Theoretical Study of Photoinduced Reactions in Ionic Crystals
Mechanisms, Energy Dissipation and Coherence Effects

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Abstract

Recent advances in laser technology have allowed driving coherent microscopic dynamics of reactive species in some chemical reactions. This technique is called coherent control or quantum control. The possibility of coherent control in reactive centres in direct contact with ionic crystals was studied theoretically on the example reactions: (1) Desorption of hydrogen from a hydroxyl ion formed due to HCl adsorption at the MgO(001) surface and (2) dissociation of the Self-Trapped Exciton (STE) in alkali halides into a pair of point defects (F-H pair). The second takes place inside a crystal lattice. A complete self-contained theoretical study of the coherent control reaction (1) is presented, involving DFT calculations and classical and quantum dynamics simulations. Reaction schemes for (2) are studied using an empirical model for the STE in a generic alkali halide.

To perform the tasks required by the aims of this project, a simple criterion for the spatial localisation of normal modes, a molecular dynamics initialisation scheme allowing dissipation dynamics at non-zero temperature and an extension of the optimal control method that greatly enhances its usability were developed. All of these techniques are applicable to a large class of theoretical problems.

Comparative studies of phonon modes localised at surfaces and surface steps in three ionic crystals lead to the conclusion that the order of these crystals with increasing localisation of surface modes is CaF$_2$(111), MgO(001), KBr(001). For MgO and KBr, step modes were found that appear to be capable of funnelling vibrational energy to the step and transport it along the step. Vibrational modes localised at the corners of a large finite cube of MgO were identified that may play an important role in the dissipation from admolecule modes of the appropriate frequency. Reaction (1) is justified by the comparatively low localisation in MgO(001) in conjunction with a low anharmonicity, promising small dissipation from the admolecule.

Density functional simulations of HCl on the MgO(001) surface at low coverage predict dissociative adsorption with chemisorption of the proton to a surface oxygen. High simulated coverage was found to be the reason for a previous contradictory study. Activation energies for hydroxyl and chlorine rotation and libration were found to be accessible at room temperature.

The first dynamical study of vibrational dissipation from a molecule adsorbed to an insulator surface was performed. This was done at a thermal population of all...
normal modes rather than at zero Kelvin. The stretch vibration of the hydroxyl was found to interact most strongly with hydroxyl rotation and libration. Vibrational energy transfer proceeds via the latter two into the crystal lattice. Dissipation starts only a considerable time after excitation. A non-symmetric collision of the proton with the chlorine ion appears to play a role in igniting the dissipation process.

A coherent control mechanism for the dissociation of OH\(^{-}\) formed at the MgO surface due to HCl adsorption was suggested and its experimental feasibility was demonstrated. Double excitations are used in the proposed excitation process. This allows a short time scale for the excitation process, which in turn diminishes the adverse effects of dissipation. A static electric field can be used to desorb atomic hydrogen from the excited molecule.

An ultrafast reaction for the dissociation of the STE was proposed. This is the first prediction of a coherent control reaction for a specific reactive centre within a crystal. The use of a bound excited state of the STE to deposit a wave packet on the dissociative flank of the STE electronic state represents a qualitatively new reaction scheme. It involves a subtle interplay between electronic and vibrational dynamics of the wave function.
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# List of Abbreviations

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<th>abbr.</th>
<th>expanded abbreviation</th>
<th>remark</th>
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<tbody>
<tr>
<td>ABM</td>
<td>Adams-Bashford-Moulton</td>
<td>as in “ABM predictor-corrector” (propagation method)</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscope</td>
<td>works with ionic substrates</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
<td>lowest unoccupied band</td>
</tr>
<tr>
<td>CAP</td>
<td>complex absorbing potential</td>
<td></td>
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<tr>
<td>ch.</td>
<td>chapter</td>
<td></td>
</tr>
<tr>
<td>cf.</td>
<td>confer</td>
<td><em>latin</em>: compare</td>
</tr>
<tr>
<td>conf.</td>
<td>configuration</td>
<td>enumerated 1 – 4 in ch. 4+5</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
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<tr>
<td>DOF</td>
<td>degree of freedom</td>
<td><em>plural</em>: DoOF</td>
</tr>
<tr>
<td>DOS</td>
<td>density of states</td>
<td></td>
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<tr>
<td>DVR</td>
<td>discrete variable representation</td>
<td>of a wave function</td>
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<tr>
<td>ECP</td>
<td>effective core potential</td>
<td>acts on valence electrons</td>
</tr>
<tr>
<td>EELS</td>
<td>electron energy loss spectroscopy</td>
<td></td>
</tr>
<tr>
<td>eq.</td>
<td>equation</td>
<td><em>plural</em>: eqs.</td>
</tr>
<tr>
<td>et al.</td>
<td>et alii/alia</td>
<td><em>latin</em>: and others</td>
</tr>
<tr>
<td>f.</td>
<td>and following (single)</td>
<td></td>
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<tr>
<td>FD</td>
<td>finite differencing</td>
<td>approximation of derivative</td>
</tr>
<tr>
<td>ff.</td>
<td>and following (several)</td>
<td></td>
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<tr>
<td>FFT</td>
<td>fast Fourier transform</td>
<td>scales with $N \log N$</td>
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<tr>
<td>fig.</td>
<td>figure</td>
<td><em>plural</em>: figs.</td>
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<tr>
<td>FROG</td>
<td>frequency resolved optical gating</td>
<td>used for theoretical analysis</td>
</tr>
<tr>
<td>GGA</td>
<td>generalised gradient approximation</td>
<td>class of DFT functionals</td>
</tr>
<tr>
<td>HAS</td>
<td>helium atom scattering</td>
<td>surface sensitive experiment</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
<td>top of VB in a crystal</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
<td></td>
</tr>
<tr>
<td>LA</td>
<td>longitudinal acoustical</td>
<td></td>
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<tr>
<td>LO</td>
<td>longitudinal optical</td>
<td>types of vibrational mode</td>
</tr>
<tr>
<td>LCAO</td>
<td>linear combination of atomic orbitals</td>
<td>electronic basis set</td>
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<tr>
<td>LDA</td>
<td>local density approximation</td>
<td>class of DFT functionals</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
<td>bottom of CB in a crystal</td>
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<tr>
<td>MSD</td>
<td>mean square displacement</td>
<td></td>
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<tr>
<td>MD</td>
<td>molecular dynamics</td>
<td>classical simulation</td>
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<tr>
<td>NPA</td>
<td>natural population analysis</td>
<td>of LCAO result</td>
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<tr>
<td>PBC</td>
<td>periodic boundary conditions</td>
<td></td>
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<tr>
<td>PES</td>
<td>potential energy surface</td>
<td></td>
</tr>
<tr>
<td>PW</td>
<td>plane wave</td>
<td><em>electronic basis set</em></td>
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<tr>
<td>QB</td>
<td>quantum beat</td>
<td><em>plural</em>: QBs</td>
</tr>
<tr>
<td>q.e.d.</td>
<td>quod erat demonstrandum</td>
<td>end of a proof</td>
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<tr>
<td>QM</td>
<td>quantum mechanics / mechanical</td>
<td></td>
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<tr>
<td>ref.</td>
<td>reference</td>
<td><em>plural</em>: refs.</td>
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<tr>
<td>RMS</td>
<td>root mean square</td>
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<tr>
<td>SBZ</td>
<td>surface Brillouin zone</td>
<td></td>
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<tr>
<td>SMD</td>
<td>self-trapped exciton</td>
<td>defect in alkali halides</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunneling microscope</td>
<td>needs conducting substrate</td>
</tr>
<tr>
<td>TA</td>
<td>transverse acoustical</td>
<td>types of vibrational mode</td>
</tr>
<tr>
<td>TO</td>
<td>transverse optical</td>
<td></td>
</tr>
<tr>
<td>TOF</td>
<td>time-of-flight</td>
<td>spectroscopic technique</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
<td>highest occupied band</td>
</tr>
<tr>
<td>w.l.o.g.</td>
<td>without loss of generality</td>
<td></td>
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<td>w/o</td>
<td>without</td>
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Chapter 1. Introduction

1.1. Motivation for Coherent Control

One of the main problems in physics is to predict the future state of a system from its present state, given a system Hamiltonian. The inverse problem of this is finding a Hamiltonian that mediates the transition between given initial and target states. This constitutes the field of quantum control.

Classically, chemical reactions are controlled by tweaking macroscopic properties of the environment such as pressure and temperature, the ratio between the reactants and the presence of certain catalysts. When controlling exclusively such macroscopic parameters, the reacting species move randomly rather than coherently during the reaction. Certain environmental conditions are controlled while the microscopic dynamics during a reaction remain uncontrolled.

This work is concerned with the endeavour to use lasers to achieve objectives such as site-specific excitations of, or dissociation along, some reaction coordinate in polyatomic systems. Optimal laser fields are sought that maximise the yield of the reaction.

Such control of the macroscopic parameters of a reaction and its dynamics means a great improvement over the mere control of thermodynamic and statistical parameters because very frequently, reactions under the same macroscopic conditions can propagate along competing microscopic pathways, producing different reaction products.

Advances in laser technology have made control of the microscopic dynamics of chemical reactions at a quantum-mechanical level possible. Such control is called coherent control of molecular dynamics. The term “coherent control” stems from the necessity of coherent motion of the reactive species during the reaction, so that the system does not get out of phase with the laser field driving the reaction during the pulse.

In the gas phase, collisions between of the reactive species with its environment are relatively rare and hence coherence times of the molecular dynamics can be quite long. In the condensed phase, however, collisions are common and hence the reactive species are subject to considerable decoherence. Coherent dynamics can then ensue only for an ultrashort timescale, i.e. on the order of hundreds of femtoseconds. Coherent control has been demonstrated in the gas phase and in some condensed phase systems (some publications on this subject are reviewed in section 1.3.2).

At the start of this project, few publications dealing with simulations of dissipative quantum systems were concerned with coherent control and most publications concerned with coherent control concentrated on small molecules in the gas phase (or in molecular beams in the vacuum). There is, however, a great interest in controlling reactions on crystal surfaces and point defects inside crystals, as these systems offer well-defined initial conditions that are otherwise only found in molecular beams whose production necessitates cumbersome equipment.

This project aims to demonstrate theoretically the possibility to achieve quantum control in physical systems involving crystals as essential parts, particularly in molecules adsorbed to the surface of a crystal and inside crystalline systems.

Crystalline systems are interesting because a crystal can play an important role in a reaction by stabilising certain reaction products which would be unstable in the vacuum – for example charged ions due to the separation of an admolecule at the surface of an ionic crystal, while in the vacuum a molecule would dissociate into neutral fragments. Other photoreactive systems, such as point defects, only exist in the context of a crystal.

1.2. Problems to be Solved

In order to demonstrate theoretically the feasibility of coherent control reactions in systems involving crystals, the following problems have to be solved:

1. Find physical systems involving a crystal as candidates whose dynamics can be controlled coherently.
   a) The reactive centre should respond vibrationally to irradiation with light so that it can be controlled.
   b) The vibrational frequencies of the reactive species and the underlying crystal should differ in order to allow for long coherence lifetimes of the reactive centre.

2. Construct model potentials for the reactants within the reactant-crystal system.

3. Run quantum dynamics simulations based on these models in order to find out whether coherent control is feasible for these systems.
   a) If the dissipation of vibrational energy from the reactive centre can be quantified, a model for the dissipation process should be developed.
   b) Dissipative quantum dynamics simulations can then be performed using this model.
and $m$ photons of frequency $\omega_n$, adding up to an excitation energy of $n\hbar\omega_m = m\hbar\omega_n$. Photons of different frequency excite the ground state wave function via different intermediate excited states to the same final electronic state. By controlling the phase relation between the two different lasers and adjusting their amplitudes such that both produce appreciable excitations, one can influence the complex phase between the two parts of the final wave function that have gone along the different excitation pathways. Controlling this phase is tantamount to control over whether there is constructive or destructive interference, or no interference at all (when the final wave packets do not overlap).

The Tannor-Rice, or “pump-dump” scheme, is illustrated in figure 1.1b. In this scheme, the system is excited electronically by a so-called “pump pulse” and left to propagate on the excited-state potential surface for a certain amount of time (which may be zero) before a so-called “dump pulse” excites it to another state (which may be a de-excitation to the ground state through stimulated emission, hence the term “dump”). As the minimum of the excited state surface is generally not at the same coordinate as the minimum of the ground state, the system geometry changes while excited – in the illustrated case, it is dissociative. This scheme can produce transitions from one ground state minimum to another one or into the continuum of vibrationally free states (dissociation) due to the momentum picked up in the electronically excited state.

It is also possible to control a system by purely vibrational excitations. When an excitation from one steady state to another is to be achieved, this could be mediated by a laser field that first excites the initial state into a non-steady vibrational state and subsequently cools the system down into the final state. Insofar such a reaction corresponds to Tannor-Rice pump-dump type control.

Common to all control schemes is that at intermediate times a mixture of eigenstates is produced and the interaction of these with the laser field produces the final state.

The use of laser pulses can be generalised to considering laser fields that have time-dependent frequency distributions and envelopes. A simple form of frequency time-dependence is “chirp”, a constant rise (positive chirp) or fall (negative chirp) in frequency over time inside one laser pulse. The time-dependent electric field of the laser pulse then has the form

$$\varepsilon(t) = E(t) \cdot \sin \left( \omega + \Delta \omega \cdot t \right) \cdot t + \varphi$$

where $E(t)$ is a time-dependent envelope function, $\omega$ is the central frequency, and $\Delta \omega$ is the chirp parameter.

Laser pulses can be chirped using optically active materials.

All coherent control schemes rely on the system to stay coherent from the beginning to the end of irradiation in order to achieve a well-defined effect (as mentioned in point 2 of section 1.4). Otherwise, the later parts of the laser field would impinge
on a collection of reactant systems in different states, each of which would respond differently. This would not lead to a well-defined final state.

1.3.2. Coherent Control Studies on Molecules

I will rely on previous work for the selection of example systems, so, in order to illustrate in more detail the main concepts pertaining to control of reactions in the gas phase and in the condensed phase, I will briefly review some publications on the subject.

1.3.2.1. Studies Using the Brumer-Shapiro Scheme

The Brumer-Shapiro technique has been used experimentally by Elliott and colleagues in atoms\(^{10,11}\) and Gordon and co-workers who used single-photon and triple photon excitation via intermediate states to control the ionisation of HCl and the photodissociation of HI and DI into different charged species.\(^{12,13}\) e.g.

\[
\text{DI} \rightarrow \begin{cases} 
\text{DI}^+ + e^- \\
\text{D} + \text{I}^+ \rightarrow \text{I}^+ + e^-.
\end{cases}
\]

Thermal dissociation of this compound and others discussed in this section requires very high temperatures, leaves the microscopic dynamics of the reactive species uncontrolled and yields neutral products. In the reaction discussed here, light is used to drive the reaction and charged species are produced. The parameter to control is the yield of dissociated molecules versus associated ones after irradiation.

Depending on the phase relation between the laser fields of different frequency, they found anticorrelating oscillatory yields of DI\(^+^\) and I\(^+^\) (Figure 1.2). This is a direct proof of control over the reaction.

The Brumer-Shapiro scheme was also used by Gordon and co-workers to demonstrate modulation of the signals of different dissociated fragment ions of HCl, H\(_2\)S and CH\(_3\)I\(^{14-16}\) and by Bersohn and co-workers\(^{17}\) to control ionisation of CH\(_3\)I, all of them varying the phase between two laser fields of frequencies \(\omega_1 = \omega_2 = \omega_3\) and by Shapiro and co-workers\(^{18}\) who used a two-photon scenario to control the electronic states of the products of the photodissociation of Na\(_2\).

Following theoretical predictions on the photodissociation of H\(_2\)\(^+\) by Charron et al.,\(^{19,20}\) experimental photodissociation of HD\(^+\) was performed by Dimauro et al.\(^{21}\) Rather than depending on the relative phase \(\phi_2 - \phi_1\) of the photons, the yield of these processes depends on \(\phi_2 - 2\phi_1\).

1.3.2.2. Studies Using the Tannor-Rice Scheme

The Tannor-Rice technique has been used experimentally by Gerber and co-workers,\(^{22}\) considering the photodissociation of the sodium dimer

\[
\text{Na}_2 \rightarrow \begin{cases} 
\text{Na}_2^+ + e^- \\
\text{Na}_2^+ \rightarrow \text{Na}^+ + \text{Na} + e^-.
\end{cases}
\]

In the so-called “pump-probe” experiment, the pump pulse excites Na\(_2\) to an electronically excited state (Figure 1.3). If the wave packet is at the inner turning point (smallest distance between the atoms) the probe pulse excites it to the molecular ion state. If it is at the outer turning point, however, the probe pulse excites the wave packet to a dissociative state because at this coordinate, the difference between these states can be bridged by the pulse energy, whereas at the inner turning point, it cannot. Consequently, Gerber and co-workers observed an anticorrelating oscillatory behaviour of the ratio between the different dissociation products Na\(^+\) and Na\(_2^+\) with respect to the delay time between the pulses. The frequency of this oscillation is the vibrational frequency of the wave packet in the intermediate electronic state.

A Tannor-Rice scheme was also used by Zewail and co-workers\(^{23,24}\) to control photodissociation channels of NaI and the formation of XeI, and by Gerber and

![Figure 1.2:](image-url) Ion yield in a Brumer-Shapiro experiment by Gordon et al. The phase between the fundamental UV and the third harmonic VUV laser is controlled by passing them through a chamber with H\(_2\) gas, whose pressure (abscissa) can be changed. The yields of DI\(^+\) and I\(^+\) oscillate with respect to the phase between the laser fields and are anti-correlated. This is direct evidence of control over the outcome of the experiment. Reproduced with permission from ref. 12.

![Figure 1.3:](image-url) (a) The ratio between the yields of Na\(_2^+\) and Na\(^+\) oscillates with respect to the delay time between the pump and the dump (or, in this case, probe) pulse. (b) Reaction path to the molecular ion Na\(_2^+\) - the probe pulse comes in as the excited state wave packet is at the inner turning point of the excited state potential. (c) Reaction path the Na\(^+\) ion - the probe pulse comes in as the excited state wave packet is at the outer turning point of the excited state potential. Reproduced with permission from ref. 22.

co-workers\textsuperscript{35} to control the photo-ionisation of Na$_2$ and Na$_3$.

A pump-dump scheme has been proposed theoretically by Brumer, Shapiro and others to control the Br to Br* branching in the photodissociation of IBr and the dissociation of Li$_2$, as well as of the hypothetical DH$_2$ complex\textsuperscript{26-28}.

Strongly chirped ultrashort pulses have been used by Warren, Melinger and co-workers\textsuperscript{29,30} to control the level of electronic excitation in few-level and multilevel systems.

1.3.2.3. Optimal Control Studies

Rice, Rabitz and co-workers\textsuperscript{31-33} have shown theoretically that optimal laser fields of generally complex shape exist for the control of transitions between bound or localised states and that for unbound states the solutions to the problem of optimal control can be enumerated by their order of control-quality.

A purely vibrational control scheme has been predicted theoretically by Sundermann and de Vivie-Riedle\textsuperscript{34} who, based on optimal control calculations, proposed a control scheme by which an excitation of the vibrational ground state of OH$^-$ to the first vibrational excited state can be performed.

Gerber and co-workers\textsuperscript{35} optimised the shape of a laser field experimentally using a feed-back loop with a genetic choice algorithm to control the ratio of products of the dissociation of Fe(CO)$_5$ in a molecular beam.

The relative ease with which some molecular systems can be controlled is essentially stipulated by the weak or absent coupling between the vibrational normal modes taking part in the reaction and the normal modes making up the environment. As a result, while excited, the systems remain coherent for a sufficiently long time.

1.3.3. Studies of Molecules on Crystal Surfaces

The situation is different if the reactants are in contact with condensed matter systems, where there is a competition between efforts to control the reaction via laser light on one hand and decoherence as well as energy dissipation caused by the coupling to the environment on the other hand.

Several approaches exist to deal with dissipation theoretically. As examples I will discuss studies using the density matrix approach and the mixed quantum-classical approach. Both studies deal with molecules adsorbed to surfaces, a type of system that I would like to study as well.

Saalfrank and co-workers have performed quantum-mechanical density matrix simulations for small molecules on metal surfaces\textsuperscript{36,37}. Starting from an electronically excited wave packet, these calculations take the finite lifetime of the electronic excitation due to coupling with the substrate into account. The density matrix approach can be employed to represent dephasing between different states of the system, which is a very important effect, as it limits the time scale on which the system stays coherent and hence controllable.

Gerber, Kosloff and co-workers have simulated the dynamics of HCl molecules on an MgO(001) surface modelled by a small cluster with effective Morse potentials, first with classical molecular dynamics,\textsuperscript{38} then with a combination of quantum mechanical wave packet dynamics for hydrogen and classical molecular dynamics for the heavier ions.\textsuperscript{39} A desorption reaction of hydrogen in which the crystal takes part by back scattering was considered.

Interference effects within the hydrogen wave function were seen at intermediate times in the simulation (fig. 1.4). The presence of these interference effects in spite of the dissipative influence of the MgO surface is suggestive of a long coherence lifetime. Hence, selecting this physical system as a candidate for coherent control appears promising.

1.3.4. Studies of Molecular Systems Inside a Dissipative Environment

In addition to a molecule adsorbed on a surface, I would like to propose a control reaction inside an ionic crystal, i.e. enclosed by a dissipative environment. This section lists some previous experimental studies of reactions within a thermal bath. However, these often deal with reactive species in molecular clusters or in liquid solution rather than inside crystals.

Parson and co-workers have performed molecular dynamics simulations of several coupled excited states on the same system of I$_2$ molecules embedded in matrices of Ar and CO$_2$ molecules\textsuperscript{40,41} at low temperatures. They calculated many classical tra-
with a complete cage(I$_2$Ar$_{16}$) at longer pump-probe delays. Dissociated intermediate evaporation states I’ Ar$_{11-13}$ were observed at short delays (fig. 1.5b). However, no dissociation was observed from the smallest complete carbon dioxide cage (I$_2$ (CO$_2$)$_{20}$). This discrepancy in the behaviour of the argon and carbon dioxide cages was explained by the authors of ref. 42 with the similarity between the vibrational frequencies of I$_2$ and rotational and librational lattice vibrations in CO$_2$, while the characteristic frequencies of argon cages are well separated from the I$_2$ frequency.

Experimental studies on liquid CH$_3$OH$^{43,44}$ have shown that the coherence lifetime for the vibrational motion in this compound is between 5 ps and 15 ps.

Several theoretical studies of model systems$^{45-48}$ (e.g. a two level oscillator coupled with a bath) have generally concluded that control is possible in solution when the coupling between solute and solvent is not too strong. Bardeen et al.$^{49}$ used positive and negative chirp of ultrashort pulses to control the formation of a non-stationary ground state component of a molecule in liquid solution.

A theoretical study modelling a realistic reaction, the controlled proton transfer in the transition from the keto to the enol form of 2-(2’-hydroxyphenol)-oxazole$^{50}$ using semiclassical mechanics concluded that the reaction can be controlled to a certain degree, in spite of considerable decoherence. In this study, the proton motion was treated as system and the remainder of the molecular modes as bath.

In experimental work on a specific excitation of the symmetric I$_2$ stretch in ethanol$^{3}$ compared to argon were seen to be the most important factors for the quenching of the dissociation and the stark contrast between the time-scales for the recovery of photon absorption (fig. 1.5c). A much stronger distortion of the adiabatic potentials of I$_2$ (fig. 1.5c) by the polar solvent CO$_2$ compared to the non-polar argon was found to be very likely. These results demonstrate that, the stronger the coupling between reactive centre and environment, the harder control of the reaction becomes.

Lineberger and co-workers$^{44}$ have studied experimentally I$_2$ molecules embedded in clusters of carbon dioxide or argon at low temperature. Pump-probe experiments at low temperatures (fig. 1.5) yielded an I$^+$ ion from the smallest argon cluster jectories to take quantum wave packet broadening and different initial configurations into account. Their conclusion is that the solvent interacts with the solute strongly enough to effectively quench dissociation from initial states in which it would occur in the free molecule. This means that the reaction coordinate for the embedded molecule is more complex than just a gas phase molecular potential.

Strong vibrational relaxation of I$_2$ together with stronger cohesive forces in the polar CO$_2$ compared to argon were seen to be the most important factors for the quenching of the dissociation and the stark contrast between the time-scales for the recovery of photon absorption (fig. 1.5c). A much stronger distortion of the adiabatic potentials of I$_2$ (fig. 1.5c) by the polar solvent CO$_2$ compared to the non-polar argon was found to be very likely. These results demonstrate that, the stronger the coupling between reactive centre and environment, the harder control of the reaction becomes.

In experimental work on a specific excitation of the symmetric I$_2$ stretch in ethanol and acetonitrile$^{51,52}$ control of aspects of the spectrum corresponding to this vibrational mode was achieved in spite of collisions with the solvent.

### 1.3.5. Studies of Control in Semiconductors

Coherent phenomena in semiconductors have been reviewed by Axt and Kuhn.$^{53}$ An overview of some experimental and theoretical work concerning coherent control in semiconductors will be given in this section.

A Brumer-Shapiro scheme has been studied for processes where charge and spin currents are generated$^{21,54-62}$ In particular, it has been shown theoretically$^{55}$ that even in the bulk with inversion symmetry, a directed charge current can be excited. This result has been confirmed experimentally in GaAs.$^{21}$ Other processes where carrier populations and optical absorption are controlled have been studied in refs. 63,64. It is also possible to employ this technique to produce spin-polarised currents,$^{57-62}$ a process which has attracted interest due to its prospective usefulness for the construction of electronic devices (spintronics).

A Tannor-Rice scheme has been used to control the optical orientation of excitons,$^{63}$ exciton and spin densities$^{66-70}$ and quantum beats (QBs) between transitions in an asymmetric double quantum well or phonon QBs.$^{71-74}$ The latter are of particular interest for this project, as I will also endeavour to control the nuclear dynamics
in the example systems considered. Theoretical studies predicted a periodic signal superimposed on the decay of an optically induced polarisation\textsuperscript{66,62,75} and experimentally verified on bulk GaAs.\textsuperscript{76} The decay of the signal in this experiment is, however, a reminder that the population of the product state is subject to dissipation and so a coherent control reaction has to be of a short timescale in order to achieve the yields desired.

Unlike these reactions in semiconductors, where predominantly the electronic states and non-local vibrational modes are controlled, this project deals with the nuclear dynamics of well-localised reactive centres in the context of ionic crystals.

1.4. Necessary Conditions for Demonstrating Coherent Control

The studies I have cited in the preceding sections demonstrate that the reactions I propose as example reactions for coherent control must be carefully chosen so that the reaction dynamics are not quenched by the environment of the reactive species. In this section I list a number of basic conditions that example systems chosen for the demonstration of a coherent control reaction must satisfy:

1. They must exhibit a branching reaction. The yield of a certain branch is the parameter to be controlled. In a dissociative reaction in particular, the branching is between dissociation vs. no dissociation.

2. The system’s reaction coordinate must couple to the thermal bath weakly enough that its dynamics remain coherent throughout the reaction. Conversely, the total time of the reaction must be much shorter than the coherence lifetime of the reaction coordinate.

3. The nuclear coordinates of the system must be sensitive to irradiation with laser light. This means that
   a) the system needs to have a dipole gradient along the reaction coordinate, so that vibrations can be excited directly by interaction with the laser field (as is the case in OH\textsuperscript{−} formed due to HCl adsorption on MgO) or
   b) an electronic transition exists to a state with a gradient in the Frank-Condon zone, so that the nuclei gain momentum after electronic excitation. This will be used to drive the reaction proposed for the STE.

The example systems chosen with these properties are then studied, e.g. their chemical and dynamical properties are simulated, in order to demonstrate directly that they are suited for control reactions.

1.5. Aims and Choice of Example Systems

The publications reviewed above deal with coherent control of molecular systems in the gas phase and of semiconductors. Molecular motion in dissipative environments has been studied extensively but coherent control processes have not been considered explicitly. My aim for this thesis was to extend the field by a study of coherent control in the context of ionic crystals, which either serve as substrate for the adsorption of a molecular system to be controlled or provide the bulk lattice defects to be controlled.

The following two systems appear as promising candidates for coherent control, as they satisfy the points outlined in section 1.4: (a) The HCl molecule adsorbed on the MgO(001) surface and (b) the Self-Trapped Exciton (STE) in alkali halides.

As the study by Gerber, Kosloff et al. on HCl adsorbed on the MgO(001) surface\textsuperscript{38,39} predicts coherence times of many periods of the hydrogen vibration, this system invites an attempt to control it coherently. However, the potential energy surface used in these publications is based on ab initio calculations\textsuperscript{77} that model a fairly high coverage with admolecules, while the control process proposed relies on isolated molecules at the surface, i.e. low coverage, in order to allow neglect of intermolecular interactions.

As I will show in chapter 4, this discrepancy leads to a description of the binding behaviour of low-coverage HCl at the MgO(001) surface which is qualitatively wrong. Physisorption was predicted in ref. 77 while my own dipole-dipole error corrected results predict chemisorption, in accordance with other results that I obtained with a method that does not feature this error by construction. Chemisorption leads to dissociation of HCl and formation of OH\textsuperscript{−} at the surface. These results are presented in detail in chapter 4.

Fig. 1.6 shows an illustration of the OH\textsuperscript{−} molecule formed at the MgO(001) surface due to HCl adsorption. Instead of a relative H-Cl coordinate, the stretch mode of OH\textsuperscript{−} has to be controlled. OH\textsuperscript{−} has a dipole gradient,\textsuperscript{*} so I will propose a purely vibrational control scheme (as in ref. 34) for the selective excitation of the OH\textsuperscript{−} stretch vibration as a precursor to the dissociation of hydrogen from the surface by a quasi-static field. The branching reaction studied (point 1 in section 1.4) is therefore dissociation versus association. The hydroxyl stretch mode is spectrally separated from the rest of the system and therefore has a dissipation lifetime of many vibrational periods (see point 2 from section 1.4).

I would also like to demonstrate coherent control inside an ionic crystal. Since my ultimate goal is to control dissociation reactions, point defects formed by dopant atoms would fail as example systems, since their diffusion would be hampered by confinement in the crystal lattice. However, some point defects formed by interstitial atoms or ions, such as the H-centre in alkali halides, can migrate through the lattice.

\textsuperscript{*}satisfying point 3a from section 1.4
Figure 1.6: Illustration of OH$^-$ formed at the MgO(001) surface due to HCl adsorption. The stretch mode of OH$^-$ is the reaction coordinate. The target of the coherent control process proposed is a selective excitation of the stretch mode vibration.

An example for such a dissociation reaction in a crystal is the separation of the Self-Trapped Exciton (STE) in some alkali halides. The STE separates into a Frenkel defect pair, an electron trapped at a vacated anion lattice site, called F-centre, and a neutral interstitial halogen associated to another halogen ion as an X$_2^-$ molecule, called H-centre (where X marks the halogen compound of the crystal).

This reaction can be seen as an analogue to the dissociation of a free NaCl molecule: An atomic metal and a halogen atom result. The F-centre corresponds to the metal and the H-centre to the halogen atom. Note that both F- and H-centre are neutral within the framework of the crystal.

Pump-probe spectroscopical evidence by Shluger and Tanimura$^7$ demonstrates that in KBr the formation of the F-centre takes place coherently (i.e. point 2 from section 1.4 is satisfied). The existence of spontaneously forming F-H centre pairs at large separation is further proof that the dissociation time is small compared to the dissipation lifetime of the reactive species.

Fig. 1.7 shows a sketch of the potential energies along the reaction coordinate of the STE and its electronically excited state. The target of the reaction is to separate the di-haloid from the vacancy, so this is again a branching of dissociation versus association.

The coherent control reaction I will propose is based on a Tannor-Rice pump-dump scheme (i.e. the reaction satisfies point 3a from section 1.4). Shown at the bottom of fig. 1.7 is the STE potential surface along the separation coordinate; above it an excited state of the STE. Note that the latter is bound, as opposed to the dissociative states usually used for pump-dump experiments of the type illustrated in figs. 1.1b and 1.3c. The excited (step 1) wave-packet is accelerated in the opposite direction (step 2) and consequently dumped on the dissociative flank of the STE potential (step 3). From there the system dissociates (step 4). This scheme relies on a subtle interplay between the electronic and the vibrational state of the system.

This increases the distance between the F-centre and the H-centre. If the distance becomes large enough, recombination is no longer ruled by the attraction between F-centre and H-centre but becomes subject to a random meeting of the two due to diffusion. The lifetime of the F-H centre pair is then greatly increased. The feasibility of this process will be demonstrated by the preparation of a transient state with non-zero momentum at the right-hand potential minimum in fig. 1.7.

1.6. Challenges to Meet and Outline of Thesis

A graphical overview of the sections in this thesis is shown in table 1.1 at the end of this chapter. The following sections list the tasks to complete in order to demonstrate coherent control processes in the chosen example systems.

1.6.1. Vibrational Properties of Clean Crystal Surfaces

It makes little sense to propose a reactive centre that is controllable when isolated and then find out that the reaction is fully quenched due to dissipation when the reactive species are in contact with a thermal bath. Therefore, substrates for molecular adsorption must be found that offer an environment where point 2 of section 1.4 can be satisfied for an admolecule of interest. This can be done by determining and analysing the surface-localised vibrational normal modes and the anharmonicity of their interatomic potentials of the substrate crystal selected.

Vibrational normal modes identify the coordinates of a physical system that interact least at geometries near the energy minimum, i.e. only to third or higher order in the displacement from the equilibrium geometry. In crystals they can be categorised according to their frequency, wave-vector and which ions participate most (for example only those near a centre of interest).
Some of the normal modes can be localised at the surface. They are the normal modes that will interact most strongly with a molecule adsorbed on the surface. Resonant coupling is enhanced when the molecular vibrations and the surface vibrations are at the same frequency. Conversely when these frequencies do not match, the coherence lifetimes of the molecular vibrations are long.

It is therefore important to ascertain the vibrational properties of the surfaces considered as substrates for admolecules whose dynamics are to be coherently controlled. An overview of techniques for the treatment of this problem is given in chapter 2. The vibrational normal modes are calculated by diagonalisation of the dynamical matrix, eq. (2.1) of the physical system. Section 2.3 introduces a simple method for the detection of localised normal modes, while in section 2.4 the Frequency-Resolved Optical Gating (FROG) data analysis method is reviewed, which is needed later.

In chapter 3, I present calculations of the normal mode structure of the surfaces MgO(001), KBr(001) and CaF$_2$(111). I have applied the detection method of localised modes introduced in section 2.3 to find normal modes localised at the surfaces.

Although I will later consider adsorption of HCl to the perfect MgO(001) surface only, I also applied this detection method to find normal modes localised at steps in the MgO(001), KBr(001) and CaF$_2$(111) surfaces and at a corner of MgO.

### 1.6.2. Adsorption Characteristics for HCl on the MgO(001)

#### Surface Terrace

After the vibrational properties of the clean surface are derived, the binding behaviour of the admolecule, in this case HCl, has to be ascertained. As I will explain in detail in section 4.3, the experimental evidence and the theoretical work regarding the adsorption behaviour of HCl on the MgO surface is partially contradictory, so I have performed ab initio DFT calculations of this physical system.

The results of these simulations are presented and discussed in chapter 4. Periodic boundary calculations with dipole-dipole interaction correction and embedded cluster calculations concurringly predict that the HCl bond breaks upon adsorption and an OH$^-$ bond forms instead. Cl$^-$ is associated to the adsorption site of the proton by Coulomb attraction.

This means that, rather than controlling the dynamics of HCl as a whole on the surface, as was predicted by earlier ab initio calculations,77 I have to concentrate my endeavours to control the system on the OH$^-$ molecule formed at the surface due to HCl adsorption, as illustrated in fig. 1.6.

### 1.6.3. Partitioning a Physical System

I have simulated coherent control reactions using wave packet propagation methods based on the Fast Fourier Transform (FFT) technique. In the course of my work on this project, I have implemented such techniques and simulated quantum mechanically the dynamics of wave functions depending on a few coordinates called Degrees Of Freedom (DsOF) of the simulation. The computational effort of the FFT-based scales as

$$N \cdot \ln N, \quad N = \prod_{i=1}^{f} d_i$$

where $f$ is the number of DsOF and $d_i$ the number of grid points used for DOF $i$. Particularly,

$$N \geq d_1 \cdot d_2 \cdot \ldots \cdot d_f$$

i.e. the computational effort increases exponentially with the number of DsOF $f$ considered.

Only a small section of the whole physical system can therefore be simulated quantum mechanically; the rest must be either neglected or taken into account implicitly as a dissipative environment. All but the few quantum-mechanically simulated reaction coordinates (the “system”) are then represented by a thermostat (the “bath”). From here on, I will denominate the entirety of system and bath as “physical system” in order to distinguish it from the small, quantum mechanically simulated part called “system”.

It is important to choose a physical system where this representation is a good approximation. A physical system can be partitioned if the interaction of the quantum mechanical system with all other modes (the bath) is weak, so that the decoherence time of the QM system is relatively long.

The dynamics of the bath coordinates should not play a role in the reaction because they will not be simulated in a time-dependent way. This means that the population of the normal modes represented by the bath should not change significantly due to interaction with the system. The bath should instead be representable only by its (constant) effect on the system.

This averaged bath influence will be present in the quantum mechanical simulation as a quantum dissipation operator acting on the density matrix of the system. This operator is constructed according to parameters extracted from properties of the coupling as acquired from other theoretical methods.

In order to make the separation a good approximation, the following condition has to hold: Write the Hamiltonian as

$$\hat{H} = \hat{H}_s + \Delta \hat{H} + \hat{H}_b$$

where $\hat{H}_s$ is the Hamiltonian of the system which will be considered quantum-mechanically, $\hat{H}_b$ is the Hamiltonian of the surrounding thermodynamic bath and...
\( \Delta H \) is the interaction Hamiltonian between the two.

Let \( |\phi_s^{(s)}\rangle \) and \( |\phi_s^{(b)}\rangle \) be the eigenstates of the isolated system and bath, respectively, and \( E_s^{(s)} \) and \( E_s^{(b)} \) their energies. The matrix elements of the isolated system and bath Hamiltonians with respect to this basis are

\[
\begin{align*}
\langle \phi_s^{(s)} | H_s | \phi_s^{(s)} \rangle &= E_s^{(s)} \delta_{ij}, \\
\langle \phi_s^{(b)} | H_s | \phi_s^{(b)} \rangle &= E_s^{(b)} \delta_{ij}.
\end{align*}
\]

Since the Hamiltonians of the isolated system and bath map system and bath eigenstates onto linear combinations of system and bath states, respectively, all matrix elements involving a Hamiltonian and at least one state of different subsystems are zero.

The corresponding matrix elements of the full interacting Hamiltonian are then

\[
\begin{align*}
\langle \phi_s^{(s)} | H | \phi_s^{(s)} \rangle &= E_s^{(s)} \delta_{ij} + \langle \phi_s^{(s)} | \Delta H | \phi_s^{(s)} \rangle, \\
\langle \phi_s^{(b)} | H | \phi_s^{(b)} \rangle &= E_s^{(b)} \delta_{ij} + \langle \phi_s^{(b)} | \Delta H | \phi_s^{(b)} \rangle, \\
\langle \phi_s^{(s)} | H | \phi_s^{(b)} \rangle &= \langle \phi_s^{(b)} | \Delta H | \phi_s^{(s)} \rangle.
\end{align*}
\]

For the system-bath separation to be useful for implicit treatment of the bath and for the system to remain coherent for a time long enough to be controllable coherently, \( \Delta H \) must have only small off-diagonal elements \( \langle \phi_s^{(s)} | \Delta H | \phi_s^{(b)} \rangle \) mediating between the system and the bath.\(^79\)

### 1.6.4. Vibrational Properties of and Dissipation from HCl on the MgO(001) Surface Terrace

Such a partitioning between system and bath modes has to be found for the OH\(^-\) dynamics in HCl adsorbed on the MgO(001) surface. The partitioning should be made between eigenstates of the dynamical matrix, as opposed to any other, general vibrational modes, as this is the partitioning with the lowest interaction between system and bath if the physical system remains near the energy minimum throughout the reaction.

The corresponding results are presented in chapter 5. The normal modes are found with the aid of lattice dynamics on the HCl molecule adsorbed on the MgO(001) surface terrace. The shell model parameters for this system are fitted to correspond to the properties derived \textit{ab initio} in chapter 4.

The modes associated with OH\(^-\) formed on the surface due to HCl adsorption are detected using the attenuation parameter introduced in section 2.3. They are localised spatially on the adsorption site and, as expected when selecting the physical system, also localised spectrally, so that selective excitation is possible.

The coupling between normal modes in the example system is simulated by performing Molecular Dynamics (MD) that allow to extract interaction strengths between vibrational modes. These are quantified by calculation of cross-correlation functions (section 5.2.5) between the modes of interest and their FROG traces (section 2.4).

A vibrational excitation of the reaction coordinate is simulated by a novel initialisation method (section 5.2.4.1). A dissipation lifetime of 2.18 ps can be assigned to this process for the construction of a quantum dissipation operator, as discussed in detail in section E.2.6 of appendix E.

Dissipation from the reaction coordinate (the OH\(^-\) stretch mode) to the surface proceeds exclusively via the OH\(^-\) rotational and librational normal modes, while chlorine plays no quantifiable role in the dissipation process. Since this rate-determining dissipation step is already sufficiently slow to allow a coherent control reaction, it is sufficient to perform one-dimensional density matrix dynamics of the OH\(^-\) stretch only, with simulated dissipation to the other normal modes.

### 1.6.5. Quantum Dynamics Simulations of the OH\(^-\) Stretch Mode in HCl Adsorbed on MgO(001)

Once the system potential and the dissipation mechanism are quantified, quantum dynamics simulations can be performed. Quantum dynamics simulations of the OH\(^-\) stretch mode in the dissipative environment of the MgO(001) surface are presented in chapter 6. The potential used for this is the same Morse potential as that used in the shell model dynamics simulations of chapter 5.

I present laser pulses generating high vibrational excitations of the OH\(^-\) stretch mode calculated with the self-consistent optimal control method. The \( \nu = 10 \) vibrational state can be generated with a yield per optimised pulse of 65%. The pulses are analysed with the FROG method.

Subsequently, the viability of the pulses in a dissipative environment is studied by density matrix propagation, using a special dissipative Lindblad superoperator for the Morse potential. The yield per pulse of the desired excitation is reduced to 45% due to dissipation but is not fully quenched.

Finally, a simulated static electric field is applied to the model potential to simulate the desorption of H\(^+\) from the surface. The yield of desorbed species is 20%. An experiment is proposed where this process is applied repeatedly to clean the surface of OH\(^-\).

### 1.6.6. Quantum Dynamics Simulations of the Separation of the STE in NaCl

Another example system, where the reaction takes place \textit{inside} a dissipative medium, is the decay of the Self-Trapped Exciton (STE) in alkali halides into F- and H-centres. This system is discussed in chapter 7. The separation of the STE has been
studied theoretically in NaCl by Gavartin and Shluger and experimentally and theoretically in KBr by Shluger and Tanimura. The latter study demonstrated that motion along the reaction coordinate remains coherent for several picoseconds. This means that a reaction that is less than one picosecond long will not be quenched by dissipation.

According to the experimental and theoretical data, I have parameterised a model potential for the F-H centre pair separation and di-haloid stretching coordinates for the NaCl STE and performed wave packet dynamics simulations on them.

I have constructed a pump-dump reaction scheme of sub-picosecond length exploiting an electronically excited state of the STE. It yields 14% separated F-H centre pairs out of all present STEs by the simulation in the two-dimensional model potential.

1.7. Thesis Road-Map

These results can be summarised in the form of a road-map for the chapters of this thesis, shown in table 1.1. The successive tasks are listed on the left. From top to bottom, different properties of the example systems are studied. At the bottom, all information from the preceding chapters is used to construct a model with which quantum dynamical simulations can be performed. On the right of each task, the sections of the thesis are listed in which this task is discussed.

<table>
<thead>
<tr>
<th>Thesis map: The components for modelling quantum control in condensed matter.</th>
</tr>
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<tr>
<td>Methods: secs. 2.1, 2.2, 2.3</td>
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<tr>
<td>Results: sec. 3.3</td>
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<tr>
<td>Quantum mechanical DFT calculations of HCl on the MgO(001) surface</td>
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<tr>
<td>Shell model lattice dynamics and normal mode analysis for terraces and steps of MgO(001), KBr(001) and CaF$_2$(111), corners in MgO(001):</td>
</tr>
<tr>
<td>Setup: sec. 3.2</td>
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<td>Methods: secs. 2.1, 2.2, 2.3</td>
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<tr>
<td>Results: sec. 6.1.2 and 7.2</td>
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</table>

Table 1.1: Thesis road-map: Main objectives and chapters dedicated to their discussion are listed on the left, particular tasks and sections where methods and results are discussed are referred to on the right. Chapter 2 contains some methods that are used in several chapters but does not contain any results. It is therefore only referred to on the right side of the table.
Chapter 2. Methods of Classical Dynamics and Data Analysis

Aims: This chapter briefly reviews some standard and non-standard methods which I have used to obtain the results presented in more than one chapter of this thesis. Methods needed only in one chapter will be reviewed in the appropriate places.

Standard lattice dynamics and molecular dynamics methods are discussed in section 2.1, the shell model used to represent the system is introduced in section 2.2, algorithms for the detection of surface modes are presented in section 2.3. The chapter concludes with a brief review of the Frequency Resolved Optical Gating (FROG) Method (section 2.4). This method was useful in analysing the evolution of quantities recorded in the different simulations in this project.

Results: I propose a simple criterion for the automated selection of localised vibrational modes from a set of modes in section 2.3.4. The localisation can be of different dimensionality (surface, line, point). I have created a computer program that applies this criterion and used it to detect the localised modes that I present in chapters 3 and 5.

2.1. Lattice Dynamics

A central element of this project is the vibrational coupling between the reactive subsystem and its environment. In a crystalline system, the natural way to classify modes of vibrational motion is by distinguishing the normal modes of the periodic system.

For this purpose, mass-weighted normal modes \( p_{n,j}(\mathbf{k}) \) are calculated\(^{81-83}\) for periodic systems with \( N \) atoms in the unit cell, where \( n \) is the number of the mode \( (n = 1, \ldots, 3N) \), \( j \) is the atom number, \( \beta \) is a Cartesian direction, \( \beta = 1, 2, 3 \), and \( \mathbf{k} \) is the wave vector of the normal mode.

The normal modes \( p_{n,j}(\mathbf{k}) \) are the eigenvectors of the mass-weighted dynamical matrix of the system, which is dominated by the Hessian of the potential energy function \( U \)

\[
\mathbf{D}(\mathbf{k}) = \left( \frac{1}{\sqrt{m_j}} \frac{\partial^2 U}{\partial r_{ij} \partial r_{j\beta}} \right)_{ij,j=1,N} \tag{2.1}
\]

and form and orthonormal system. The eigenvalues are the squares of the circular frequencies of the normal modes, \( \omega^2 \).

If normal mode \( n \) at the wave vector \( \mathbf{k} \) has population \( X_{n\mathbf{k}} \) the displacement \( x_{n\mathbf{k}} \) from the equilibrium configuration of atom \( i \) in the direction \( \alpha \) at the time \( t \) can be expressed classically as

\[
x_{n\mathbf{k}}(t) = \frac{1}{\sqrt{P_3}} \sum_{\mathbf{k}} \sum_{n=1}^{3N} X_{n\mathbf{k}} p_{n,\mathbf{k}}(\alpha) e^{i(\mathbf{k}_r \cdot \mathbf{x}_i(t))}. \tag{2.2}
\]

Phonons, the pseudo-particles of the normal mode population are bosons and are therefore subject to the Bose-Einstein distribution. Quantum-mechanical extension of eq. (2.2) by the usual creation and annihilation operators then leads to

\[
\langle \hat{x}_{n\mathbf{k}}^2 \rangle = \frac{\hbar}{2\rho} \sum_{\mathbf{k}} \sum_{n=1}^{3N} |p_{n,\mathbf{k}}(\alpha)|^2 \coth \left( \frac{\hbar \omega_{\mathbf{k}}(\alpha)}{2k_B T} \right). \tag{2.3}
\]

2.2. The Shell Model

The normal modes and their frequencies calculated with Lattice Dynamics are, of course, dependent on the model used to represent the ions and their interactions. On one hand, highly accurate ab initio methods can be used to calculate the dynamical matrix.

Through much of this project, however, the unit cells considered will be too large to be treated by such demanding methods. I will therefore use simpler methods based on representing the ions by point charges that interact via pair potentials.

The model system for control of a molecule at a crystal surface in this project is HCl on the MgO(001) surface. The magnesia crystal, however, has highly polarisable ions. Using a single point charge to represent oxygen would fail to take polarisation into account. This would mean overestimated optical phonon frequencies, as the polarisation-induced damping is neglected.

One way to avoid this problem is to employ the shell model.\(^{84}\) The polarisable ions are modelled by two point charges, one of which has a mass and represents the core, while the other is massless and represents the polarisable component of the shell. Core and shell are connected by a harmonic spring whose spring constant represents the polarisability. Fig. 2.1 shows an illustration of the difference between rigid ion and shell model. The analytic pair potential functions used in this project to model the interionic interactions are reviewed in Appendix D.
2.3. Detection of Surface Modes

If a surface is present, there may be vibrational modes in which atoms near the surface take part to a higher degree than atoms far away from the surface. If the degree of participation decays exponentially with the distance from the surface, these modes are called localised at the surface or surface (phonon) modes. All other modes are called bulk vibrational modes.

Surface modes are particularly interesting for studying the interaction of an adsorbed molecule with a surface. Surface vibrational modes are relevant for other processes as well, such as dissipation of energy from the tip of a scanning probe microscope, for example a scanning tunnelling microscope (STM) or a non-contact atomic force microscope (AFM). This is because they contribute most to the motion of substrate atoms at the surface. Conversely, a displacement of a surface atom from its equilibrium position has a higher overlap with surface modes than with bulk modes. This can be seen by recalling that the normal modes are orthonormal (\(|p_n|^2 = 1\), i.e. a surface mode \(p_n\) has larger components \(p_{n(i)}\) at a surface ion \(i\)) and looking at the equation

\[
\langle \hat{X}^2_{\alpha n} \rangle_n = \frac{\hbar}{2 \mu_i} \frac{|p_{n(i)}|^2}{\omega_n} \left( N_n + \frac{1}{2} \right),
\]

giving the expectation value of the quantum mechanical displacement operator of ion \(i\) in the Cartesian direction \(\alpha\), where \(N_n\) is the population number of the vibrational mode \(n\), \(\omega_n\) is its frequency and \(\mu_i\) the ion mass. The equation connects the mean square displacement of ion \(i\) with the population of vibrational mode \(n\). Particularly

\[
\langle \hat{X}^2_{\alpha n} \rangle_n \propto |p_{n(i)}|^2.
\]

The domination of surface atom displacements by surface modes also means that surface modes are more susceptible to a vibrational excitation due to energy injected at the surface, for example through the ad molecule.*

*Interaction with surface vibrational modes is relevant for other kinds of excitation as well, such as dissipation of energy from the tip of a scanning probe microscope, for example a scanning tunnelling microscope (STM) or a non-contact atomic force microscope (AFM).

2.3.1. Participation of Atoms in a Specific Mode

The participation of atom \(j\) in the motion of mode \(n\) that I have used tentatively in the previous sections is strictly defined as

\[
P_{\text{atom}}(n,j) = \sum_{\beta=1}^{3} p_{n(j)}^2
\]

Note that, due to the normality of the phonon mode, this has to be seen in relation to unity. Note also that, away from the \(\Gamma\)-point (where \(k=0\) and \(D\) is symmetric rather than generally Hermitean), the components of the vectors \(p_n\) are generally complex, allowing for non-zero phases between the mode components.

Sangster and Strauch\(^{65}\) considered the normal mode structures of diatomic linear chains with single defects using Green’s function methods. They found that normal modes with energies split from the main band appeared only when the changes were strong enough and did not act to cancel each other out (by, for example, increasing a mass but increasing the force constants acting on it as well).

Most importantly, they found that when a mode has a frequency outside the
perfect crystal bands, it is necessarily localised at the defect. Note that the converse
is not true, i.e. there may be normal modes that are localised at a defect but not
split from the main band. These are called resonant local modes or “resonances”.
This means that localised vibrational modes cannot be detected purely by analysing
the spectral properties of a crystal. It may even be difficult to detect spectrally
separated local modes in computational applications, as there the model system is
always finite and hence the spectrum is discrete.

In a three-dimensional lattice defects of different dimensionality may occur.
Some examples (with decreasing dimensionality) are surfaces, steps at a surface,
or kinks in steps, corners, vacancies or substituted ions.

I will show in chapter 3 that in MgO, KBr and CaF$_2$ normal modes localised at
surfaces exist, and that these localised modes may be split from or resonant with
the main bands. To detect these localised modes I have used the analysis methods
presented in the following sections.

2.3.2. Analysis of Lattice Dynamics Results

It is important to establish a well-defined criterion to decide whether a mode is
localised at a chosen point, line or surface, in order to be able to analyse the results
of large calculations automatically. Such a criterion in the form of an algorithm
would ideally be usable for any localisation problem and useful to decide unambigu-
ously about the localisation property of any mode. At least it should offer a means
of measuring localisation at a chosen location, in order to characterise modes and
postulate a meaningful threshold value beyond which a mode would be viewed as
localised. An algorithm based on such a criterion allows to decide cases which are
ambiguous to the naked eye and to analyse results of calculations with very many
ionic coordinates (and hence equally many normal modes).

2.3.3. The Participation Function

In order to get a general overview of the degree to which a mode $n$ is localised, the
value of the participation function, also called participation ratio can be used. It
was initially introduced for the analysis of wave functions.$^{86}$ For the time being, it
can be defined intuitively as

$$P(n) = \sum_{j=1}^{N} P_{\text{atom}}(n, j)^2 = \sum_{j=1}^{N} \left( \sum_{j=1}^{3} p_{n,(j)}^2 \right)^2.$$  \hspace{1cm} (2.5)

In order to interpret the participation function, two extremal cases can be considered:

1. All atoms participate in the mode to the same degree, i.e. $P_{\text{atom}}(n, j) = \frac{1}{N}$ for
all $j$ due to the normality of the phonon mode. In this case, the mode is fully

delocalised and the participation function is

$$\tilde{P}(n) = \sum_{j=1}^{N} \frac{1}{N} = \frac{1}{N} \ll 1.$$ \hspace{1cm} (2.6)

2. The mode is localised on a single atom, in which case it is obvious that $\tilde{P}(n) = 1$.

The participation function measures to which degree a mode is localised. The inverse
participation function

$$P^\text{inv}(n) = \frac{1}{P(n)}$$ \hspace{1cm} (2.7)

then gives a measure of the number of atoms that participate in the mode. Note
that this approach replies on a finite number of atoms in the model, as otherwise
for delocalised modes $\tilde{P}(n) = 0$. In practical applications, information about the
localisation of a mode is usually given in this form and therefore the inverse partici-
pation function is often referred to as participation function. The form used can be
recognised by the limit compared with, which is unity for the participation function
and the total number of atoms in the simulation cell for its inverse.

The localisation length of a mode $n$ is measured with the function

$$P_k(n) = \frac{\sum_{j,j'=1}^{N} P_{\text{atom}}(n, j) P_{\text{atom}}(n, j') r_{jj'}^2}{\sum_{j,j'=1}^{N} r_{jj'}^2}.$$  \hspace{1cm} (2.8)

This allows to gauge whether the atoms participating in a mode form a cluster or are
spread over an extended region, like in a mode involving a sublattice. This approach
also originates from the analysis of wave functions and was initially introduced under
the name quantum connectivity function.$^{87}$ Surface and step modes, however, extend
parallel to the surface and therefore cannot be distinguished from bulk modes by
the function $P_k$.

Participation function and localisation length are formulated here in analogy to
functions used to gauge localisation of electronic orbitals for which purpose they
were first introduced. The normal mode eigenvector components are substituted for
the LCAO coefficients centred at a certain atom.

In theory, participation function and localisation length can be used to find normal
modes localised at a defect in a periodic lattice.$^*$ Unfortunately, there are problems
in the computational application of the participation function and the localisation
length on simulations using a supercell model. Some of the normal modes detected
as localised by the participation function may in fact be delocalised, as a few ions
per unit cell participating in a certain normal mode may form sublattices extending
over the whole crystal. Normal modes avoiding the defect that are in fact extended
only involve a subset of the supercell ions. In a calculation where the size of the

$^*$Such as surfaces or point defects.
system is of the same order as the localisation length of localised normal modes
(as is the case in the calculations presented here); these are also falsely detected as
localised by \( \tilde{P} \) and \( P_x \).

In an infinite or semi-infinite periodic crystal, the sublattice modes and bulk modes
avoiding the defect would not be detected as localised by the participation function
\( \tilde{P} \) but since the model has a finite size, this distinction cannot be made.

Additionally, neither participation function nor localisation length give information
as to where a normal mode is localised, for example in a problem where two or
more defects exist.\(^*\) The information that the participation function can provide
can be used as a supplemental information measuring the degree of localisation of
a mode that has already been identified as localised at the location of interest.

2.3.4. A Parameter to Quantify Mode Localisation

Due to the problems described in the previous section, I propose a simple criterion
for normal mode localisation that is applicable to finite model systems. Note that
in a finite model, the localisation problem is ill-defined, as only a finite number of
ions exist that may participate in any given normal mode. However, the decay of
ionic participation with growing distance from the defect can be measured. This is
the basic idea used in the construction of the new criterion.

I will use the example of surface modes to exemplify the proposed criterion but
the method I propose is also transferable to special locations of any dimensionality.
To model a crystal surface, I have used a slab of \( 2b - 1 \) crystallographic planes with
vacuum gaps above and below. This means that the slab has two surfaces which
have to be taken into account.

Due to the introduction of a surface, a mode present in a bulk crystal may change
its frequency to a range occupied by no other modes or a band with different sym-
metry to the one the mode came from, in which case it will necessarily be a surface
mode. Otherwise it will be a “mixed mode” or “surface resonance”. Only an analysis
of the participation of atoms in this mode can establish whether it is of surface
nature.

Just looking at the participation of the atoms in the surface monolayers is not
sufficient to detect surface modes, for example, as these may be large for an extended
mode that only involves a sublattice. Instead, one should look for modes in which
the participation of atoms decays systematically with the distance from the surface.
Previously,\(^88\) so-called “surface attenuation curves” were analysed:
The surface attenuation curve is formed by the summing up the atomic partici-

cations of all atoms in the crystallographic planes. Because the numbering of the
crystallographic planes from the surface is a discrete parameter, it would be more
appropriate to refer to the attenuation curve as attenuation profile. Let \( n \) be the
\(^*\)E.g. a surface (two-dimensional defect) with an admolecule (zero-dimensional defect).

![Figure 2.3.](image)

(a) Attenuation profile of a fictitious subsurface mode in a 17 layer slab \((b = 9)\).
The participation of atoms in this mode decays systematically with distance from the surface and
therefore the mode should be detected as a mode localised near the surface.
(b) Weighting function for the attenuation profile for a 23 layer slab \((b = 12)\). Maximum \((\approx 0.92)\),
imimum \((\approx 0.04)\), value 0.5 at \( \frac{a}{2} \) and integral from 0 to \( b \) \((\approx 0.35\ b)\) are shown. This weighting
function multiplied with the attenuation profile shown in (a) will give a large number near 0.92,
while the attenuation profile of a bulk mode (with small displacement in the surface layers) will
give a small number near 0.04.

\[^{2.3.4.}\]A. Markmann (2004) Ph.D. Thesis

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when the surface character of a mode could not be determined by its frequency or symmetry. However, since the simulation of systems with steps or with adsorbed molecules involves very many atoms, this is impracticable which is why I need to develop criteria in the form of algorithms for the detection of surface modes.

Since the decay of participation of the atoms in an ideal, reference surface mode is exponential, it would be natural to estimate the exponent by calculating the average of the logarithms of the ratios between the participations of adjacent planes

$$a_{surf}(n) = \frac{1}{b-1} \sum_{c=1}^{b-1} \ln \left( \frac{P_{\text{plane}}(c)}{P_{\text{plane}}(c+1)} \right) + \frac{1}{b-1} \sum_{c=b+1}^{2b-1} \ln \left( \frac{P_{\text{plane}}(c)}{P_{\text{plane}}(c-1)} \right)$$

(2.9)

where the second sum takes the lower part of the slab into account. However, the elements of the sum may become singular if $P_{\text{plane}}(c) \ll 1$ for some $c$ (as can be seen in the example fig. 2.3a between planes 3 and 4) and therefore this approach is numerically unstable – large negative exponents frequently outweigh the ones reflecting the general tendency of decaying participation into the slab.

Also, the sums are telescopic (also known as “balancing pairs”) due to

$$\ln \left( \frac{P_{\text{plane}}(c)}{P_{\text{plane}}(c+1)} \right) = \ln (P_{\text{plane}}(c)) - \ln (P_{\text{plane}}(c+1)),$$

i.e.

$$\sum_{c=1}^{b-1} \ln \left( \frac{P_{\text{plane}}(c)}{P_{\text{plane}}(c+1)} \right) = \ln (P_{\text{plane}}(b-1)) - \ln (P_{\text{plane}}(1)),$$

which thwarts the original attempt to compare adjacent layer participations.

The use of different means (for example the geometric mean) suffers from the same numerical instabilities as the arithmetic mean, so the initial idea of estimating an exponential decay rate was abandoned.

Instead, I propose a simpler way to analyse the attenuation profile based on the values of the attenuation profile points rather than their ratios. As before, the slab consists of $2b-1$ planes, enumerated by $c$, such that the plane in the middle of the slab is numbered $c = b$. I first consider the part of the slab enumerated from 1 to $b$. The other part can then be treated symmetrically. Let $w_b(c)$ be a weighting function defined by

$$w_b(c) = \frac{1}{2} - \frac{1}{\pi} \arctan \left( \frac{12(c - \frac{b}{2})}{b} \right).$$

(2.10)

This function, as shown in fig. 2.3b for $b = 12$, has the following numerical properties for every $b > 0$:

1. $\lim_{c \to \infty} w_b(c) = 0$, $\lim_{c \to -\infty} w_b(c) = 1$,
2. $w_b \left( \frac{b}{4} \right) = \frac{3}{4}$, $w_b \left( \frac{3b}{4} \right) = \frac{1}{4}$, hence $w_b \left( \frac{b}{4} \right) = \frac{1}{4}$,
3. $w_b(0) \approx 0.92$, $\int_0^b w_b(x) \, dx \approx 0.35 \cdot b$, $w_b(b) = 0.04$.

A change of the parameter $b$ converts corresponds to a stretching of the abscissa. Summation of the $w_b$–weighted attenuation profile values yields a parameter that can be used for deciding on the degree of surface localisation of a certain mode:

$$a_{surf}(n) = \sum_{c=1}^{b} w_b(c-1) \cdot P_{\text{plane}}(n,c) + \sum_{c=b+1}^{2b-1} w_b(2b-1-c) \cdot P_{\text{plane}}(n,c).$$

(2.11)

The second sum in (2.11) takes the lower half of the slab with plane indices from $p = b$ to $p = 2b-1$ into account. Note that summation starts at $p = b+1$ to avoid double counting of the middle layer. Due to the normality property (2.8), the behaviour of this parameter can now easily be connected to the degree of localisation at the surface:

The displacements of atoms near the surface are weighted higher than the displacements of atoms inside the slab. If and only if mode $n$ is a surface mode, atoms at the surface are participating most, resulting in a value of $a_{surf}$ near unity. If all planes participate equally in mode $n$ then $P_{\text{plane}}(n,c) = \frac{1}{m}$ for all $c$ and a value of $a_{surf}$ of around $\frac{35 \cdot 1}{m^2} \approx 0.35$ results (the factor of two stems from the sum over the two sides of the slab). The mode could even be localised at the centre of the slab, in which case $a_{surf}$ almost vanishes.

I therefore propose the following criterion for detection of a surface mode:

Mode $n$ is considered a surface mode if the function $a_{surf}$ exceeds a certain critical value $0.35 < a_{crit} \leq 0.92$:

$$a_{surf}(n) > a_{crit}.$$ (2.12)

Note that the weighting function is not perfectly flat anywhere. If it were nearly flat near the surface, surface and sub-surface modes could not be distinguished. Due to the larger derivative (modulus) of the weighting function in the intermediate area, however, surface and subsurface mode $a_{surf}$ values are still sufficiently separated from bulk mode values.

#### 2.3.5. Properties of the Proposed Criterion

1. It is numerically stable. Singularities as in (2.9) do not occur.
2. It is smoothly scalable. It can be applied to slabs of all thicknesses by adapting the parameter $b$ in eq. (2.10), yielding comparable results. Imagine for example doubling the number of planes by doubling the distance between the old planes and inserting a new one between every two old ones. The newly introduced planes will be weighted similarly to their neighbours.
3. The cutoff value $a_{crit}$ is arbitrary and can therefore be parameterised, based on a histogram of the values $a_{surf}(n)$ over all $n$.
4. The criterion is applicable to other localisation problems. Instead of using the number $p$ of the plane, starting from the surface, as argument for the weighting function, the distance from any defect of interest can be used. The parameter $b$ in (2.10) will then be the maximum distance. This way, localisation at a
line (e.g. a step at the surface) or at a point (e.g. a point defect, kink or adsorbed molecule) can be analysed, forming criteria \( a_{\text{line}} \) and \( a_{\text{point}} \). Due to the smoothness of the weighting function, all distances are treated properly. This is a considerable extension of applicability compared to attenuation profile approaches that rely on a layered structure in the supercell.

5. It can be generalised. Consider the new weighting function

\[
\psi_b^{(\sigma, \tau)}(c) = \frac{1}{2} - \frac{1}{\pi} \arctan \left( \frac{\sigma (c - \frac{b}{2})}{b} \right)
\]

Previously, I have described \( \psi_b = \psi_b^{(12,3)} \). This choice of parameters \( \sigma = 12, \tau = 3 \) is essentially arbitrary but was chosen to yield a good resolution for the problem of finding surface modes. Now

\[
\psi_b^{(\sigma, \tau)} \left( \frac{b}{\tau} \right) = \frac{1}{2},
\]

i.e. \( \tau \) is the position of the half maximum in units of \( b \) and

\[
\psi_b^{(\sigma, \tau)} \left( \frac{b}{\tau} - \frac{b}{\sigma} \right) = \frac{3}{4} \psi_b^{(\sigma, \tau)} \left( \frac{b}{\tau} + \frac{b}{\sigma} \right) = \frac{1}{3},
\]

i.e. \( \sigma \) is the steepness of the transition from one to zero in units of \( b \).

This means that \( \tau \) specifies how deep into the slab modes are allowed to penetrate to still be considered surface modes and \( \sigma \) specifies how closely this demand has to be followed. Criteria with different properties can thereby be constructed. However, I expect this change only to affect the resolution of the criterion, rather than its qualitative result.

Other weighting functions of similar shape may be used, such as Fermi functions or cosine functions such as

\[
\frac{1}{2} + \cos \left( \frac{f(c)}{b} \pi \right), \quad f(1) = f(2b - 1) = 0, \quad f(b) = b
\]

to subtly influence the behaviour of the criterion.

As the criterion functions \( a_{\text{surf}}, a_{\text{line}} \) and \( a_{\text{point}} \) measure the decay or attenuation of ionic participation with the distance from the defect studied, I call them respectively surface, step and point defect attenuation parameter, depending on the defect studied.

2.4. Data Analysis Using the Simulated Frequency Resolved Optical Gating (FROG) Method

Frequency Resolved Optical Gating is an experimental technique used to analyse laser fields. I will use it to analyse laser fields constructed with the optimal control method and molecular dynamics trajectories.

A density function \( F(T, \omega) \) is generated which measures the distribution of frequencies \( \omega \) at a given time \( T \) in the function to analyse. Experimentally, this is done by measuring the cross-correlation of a field \( \varepsilon(t) \) with a Fourier limited pulse \( g(t) \) or, more usually, the autocorrelation of \( \varepsilon(t) \). This choice is born out of necessity for very short pulses (where pulses of even shorter length are not available). It also guarantees that time and frequency resolution are balanced.

Computationally, the time dependence of the frequency of the function \( \varepsilon \) can be calculated via

\[
\frac{d}{dt} \int_{-\infty}^{\infty} g(T - t) \varepsilon(t) e^{i\omega t} dt = g(T) \varepsilon(T)
\]

which is essentially the Fourier transform of \( g(T - t) \cdot \varepsilon(t) \), i.e. the pulse multiplied by a gate function \( g \). Fig. 2.4 shows an illustrative example of the transformation process, where the FROG trace of a linearly chirped pulse is calculated. It can be seen that the gate function is slid over the data to be analysed and for each gate function position the Fourier transform is determined. Note that choosing a very broad gate function results in reduced time resolution while choosing a very sharp one results in reduced frequency resolution. This necessitates a compromise in the choice of gate function.

In step (3), the spectra corresponding to the different gate function positions are collected and drawn as a contour plot with time along the abscissa and frequency shown in the ordinate. Images of this kind are presented in chapters 5 and 6. They allow to gauge the time-dependence of the frequency (also called “chirp”). For the calculation of simulated FROG traces I have used a Gaussian gate functions

\[
g(T) = \frac{1}{\sqrt{2\pi} \sigma} e^{-\frac{(T - T_0)^2}{2\sigma^2}}
\]

where \( \sigma = \frac{T}{10} \) when \( T \) is the total pulse time or total time of the trajectory. This yields a good resolution for the benefit of discussing the structure of the pulse.
Figure 2.4.: Illustrative example for theoretical construction of a FROG trace. (a) An artifical pulse with a Gaussian envelope and a linear chirp is (1) multiplied with a gate function \( g(T - t) \) for different times \( T \). (b) Temporally confined pulses with the gate function as envelope and a narrower frequency distribution. Shown from top to bottom are the pulses resulting from \( T = \frac{1}{4}T \), \( T = \frac{1}{2}T \) and \( T = \frac{3}{4}T \), where \( T \) is the total time of the pulse shown in (a). (2) The spectra of these pulses are calculated by the Fast Fourier Transform (FFT) technique. (c) Note that the spectra of the gated pulses have a finite width since the gating function has a finite width. The narrower the gate function is, the wider will the corresponding spectrum become. (3) The gated pulse spectra are assembled in a contour plot (d). It clearly demonstrates the linear chirp.

Chapter 3. Localisation of Vibrational Modes at Ionic Crystal Surfaces

Aims: This chapter deals with the calculation of the normal mode structure at the surfaces KBr(001), MgO(001) and CaF$_2$(111). This allows to gauge the frequency ranges of crystalline vibrations localised at the surface which is important for the interaction with adsorbed molecules.

Since surface defects such as steps are preferred adsorption sites, systems with such defects are also modelled for the three surfaces. Phonon mode localisation at steps is analysed. Zero-dimensional defects, such as kinks in surface steps, are exemplified by considering normal modes localised at the corners of a large cube of MgO.

Methods: Lattice dynamics (section 2.1) within the shell model (section 2.2) are employed as implemented in the GULP$^{93}$ program. The crystal surface is modelled within the periodic slab approach or, for corners, by a finite cluster. The attenuation parameters \( a_{\text{surf}} \), \( a_{\text{line}} \) and \( a_{\text{point}} \) presented in section 2.3.4 are used to analyse normal mode localisation at surfaces, steps and corners.

Results: Surface modes for the MgO(001), KBr(001) and CaF$_2$(111) surfaces are detected and described. Surface modes exist at frequencies unoccupied by the bulk spectrum (in lagoons of MgO and CaF$_2$ and in the vibrational gap in KBr) but also overlapping with it (resonant surface modes). Ambiguous modes exist due to the finite size of the supercell model but a physically relevant criterion cutoff can be extracted from histogrammatic considerations.

Normal modes that have a frequency split from the bulk spectrum are generally localised more strongly than resonant local modes. Out of the materials studied, normal modes localised at a surface step ("step modes") exist only in MgO and KBr. The maximum degree of localisation is weaker in MgO, as it has no pronounced phonon band gap. Normal modes localised at the corners of an MgO cube exist; their
counterparts in a surface step with a kink are extrapolated from the displacements of the corner modes.

3.1. Introduction

Molecules adsorbed on a crystal surface can exchange energy with it by vibrational interaction. The natural coordinates for describing vibrations in crystals are vibrational normal modes, the modes of collective motion of atoms that do not interact with each other in the harmonic approximation. These vibrational normal modes can be distinguished by their frequency (or energy), their wave vector and by the degree to which certain atoms participate in the mode.

The aim of this chapter is to calculate vibrational modes of three ionic crystal surfaces – MgO(001), KBr(001) and CaF$_2$(111) – and analyse them to find out whether surface modes exist and what their properties are. The introduction of a surface to an infinite bulk crystal can be seen as a two-dimensional crystal defect. The introduction of a step at the surface represents an additional one-dimensional defect. The presence of modes localised at steps is another question treated in this chapter. It is important because at steps the polarisability of anions is often increased due to their lower coordination and hence steps can become preferred adsorption sites for admolecules at a surface.

The analysis of the surface-localised vibrational normal modes of some ionic crystals presented in this chapter will serve to justify the choice of HCl on the MgO(001) terrace used in the next few chapters as example system for quantum control at a crystal surface.

Note that, in contrast to the molecular dynamics calculations discussed in the second half of chapter 5, atoms are not displaced from their minimum energy positions in lattice dynamics and the dynamical properties of the crystal are described well only if the harmonic approximation is valid and the system remains near the equilibrium geometry.

3.1.1. Previous Results

A well-known example for a surface mode is the Rayleigh wave which was predicted by Rayleigh in 1885 as a special solution to the problem of vibrations in a continuous, semi-infinite elastic medium. It is characterised by a rapid decay of vibration into the medium, such that 90% of the vibrational energy is found up to a depth of one wave length.

First microscopic calculations of surface modes of atomic lattices, using Green’s functions, were carried out by Lifshitz and Rosenzweig in 1948. The first calculations of surface phonon dispersion curves using an atomistic model were done by de Wette and co-workers in 1971.

Figure 3.1.: Theoretical MgO dispersion curves. (a) Shell model unrelaxed slab calculation with 15 layers (dashed). (b) Rigid ion model slab calculations with 15 layers. Lower panel: with charge transfer at the surface. The k-point labels are $\Gamma = (0,0,0)$, $X = (0,0,5,0)$ and $M = (0,5,0,0)$. Both taken from ref. 101. Permission requested but no reply.

The lowest energy mode in atomistic models of an ionic slab usually has Rayleigh-mode character. However, the participation of atoms in this mode often decays more slowly than the Rayleigh wave with distance from the surface. It is then called “generalised Rayleigh wave”.

The presence of a surface introduces two perturbations to the model of the infinite bulk crystal: A change of the Madelung field due to the truncation of the crystal and a change in the short-range forces acting on the surface atoms due to their reduced coordination. In purely ionic crystals, this often causes the force constants near the surface to decrease, i.e. the frequency of surface modes is lowered with respect to the unperturbed modes. This is in contrast to predominantly covalent systems like silicon or germanium, where the force constants frequently increase near the surface. In mixed ionic/covalent systems, surface modes of increased frequency also exist (see for example ref. 99).

Slab calculations of ionic crystal surfaces predict that modes localised at the surface plane have lower frequency than modes localised at the first sub-surface plane and so on up to a depth that is determined by the strength of the perturbation caused by the introduction of the surface (depending on the crystal).

Experimental measurements of surface phonon dispersion curves have been developed by Ilbach and Mills using Electron Energy Loss Spectroscopy (EELS) and by Toennies and co-workers using Inelastic Helium Atom Scattering (HAS). The HAS technique is widely used, mostly to measure low-energy mode excitations, due to its favourable properties such as high intensity, low energy, monochromatism, sensitivity only to the surface, charge neutrality (avoiding the charging problems of EELS), chemical inertness and high resolution. It has recently been further developed in order to find higher energy modes such as shear horizontal and optical surface modes in the NaCl(001) surface and high frequency surface modes such
Localisation of Vibrational Modes at Ionic Crystal Surfaces

Chapter 3

Figure 3.2: Comparison of theoretical and experimental KBr dispersion curves. (a) Comparison of shell model relaxed slab calculation with 15 layers (dashed) and helium atom scattering (HAS) measurement \cite{106} (symbols). (b) Comparison of breathing shell model Green’s function calculation (no surface relaxation) \cite{109} with the same experimental results. The k-point labels are \( \Gamma = (0, 0, 0) \), \( M = (0.5, 0.0, 0) \) and \( X = (0.5, 0.5, 0) \). Note that the frequencies are supplied as angular frequency \( \omega \) in units of \( 10^{13} \text{rad s}^{-1} \), which translate to a frequency \( \nu \) in units of \( 10^{12} \text{THz} \). Both figures reproduced from ref. 101. Permission requested but no reply.

as in CaO(001) \cite{106}. Furthermore, all-optical techniques using time-resolved second-harmonic generation have been developed by Tom and co-workers, which allow to probe modes at buried interfaces \cite{107}.

Fig. 3.1a shows a dispersion spectrum from a shell model slab calculation for the MgO(001) surface \cite{102}. Note that the frequencies are supplied as angular frequency \( \omega \) in units of \( 10^{13} \text{rad s}^{-1} \), which translate to a frequency \( \nu \) in units of \( 10^{12} \text{THz} \). The maximum frequency in fig. 3.1a is therefore \( \omega = 135 \text{THz} \rightarrow \nu = 21.5 \text{THz} \). The dispersion spectra from rigid ion calculations in fig. 3.1b (ref. 101) show the typical overestimate of optical frequencies mentioned in section 2.2. A calculation taking polarisation at the surface into account is shown in the lower panel of fig. 3.1b. It predicts a larger number of surface modes split off from the lowest bulk band. For both models, the overall shapes of the dispersion spectra agree, with lagoons predicted around the \( \Gamma \) and \( X \) points.

A comparison of shell model slab calculation and HAS results for the KBr(001) surface can be seen in Fig. 3.2a. Due to the larger anion-cation mass ratio, KBr has a gap between the acoustic and optical bands, at 2.8 THz. Lagoons are reported in the optical band at the \( X \) point and, to a small extent, the \( \Gamma \) point. A good quantitative agreement between theory \cite{108} and experiment \cite{109} is reported, especially for the modes that are split from the bulk bands. Fig. 3.2b shows a comparison of the same experimental results with breathing shell Green’s function calculations (using the unrelaxed surface) \cite{109}, where the polarisation of the modes is depicted. Again the agreement between theory and experiment is quite good. Note that the measured surface-localised branch in the right-hand third of the dispersion spectrum is not predicted theoretically. The maximum frequency in fig. 3.2a is \( \omega = 31 \text{THz} \).

Figure 3.3.: Theoretical CaF\(_2\) dispersion curves from a shell model unrelaxed slab calculation with 19 layers. The k-point labels are \( \Gamma = (0, 0, 0) \), \( M = (0.5, 0.0, 0) \) and \( K = (\frac{1}{2}, \frac{1}{2}, 0) \).

Theoretically predicted surface modes and resonances are marked by full and dashed lines, respectively. Experimental points are marked by filled circles. Image from Jockisch et al. \cite{111} Permission requested but no reply.

\[ \rightarrow \nu = 4.9 \text{THz} \]

The CaF\(_2\)(111) surface phonon Density Of States (DOS) based on a shell model has been calculated and compared to the bulk DOS by Allan and Mackrodt \cite{110}. CaF\(_2\) surface dispersion curves have been presented by Jockisch et al. \cite{111} Lagoons are predicted at the \( K \) point and between the \( M \) and the \( \Gamma \) points. Experimental points are marked by filled circles.

I will repeat these calculations using shell model parameters that are specially geared towards reproducing elastic properties of the crystals and extend previous results by analysing the surface localisation quantitatively using the attenuation parameter and adding a study of phonon mode localisation at steps in the surfaces and at corners of an MgO cube.

3.2. Setup of Calculations

3.2.1. (001) Surfaces of MgO and KBr

The MgO and KBr bulk structures can, in analogy to NaCl, be built up as a face-centred cubic Bravais lattice with a primitive unit cell consisting of the cation at \( (0, 0, 0) \) and the anion at \( (1, 1, 1) \).

To build up the supercell used for the (001) surface, an odd number of atomic layers consisting of one cation and one anion each are stacked in alternating positions (as illustrated in fig. 3.4a). The surface translational vectors then enclose an angle of 90° (fig. 3.4b). An odd number of layers is used in order to avoid a macroscopic total dipole-moment due to different surface relaxation of anions and cations which may lead to supercell interaction errors in a periodic calculation. Three-dimensional periodic boundary conditions (PBC) are used, i.e. an alternation of crystal slabs with finite vacuum gaps is used to model surfaces.

Using a variant of the Ewald summation technique, lattice dynamics can also

Figure 3.4: Setup of surface mode calculations in MgO and KBr. (a) Side view of the unit cell with an odd number of atomic layers and two atoms in the surface unit cell. (b) Top view at the surface with the unit cell atoms in black. The surface is built up by translating the unit cell along multiples of the lattice vectors (shown as arrows). Images of the unit cell under this operation are shown in gray to illustrate the orientation of the crystal relative to the surface lattice vectors.

The calculation of surface steps requires a larger unit cell in order to minimise interaction between steps (that are periodically repeated parallel to the surface). A side view of the unit cell is shown in fig. 3.5. It is two atoms deep and 2y atoms wide, were y is the width of the terraces between the steps. The slab has two different thicknesses, b in the thinner and b + 2 in the thicker half, modelling atomic steps at the top and the bottom of the slab. The surface lattice vectors are collinear with the lines connecting nearest neighbour ions. In the largest calculations used, y = 16 and b = 13. Note that each unit cell has four steps, A, B, C, D. All these places of localisation are to be observed when deciding on whether a given normal mode is a step mode.

With the exception of Γ-point and bulk calculations, all calculations in this chapter were performed using eleven sampling k-points per segment connecting the corners of the irreducible part of the Brillouin zone.

An extension of this approach to kinks in surface steps would make the unit cell too large for a viable calculation. Therefore a corner in MgO was simulated by using an isolated block of 8 × 8 × 8 ions. Note that this means that no periodicity is implied.

Table 3.1: Shell model parameters for the simulation of MgO and KBr. Top: shell model charges and force constants; bottom: Buckingham potential \( b(r) = A e^{-r} - \frac{C}{r^6} \) parameters. Interaction between Mg and Mg is Coulombic only. MgO parameters are due to ref. 112, KBr parameters are due to ref. 113.

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{ion} & \text{charge } [e] & \text{core-shell spring constant} \\
\hline
\text{Mg core} & 2.000 & \\
\text{O core} & 0.8107 & \\
\text{O shell} & -2.8107 & 46.128 \text{ eV/ Å} \\
\text{K core} & 0.988 & \\
\text{Br core} & 1.717 & \\
\text{Br shell} & -2.705 & 24.66 \text{ eV/ Å} \\
\hline
\text{ion1} & \text{ion2} & A [\text{eV}] & \rho [\text{Å}] & C [\text{eVÅ}^6] & \text{cutoff } [\text{Å}] \\
\hline
\text{Mg core} & \text{O shell} & 1275.2 & 0.5012 & 8.0 \\
\text{O shell} & \text{O shell} & 12761.301.1490 & 20.37 & 8.0 \\
\text{K core} & \text{K core} & 3796.9 & 2663 & 183.8 & 4.8 \\
\text{K core} & \text{Br shell} & 2944.0 & 0.3295 & 0 & 4.8 \\
\text{Br shell} & \text{Br shell} & 2948.2 & 0.3164 & 183.8 & 4.8 \\
\hline
\end{array}
\]


*At the time of writing this, a new version of GULP is in its testing phase that can use two-dimensional boundary conditions.
To model the interionic interactions, the shell model was used. As already mentioned in section 2.2, this is a useful compromise between the rigid ion model, which suffers from overestimated optical frequencies, and higher accuracy methods such as the breathing shell model or ab initio methods which would prove too demanding for the purposes of this project.

Table 3.1 reviews the shell model parameters used to model MgO and KBr. The Buckingham potential is discussed in more detail in appendix D. The parameters for MgO are due to Stoneham and Sangster and have been used in a number of studies, for example to model an AFM tip. The KBr parameters are due to Catlow et al. The parameters used are specifically fitted to reproduce elastic properties of the crystals, which is what is needed for this chapter.

### 3.2.2. The CaF\(_2\)(111) Surface

The CaF\(_2\) crystal can be built up using a face-centred cubic Bravais lattice with three ions in the primitive unit cell, Ca\(^{2+}\) at \((0,0,0)\), and one F\(^-\) each at \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\) and \((\frac{3}{4}, \frac{3}{4}, \frac{3}{4})\). The bulk crystal can also be built up by the supercell shown in fig. 3.6a with the coordinate system aligned such that the (111) surface normal is in z-direction. This unit cell consists of three layers with one Ca and two F ions each. Note that these layers are not perpendicular to the (111) vector. More layers can be added by continuing the sequence A–B–C periodically.

A supercell with 15 ions, i.e. five layers, was chosen for the calculations of the (111) surface. This allowed fast calculations and was sufficiently extended to observe surface localisation. A view onto the surface is shown in fig. 3.6b. Note that the fluoride ion 2 protrudes from the rest of the crystal, while the fluoride ion 1 is below the calcium cation in that layer. The surface lattice vectors are indicated by arrows.

The (111) surface is the most stable in CaF\(_2\). This can be rationalised by looking at fig. 3.6a as follows: a crystal cleaves along the planes where the layer distance is largest and with it the interlayer cohesion is weakest. In the MgO and KBr lattices, this is the (001) plane. Figure 3.6a demonstrates the large interlayer distance \(d\) along the (111) vector. The surface consists of stoichiometric layers and hence is also stoichiometric. The ions at the boundary are fluoride ions.

Fig. 3.6b also shows an alternative, straight shape of the unit cell. This can be constructed by translating ion 2 along the negated translational vector II. This unit cell lends itself to the construction of a rectangular surface supercell which can be used to set up a supercell with a surface step. A view down onto a surface with a step is shown in the top panel (top view) of fig. 3.7.

Unlike for the MgO and KBr (001) surfaces, where a single layer of ions can be removed, the only stoichiometrically correct way to remove ions from the CaF\(_2\) surface is to remove a triple ionic layer, as shown in the lower panel (side view) of fig. 3.7.
ion charge [e] | core-shell spring constant
--- | ---
Ca core | 0.719
Ca shell | 1.281
F core | 0.378
F shell | -1.378

Table 3.2: Shell model parameters for the simulation of MgO and KBr. Top: shell model charges and force constants; bottom: Buckingham potential \( b(r) = A e^{-\alpha r} - \frac{B}{r} \) parameters from ref. 116.

The dashed grey circles specify the positions where ions have been cut away, leaving a raised terrace in the middle of the supercell, analogous to the raised terrace in fig. 3.5 for MgO and KBr.

It is not clear a priori which of the positions 1 or 2 the F ion at the left step will take. According to ab initio Hartree-Fock calculations done by Huisenga, Reichling and co-workers, the structure with the fluoride ion at position 1 is more stable, so I have used this configuration in the calculations presented.

As before, \( b \) and \( b + 2 \) denote the number of monolayers in the slab, respectively (3b to \( 3b + 6 \) ionic layers in CaF\(_2\)), while \( y \) denotes the width of the terraces. The step localisation analysis below has been performed on a supercell with \( y = 12 \) and \( b = 6 \).

As before, the shell model is used as a compromise between accuracy and computational effort. Table 3.2 reviews the shell model parameters used to model CaF\(_2\). They were modified by Foster from a set developed by Binks specifically to reproduce well the experimental bulk elastic and dielectric constants. These are properties that are relevant for lattice dynamics calculations, so it is important that this parameter set was chosen.

Monolayers at the CaF\(_2\)(111) surface consist of three ionic layers. For the purpose of defining the \( a_{\text{plane}} \) attenuation parameter, the ionic layer furthest from the middle of the slab is postulated as location of the surface. The weighting function \( w_R(r) \) assigns different weights to different ionic layers within one monolayer. \( w_R(r) \) is, however, flat enough near the surface that this will not affect the physical relevance of the result. This argument holds similarly for the step in the surface.

### 3.3. Results

#### 3.3.1. Bulk Densities of States

To demonstrate the different vibrational properties of the bulk crystals, I have calculated the bulk Densities Of State (DsOS) of the three compounds considered in this study with a k-point sampling of \( 15 \times 15 \times 15 \) k-points in the Brillouin zone.

#### 3.3.2. Thin Films as Model for a Crystal Surface

A crystal surface can be modelled in one of several ways. Leaving aperiodic approaches aside, a supercell may be used to model the system where, to conserve computational effort, lattice dynamics are to be performed only on the ions near the surface of the film. This would have the advantage that the “fixed” ions in the supercell could be placed at their bulk coordinates, so that a semi-infinite surface could be approximated.

I have performed calculations of the MgO(001) surface with this setup. Among others, modes localised at the interface between the lattice dynamics region and the fixed region resulted (as illustrated in fig. 3.9). This implies that the interface acts as an open end to the phonons, a behaviour that is clearly unphysical as the interface is artificial. Therefore, this model for a semi-infinite crystal has to be discarded for the purpose of dynamical calculations. Instead, I have used a supercell where all ions take part in the lattice dynamics calculation.

The interest of this project lies with the normal modes of the slab and their frequencies. These properties are very sensitive to stress, so the translation vectors of the unit cells parallel to the surface were relaxed to zero stress. Strictly speaking, the results presented below correspond to the vibrations in a thin film (which may
3.3.3. Surface Relaxation

3.3.3.1. Surface Relaxation of the MgO(001) Surface

As a first step, the bulk lattice constant within the shell model of MgO was determined. It is 4.209 Å. In a slab, the ions near the surface react to the presence of the surface by relaxing with respect to their positions in the perfect lattice. The change $d_{12}$ of the spacing $d_{12}$ between the surface and subsurface layers is given as a percentage of the perfect lattice spacing (half of the lattice constant) $d$

$$\delta d_{12} = \frac{d_{12} - d}{d} \cdot 100\% = \left( \frac{d_{12}}{d} - 1 \right) \cdot 100\%. \quad (3.1)$$

From experimental evidence, most directly through atomic force microscopy,$^{119}$ it is known that the MgO and KBr (001) surfaces do not reconstruct, so the ions in the surface must, by symmetry, retain the perfect crystal structure parallel to the surface (x and y-directions). Normal to the surface (in z-direction), the symmetry is broken, so that anions and cations can have different z-coordinates near the surface. The surface rumpling $\Delta_1$ is defined as the difference between the z-coordinates of anions and cations in the surface plane, again as percentage of the ideal lattice spacing:

$$\Delta_1 = \frac{z_{anion} - z_{cation}}{d} \cdot 100\%. \quad (3.2)$$

The lattice constant is defined ambiguously in slab calculations, as the thickness of the slab is finite and therefore the lattice constants parallel and normal to the surface are different. The lattice constant parallel to the surface, denoted as $d^p$, be deposited on a substrate with which it interacts very weakly). It may be hoped, however, that at a sufficient thickness the results approach the surface vibrations of a semi-infinite crystal. It must be stressed that the model system is finite in the direction of the surface vector, so the problem of surface-localisation is ill-defined. However, normal modes whose ionic participation decays towards the slab middle will be identified as surface modes.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
<th>Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{12}$</td>
<td>2.1276 Å</td>
<td>$\Delta_1^{anion-cation}$ = 0.0519 Å</td>
</tr>
<tr>
<td>$d^p$</td>
<td>2.1137 Å</td>
<td>$\Delta_1^{cation}$ = +0.66%</td>
</tr>
</tbody>
</table>

Table 3.3.: Relaxation of the MgO surface in shell model calculations as defined in eqs. (3.1) and (3.2). PW-DFT and EC-DFT results presented in the following chapter as well as some experimental results are shown for comparison. More experimental results and detailed discussion can be found in section 4.3.1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
<th>Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{12}$</td>
<td>3.2543 Å</td>
<td>$\Delta_1^{anion-cation}$ = 0.1027 Å</td>
</tr>
<tr>
<td>$d^p$</td>
<td>3.262 Å</td>
<td>$\Delta_1^{cation}$ = -0.002 Å</td>
</tr>
</tbody>
</table>

Table 3.4.: Relaxation of the KBr surface in shell model calculations. Relaxation parameters as defined in eqs. (3.1) and (3.2).

results from the relaxation of the unit cell dimensions and is uniform over the whole slab, while the lattice constant perpendicular to the surface, denoted as $d^s$, is taken as the distance between two layers in the middle of the slab, because there the bulk situation is approximated. The parameter $\delta d_{12}$ then measures the percentage difference between the outermost layer distance and the innermost one in the slab. The relaxation can also be compared to the bulk lattice constant $d^b$, determined with the same shell model parameters. The corresponding relaxation parameters are shown in table 3.3.

The relaxation of the surface layer $\delta d_{12}$ is more susceptible to the difference in the choices of lattice constant than the rumpling $\Delta_1$ (compare the definitions, eqs. 3.1 and 3.2). Compared to the bulk calculation, the slab contracts by 0.67% parallel to the surface and expands by 0.2% normal to the surface.

A comparison of surface relaxation parameters for MgO derived from different experimental and theoretical techniques (ref. 120 and refs. therein) is presented in the context of ab initio calculations in the next chapter, tables 4.1 and 4.2. For the moment, it suffices to say that the surface relaxation as calculated within the shell model agrees well with the present data.

3.3.3.2. Surface Relaxation of the KBr(001) Surface

In MgO, the value of the lattice spacing $d$ depends on the direction in the slab calculations and both values are different from the bulk value. In KBr, all these values are approximately the same, at 3.262±0.002 Å.$^{121}$ Table 3.4 therefore shows only one set of rumpling parameters according to $d = 3.262$ Å. These relaxation parameters agree well with previous results.$^{121}$

$^{119}$The relaxation with respect to the bulk distance due to formation of the surface is less than 0.05%. This is well within the error intrinsic to the model.

3.3.3. Surface Relaxation of the CaF$_2$(111) Surface

The hexagonal symmetry seen in the fig. 3.6b is present due to the fact that the surface does not reconstruct. As in the MgO and KBr (001) surfaces, the symmetry cannot be broken parallel to the surface in CaF$_2$(111), so the only parameter that can relax in this direction is the lattice vector. It is 3.7921 Å (3.8453 Å in the bulk shell model), i.e. the slab contracts by 1.38% parallel to the surface with respect to the bulk.

Normal to the surface, the slab has a layered structure, as shown in fig. 3.6a, which is not collinear with any bulk lattice vector, so the comparison of the relaxed surface slab with the bulk situation is not as straightforward as for MgO and KBr. However, the values measured in the surface result can be compared to the analogous values of a surface slab that is imagined to be embedded in the bulk, as seen in fig. 3.6a.

The relaxation of the distance between the surface and subsurface layer $\delta d_{12}$ is calculated as before (eq. 3.1), but the rumpling $\Delta z_1$ is replaced by the change in the difference of the $z$ coordinates of the calcium ion and the fluorine ions in the same layer, above and below the calcium (where “above” means further from the centre of the slab):

$$\Delta z_1^\text{surf} = \frac{z_1(\text{anion}) - z_1(\text{cation})}{d_{\text{bulk}}} - \text{sgn}(\alpha) \cdot \frac{z_{\text{anion}} - z_{\text{cation}}}{d_{\text{bulk}}} \cdot 100\%,$$

where $\alpha$ can be “above” or “below”:

$$\text{sgn}(\alpha) = \begin{cases} +1, & \alpha = \text{above}, \\ -1, & \alpha = \text{below}. \end{cases}$$

$z_{\text{bulk}}^X$ refers to the $z$ coordinate of ion X in the bulk at the same orientation and $d_{\text{bulk}}$ refers to the distance between the layers in the bulk. This construction makes the result comparable with the rumpling values $\Delta z_1$ in MgO and KBr defined in (3.2) and where $z_{\text{anion}} - z_{\text{cation}} = 0$. Just like in (3.2), a positive sign means that the anion is moving away from the centre of the slab compared to the bulk situation. Similar to (3.2), 100% corresponds to the distance between two successive layers. However, the distance between the layers in CaF$_2$ is $\sqrt{3}/2 \approx 0.82$ times the lattice constant, while in MgO and KBr (001) surfaces it is $\sqrt{3}/2$ times the lattice constant.

In order to specify the average position of a layer, the arithmetic average (denoted by “avg”) can be used or the ions can be weighted by the magnitude of their charge, i.e. Ca ions enter with twice the weight of F ions (denoted by “wgt”). Table 3.5 shows an overview of the relaxation of a CaF$_2$ slab consisting of nine layers, i.e. 27 ions.

When two values are the same due to symmetry constraints, the columns in table 3.5 are joined. A comparison of $\delta d_{\text{wgt}}$ and $\delta d_{\text{avg}}$ at the surface shows that the fluorine ions move further away from the centre of the slab than the calcium ions, an observation which is confirmed by the $\Delta z_1^\text{surf}$ values.

The $\Delta z_1^\text{surf}$ values are, at 0.1% to 0.4%, much smaller than in MgO and KBr (~3%). This indicates that the perturbation of the potential felt by the surface ions due to formation of the surface is much smaller in CaF$_2$ than in MgO and KBr.

### Table 3.5.

<table>
<thead>
<tr>
<th>location</th>
<th>$d_{\text{avg}}^{\text{surf}}$</th>
<th>$d_{\text{wgt}}^{\text{surf}}$</th>
<th>$\delta d_{\text{avg}}^{\text{surf}}$</th>
<th>$\delta d_{\text{wgt}}^{\text{surf}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface</td>
<td>3.1484 Å</td>
<td>3.1470 Å</td>
<td>+0.28%</td>
<td>+0.23%</td>
</tr>
<tr>
<td>centre of slab</td>
<td>3.1616 Å</td>
<td>3.1612 Å</td>
<td>+0.70%</td>
<td></td>
</tr>
<tr>
<td>bulk</td>
<td>3.1397 Å</td>
<td>3.1400 Å</td>
<td></td>
<td>-0.03%</td>
</tr>
</tbody>
</table>

### Changes in the Vibrational Densities of State due to Formation of a Surface

#### 3.3.4.1. Spectral Changes in MgO

In order to avoid a macroscopic total dipole-moment in the slab which would, due to periodicity, lead to errors in the calculation, the number of layers in all slab calculations is odd. This means, however, that bulk calculations corresponding to the slab supercells cannot be performed just by setting the vacuum gap to zero since that would cause ions of the same charge to touch at the interface.

Instead, the DOS resulting from lattice dynamics of the bulk unit cell with the Monkhorst-Pack k-point sampling scheme presented above in fig. 3.10a is used. The surface DOS is formed by sampling the boundary of the irreducible part of the Surface Brillouin Zone (SBZ). For the (001) surface of MgO and KBr, this is simply the isosceles triangle $\Gamma = (0,0,0)$, $M = (0.5,0,0)$, $X = (0.5,0.5,0)$ in reciprocal space, as illustrated in fig. 3.10b. This sampling was chosen because the results of this calculation can immediately be used to produce dispersion spectra.

Fig. 3.10a shows a comparison between the MgO surface DOS of a slab 15 layers thick and the bulk DOS. MgO is a comparatively hard crystal, with a maximum frequency of around 21.5 THz, and has no vibrational band gap. It is purely ionic, i.e. surface-localised normal modes are expected to be lowered in frequency with respect to their bulk counterparts. As no phonon band gap exists, high-frequency surface-localised normal modes must be resonant with the bulk spectrum.

Note that the resolution of the surface DOS (blue line in fig. 3.10a) is higher than that of the bulk DOS. Only the main structures should be considered. The surface DOS does not feature frequencies absent in the bulk DOS, i.e. surface modes are...
expected to be resonant with the bulk DOS. This is in accordance with previous work.\textsuperscript{101}

The change of the phonon density of states (DOS) due to the introduction of the surface can also be estimated by comparing the normalised DsOS of slabs with increasing thickness. This is because at larger thicknesses, the impact of surface modes diminishes due to the increasing number of bulk modes and constant number of surface modes.

Fig. 3.11a shows a comparison of the vibrational DOS at the $\Gamma$-point for MgO(001) slabs of different thickness. The DsOS were produced from the discrete lattice dynamics spectrum using Gaussian broadening. The width used is $\sigma = 0.05$ THz to yield a satisfactory resolution. It can be seen that, with the exception of the zero-frequency Rayleigh mode, no isolated spectral lines appear as the thickness progresses from fifteen (more bulk-like) to seven (more surface-like). This can also be seen by looking at the phonon DOS difference between the fifteen and seven layer calculations. This confirms that if surface-localised normal modes exist, they must be resonant with the bulk spectrum. This means that, rather than expressing itself in newly appearing peaks separated from the spectrum, surface localisation merely shifts some normal mode frequencies within the DOS.

3.3.4.2 Spectral Changes in KBr

Fig. 3.12 shows a comparison between the KBr surface DOS of a slab 15 layers thick and the bulk DOS presented above in fig. 3.8b. As for MgO, the surface DOS is formed by sampling the boundary of the irreducible part of the quadratic SBZ.

The surface DOS adds a small amount of density in the vibrational gap of the bulk spectrum but also introduces considerable changes resonant with the bulk spectrum. Surface modes are therefore expected to be found in the gap as well as resonant with the bulk DOS. This is in accordance with previous work.\textsuperscript{101}
3.3.4.3. Spectral Changes in CaF$_2$

Fig. 3.13 shows a comparison between the CaF$_2$ surface DOS of a slab 15 atoms thick and the bulk DOS presented above in fig. 3.8c. The surface DOS is formed by sampling the boundary of the irreducible part of the SBZ. For the (111) surface of fluoride structure crystals, this is the triangle $\Gamma = (0,0,0)$, $M = (0.5,0,0)$, and $K = (\frac{1}{2},\frac{1}{2},0)$, as illustrated in fig. 3.13b.\* 

The surface DOS does not feature frequencies absent in the bulk DOS, i.e. surface modes are expected to be resonant with the bulk DOS. This and the DOS change are in accordance with the calculation of the surface DOS by Allan and Mackrodt,\textsuperscript{110} where, however, a different parameterisation was used. The frequency range predicted here is somewhat smaller (maximum frequency of ~12 THz vs. ~14 THz).

3.3.4.4. Changes in the Dispersion Spectrum, Exemplified by MgO

It is instructive to observe the split of some surface vibrational modes from the dispersion spectrum of a slab with an even number of atomic layers by conducting lattice dynamics with changing vacuum gap. I have used slabs with eight atomic layers. Fig. 3.14 shows dispersion spectra from these calculations for four different distances. At each k-point, the lines can be read as stick-spectrum from bottom to top.

Fig. 3.14a shows the bulk crystal, i.e. the supercells touch. K-points perpendicular to the prospective surface were not used as they become irrelevant as soon as the gap is opened. Note that in these as in all following dispersion spectra, points are connected on the basis of the order of the frequencies of the modes, i.e. the lines do not cross, even though in a figure based on the symmetry of the modes they might.

Some of the degeneracies in fig. 3.14a split when a surface is introduced – most modes become slightly softer when the slabs are moved 0.5 Å apart (fig. 3.14b) due to the lower coordination of atoms at the surface. No clear qualitative changes can however be observed.

The situation changes drastically when the distance between the slabs is increased to 1 Å (fig. 3.14c). The perturbation introduced by the surface becomes strong enough to lift most degeneracies. The characteristic lagoons (empty spaces in the dispersion spectrum) can now be identified because the split modes densely populate the remainder of the spectrum. Some isolated surface modes can be identified because they reside in lagoons. One example for this is the Rayleigh mode that is split from the bottom of the transverse acoustic band. Another is the mode split off from the longitudinal optical band into the lagoon to the left from $k = (0.5,0.5,0)$ and around $f = 17$ THz.

The final image at the full distance of double the slab thickness (about 32 Å) (fig. 3.14d) is almost indistinguishable from the previous one, which is, incidentally, a good indication that the results discussed previously and in the following are converging with respect to the vacuum gap.
However, it has to be expected that surface modes other than those immediately identifiable by their splitting from the main bands exist. These are resonant energetically with bulk modes and hence play a more important role in the vibrational coupling of admolecules to the bulk than split surface modes. Such resonant normal modes obviously cannot be found by considering the normal mode spectra alone. Atomic participation in each mode has to be analysed in order to decide whether a normal mode is a resonant surface mode.

Automated algorithms for the detection of localised normal modes have been described in section 2.3.4. To analyse localisation at the surface, the $a_{\text{surf}}$ criterion function is used while localisation at lower-dimensional loci are analysed using the analogous criterion functions $a_{\text{line}}$ and $a_{\text{point}}$.

### 3.3.5. Surface Modes Detected with the $a_{\text{surf}}$ Criterion

Histograms of the surface localisation criterion function $a_{\text{surf}}$ from section 2.3.4 and the participation function $\hat{P}$ from section 2.3.3, eq. (2.5) for 15 layer slab calculations of MgO, KBr and CaF$_2$ are shown in fig. 3.15. The $\hat{P}$ histograms (shown in red) have peaks at or below 0.2. These stand for the majority of normal modes that involve almost all ions in the supercell. The tails at high values are made up of modes involving only few ions in the supercell. Some of these normal modes may, however, be delocalised, as the few ions participating may form sublattices extending over the whole supercell. Among the normal modes in the $\hat{P}$ histogram tail are also normal modes localised at the centre of the slab that are present due to the finite slab thickness.

In a semi-infinite periodic crystal, the sublattice modes and bulk modes avoiding the surface would not be detected as localised by the participation function $\hat{P}$ but since the model has a finite width, this distinction cannot be made.

The $a_{\text{surf}}$ criterion can distinguish between surface modes, normal modes localised at the slab centre and sublattice modes. The $a_{\text{surf}}$ histograms (shown in blue) have a broad peak around the medium value of 0.35 which was predicted as average value for a bulk phonon (the integral under the attenuation weighting function, as shown in fig. 2.3b). This demonstrates bulk type characteristics for the majority of vibrational modes. The tails of the histograms at higher values contain the most localised vibrational modes. Criterion threshold values, indicated by dotted lines, can be set such that only a few normal modes with the highest $a_{\text{surf}}$ values are identified as surface modes. Due to the more diffuse nature of the CaF$_2$ histogram, the threshold there has to be set lower to obtain a comparable number of surface modes.

**Figure 3.15:** Histograms for 15 layer slab calculations of some ionic surfaces of the $\hat{P}$ function of eq. (2.5) and the $a_{\text{surf}}$ function from section 2.3.4. From top to bottom MgO, KBr and CaF$_2$. Cutoff values to be used to identify surface modes are shown as dotted lines. It can be seen that the CaF$_2$ $a_{\text{surf}}$ histogram is more diffuse, while the $\hat{P}$ histogram is more sharply peaked at low values than for MgO and KBr.

3.3.5.1. Surface Modes of the MgO(001) Surface

Fig. 3.16 shows the dispersion spectrum of a 15 layer MgO slab with surface modes marked. Note that the order of the k-points in fig. 3.16 is reversed with respect to the previous results of fig. 3.1 (as are the dispersion diagrams for the other crystals). Lines in fig. 3.16 represent the dispersion relations for the 90 modes and points mark modes that were labelled as surface mode with the respective cutoff value of the $a_{surf}$ criterion function.

Fig. 3.16 demonstrates that the generalised Rayleigh wave is clearly split from the bulk and accordingly yields a comparatively high $a_{surf}$ criterion function value.

Optical surface modes can be found at the top end of lagoons around the $\Gamma$-point (this lagoon was not recognised earlier as it is not very wide) and $k = (0.5, 0.5, 0)$. Note that, at a threshold value of 0.6, another surface mode is detected at the bottom of the same lagoon. This means that it has split off from the top of its band, a sign that for this mode, the introduction of the surface increases the force constant. All other surface modes are resonant with bulk modes. A comparison with the earlier results in fig. 3.1a shows good agreement, however more detailed information about the degree of localisation at the surface can be extracted from fig. 3.16.

Resonant surface modes exist at the centre of the dispersion diagram and on the left below 10 THz (circled in the middle panel of fig. 3.16). These were not classified as surface localised in previous theoretical studies (fig. 3.1). This demonstrates that the surface attenuation parameter $a_{plane}$ is useful for comparing surface modes of different character on an equal footing, preventing such oversights.

The results seen in fig. 3.16 for different threshold values can be summarised by plotting the $a_{surf}$ value as height value in a three-dimensional plot (upper panel of fig. 3.17). The generalised Rayleigh mode, the lagoon modes and the section of k space where resonant acoustic modes exists (on the right) are clearly visible. The more weakly localised modes in the centre, which show up when lowering the threshold value of the criterion clearly contrast the $a_{surf}$ values of the surrounding modes and should therefore be labelled as surface modes.

Note that, as before, points are connected in fig. 3.17 based on the order of the frequencies of the modes, i.e. there are no crossings. Rather than appearing as a connected ridge of increased elevation, some surface modes show up as an unconnected series of peaks because of this.

The lower panel of fig. 3.17 shows a plot of the complementary participation function, which is the number of atoms minus the participation function (as defined in eq. 2.7)

$$P(n) = N - P'(n).$$

As the participation function has values between 1 and $N$, this has values between 0 and $N - 1$ and is high when a mode is localised, i.e. few atoms participate in it. While surface modes can be distinguished clearly in the upper panel of fig. 3.17, the threshold value is relaxed from 0.8 through 0.7 to 0.5-0.6.

Figure 3.16: Dispersion spectrum of 15 layer MgO slab with surface modes. From top to bottom, the threshold value is relaxed from 0.8 through 0.7 to 0.5-0.6.
Figure 3.17: Three-dimensional plots of the $a_{surf}$ value (upper panel) and participation function (lower panel) over the dispersion spectrum of the MgO(001) surface. The colour palette is goes from blue for 0% via green to red for 100%.

Figure 3.18: Displacement diagrams of some MgO slab modes. The dash-dotted line at the bottom shows the middle of the slab, i.e., the surface is drawn at the top. (a) Rayleigh type surface mode at $k = (0, 0, 0), f = 1.0$ THz, (b) surface mode (lagoon mode) at $k = (\frac{1}{2}, \frac{1}{2}, 0), f = 18.2$ THz, (c) surface mode at $k = (\frac{1}{2}, 0, 0), f = 12.7$ THz, (c) bulk mode at $k = (\frac{1}{2}, \frac{1}{2}, 0), f = 18.7$ THz, participation of ions in the middle is bigger than at the surface.

showing the results of the $a_{surf}$ criterion function, surface modes are largely drowned out by the abundance of modes with moderate participation function values in the lower panel. This demonstrates the better selectivity of the $a_{surf}$ criterion function compared to the participation function.

The graph of the complementary participation function has peaks wherever the graph of the $a_{surf}$ criterion function value has peaks. However, it has peaks elsewhere as well, belonging to modes localised in the middle of the slab, for example, or extended modes that involve only a sublattice of ions. As expected, this demonstrates the inability of the participation function to qualify the location of a localisation in a finite model.

The average participation function (over all k-points) of the 15 layer MgO slab is 14.3 (out of 30 ions). The peaks of the surface modes are, however, higher than the peaks belonging to modes localised elsewhere, so with a carefully chosen threshold value it may be possible to distinguish surface modes and modes localised elsewhere. However, use of the participation function alone does not provide any help with the choice of this threshold value. It can only be defined a posteriori with the knowledge of all surface modes in mind.

Fig. 3.18 illustrates the properties of some modes in MgO in the form of displacement diagrams. Note that the lengths of the vectors shown correspond to
mass-weighted eigenvectors as resulting from the diagonalisation of the dynamical matrix rather than actual displacements. The relation between the mass-weighted eigenvectors and the actual displacements was shown in eq. 2.3 on p. 43.

The different directions of the arrows in fig. 3.18 have to be explained: Away from the Γ-point, where the dynamical matrix (eq. 2.1) is Hermitean but not symmetric, the vibrational mode displacements have non-real eigenvalues. Let

\[ p_1 = |p_1| \cdot e^{i\omega_1} \text{ and } p_2 = |p_2| \cdot e^{i\omega_2} \]

be two eigenvector components, with an eigenvalue \( \omega \). The atomic displacements at time \( t \) from the equilibrium position then are

\[ x_1 = \frac{|p_1|}{\sqrt{p_1}} e^{i(\omega t + \omega_1)} \text{ and } x_2 = \frac{|p_2|}{\sqrt{p_2}} e^{i(\omega t + \omega_2)}, \]

so the relative phase between the eigenvector components is equal to the relative phase between the two different ion displacements. If there is a non-zero phase between two coordinate components of the displacement of the same ion, this ion will vibrate on an elliptical path rather than a linear one. Such a path cannot be shown, however, in a diagram of this kind.

What is shown, are the phases between ions. E.g. in fig. 3.18b the arrows pointing towards ions signify that at \( \omega t = 2\pi n \) the ion is displaced and at \( \omega t = 2\pi n + \frac{\pi}{2} \) it is at its equilibrium position, contrary to the intuitive notion that is valid for ions with arrows pointing away from them, where the ion is at its equilibrium position at \( \omega t = 2\pi n \) and displaced at \( \omega t = 2\pi n + \frac{\pi}{2} \).

The surface mode shown in fig. 3.18a is of Rayleigh type. The modes shown in fig. 3.18b and (c) are surface modes. Fig. 3.18d shows a mode with displacements increasing towards the middle of the slab, to contrast the surface modes.

### 3.3.5.2. Surface Modes of the KBr(001) Surface

The phonon dispersion spectrum of KBr (fig. 3.19) shows a marked contrast to that of MgO (fig. 3.16): MgO features much higher vibrational frequencies than KBr, (maximum frequencies – MgO: \( \sim 21.5 \) THz, KBr: \( \sim 6 \) THz). Due to the larger anion-cation mass ratio, KBr has a phonon band gap, so that modes appearing in the phonon band gap can immediately be identified as surface modes.

I will show in the following, however, that normal modes localised at the surface and resonant with the bulk spectrum exist in KBr as well. Unlike in MgO, the generalised Rayleigh wave is not so clearly split from the bulk spectrum and accordingly yields a lower \( \omega_{surf} \) criterion function value.

The normal mode of highest frequency is a longitudinal optical mode around \( 4.9 \) THz, in agreement with ref. 108. Overall, the results presented here agree very well with the previous results.

KBr has a phonon band gap between the optical and acoustic bands. Two normal modes between 2.5 THz to 3.5 THz exist at all k-points, showing up as uninterrupted
strings of dots in the dispersion spectrum. The higher of these is resonant with the bulk bands and would not be detected without inspection of the ionic displacement in the modes.

The lowest frequency surface mode is the generalised Rayleigh wave. Due to its extended nature, it is not detected at all k-points with higher threshold values. The number of atomic layers is, however, comparatively small at 15, so detecting these modes with the threshold value 0.6 (in the bottom panel of fig. 3.19) is satisfactory.

Several other surface modes do not span the whole k-space, most notably modes around (0.5, 0.5, 0). The lowest of these is a bulk resonant mode, while the two others split from the bottom of sub-bands into lagoons in the dispersion spectrum. At the threshold value of 0.6, a further mode is identified as a surface mode at the bottom of the optical band around (0.5, 0, 0).

By relaxing the criterion threshold value from 0.8 through to 0.5, more and more modes are designated as surface modes. The bulk resonant modes around the Γ-point from 2.3 THz downward (circled in bottom panel of fig. 3.19) are marked in fig. 3.2 as experimental results but not theoretical ones. The reason for this, it can now be said, is the weak localisation of these modes ($a_{surf} \leq 0.6$).

The results seen in fig. 3.19 for different threshold values can be summarised in a three dimensional plot of the $a_{surf}$ value (upper panel of fig. 3.20).

The generalised Rayleigh mode, the gap mode and the resonant optical surface mode are clearly visible, alongside with the lagoon modes and the section of k space where resonant acoustic modes exists (on the right). The less localised modes on the left are seen in comparison to their surroundings.

The lower panel of fig. 3.20 shows a similar plot of the complementary participation function. The average participation function (over all k-points) of the 15 layer KBr slab is 13.1 out of 30 ions. As before, the graph of the complementary participation function has peaks wherever the graph of the $a_{surf}$ value has peaks, however, it has peaks elsewhere as well, belonging to modes localised in the middle of the slab. This can be seen most clearly at the top frequencies below the lagoon and at the top frequency.

The diagrams in fig. 3.21 illustrate the atomic displacements corresponding to some modes in KBr. The surface mode shown in fig. 3.21a is an optical surface mode. The mode shown in fig. 3.21b shows the gap mode, an optical surface mode that only involves only a sublattice, i.e. has nodes on the ions to the right. (This immediately means that it is degenerate with a mode that involves the other sublattice.)

To contrast the surface modes to a bulk mode, which form the overwhelming majority of modes, I present in fig. 3.21c an optical mode which is actually localised around the middle of the slab, as the displacements become bigger with distance from the surface.
Figure 3.21.: Displacement diagrams of some KBr slab modes, all at $k = \left(\frac{1}{2}, 0, 0\right)$. The dash-dotted line at the bottom shows the middle of the slab, i.e. the surface is drawn at the top. (a) Optical surface mode at $f = 3.6$ THz, (b) sublattice optical surface mode (gap mode) at $f = 3.0$ THz, (c) bulk mode at $f = 2.2$ THz, participation of ions in the middle is bigger than at the surface.

Figure 3.22.: Dispersion spectrum of 15 layer CaF$_2$ slab with surface modes for criterion threshold values 0.85, 0.75 and 0.65.

3.3.5.3. Surface Modes of the CaF$_2$(111) Surface

Fig. 3.22 shows the dispersion spectrum of CaF$_2$ calculated with the present model. The overall shape agrees well with the previous shell model publication by Jockisch et al.\textsuperscript{111} but I find lagoons around the K and $\Gamma$ points, not between the M and $\Gamma$ points. I attribute this discrepancy to the fact that the results of ref. 111 are based on a slab model fixed at the bulk structure. The frequencies of surface modes detected for the threshold values 0.85, 0.75 and 0.65 are marked in the framework of the dispersion spectrum. These values were used as fewer normal modes reach $\alpha_{\text{surf}}$ values of 0.8 as seen in MgO and KBr. As it is possible to fill in the dispersion spectrum with more and more surface modes detected according to decreasing cutoff values, some experimental data points (fig. 3.3) around the K point ($\frac{1}{2}, \frac{1}{2}, 0$) at about 7 THz and around the $\Gamma$-point from 6.7 THz downward can now be assigned (circled in fig. 3.22).

Other features of the previous study are qualitatively reproduced, although the frequency range is different due to the different shell model parameter set. In terms of the range of vibrational frequencies, CaF$_2$ is intermediate between MgO and KBr, with a maximum frequency of 11.4 THz. Lagoons between the LO band and the TO band open up around the $\Gamma$, M and K points. Spectrally localised surface modes are seen in these areas, at 9 to 10 THz. Resonant surface modes can be found at frequencies between 5 and 8 THz, mainly near the $\Gamma$-point.

Fig. 3.23 shows displacement diagrams of some normal modes of a fifteen layer CaF$_2$ slab that are detected as localised at the surface with a cutoff value of $\alpha_{\text{crit}} =$
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Figure 3.24.: Histograms of the localisation criterion functions for MgO with step. (a) Surface localisation criterion function $a_{\text{surf}}$, (b) step localisation criterion function $a_{\text{line}}$.

The number of ions in the surface unit cell of a fifteen layer slab of MgO and KBr is $N = 30$, i.e. the number of non-trivial normal modes in these calculations is $3N - 6 = 84$ for each k-point. The number of ions in the step unit cell is 448, so the number of non-trivial normal modes is 1338.

Due to this vastly increased number of normal modes, a visual inspection of all normal modes becomes prohibitive in step calculations and an automated algorithm for detection of localised modes is a necessary ingredient to the detection of normal modes localised at steps (called step modes in the following).

3.3.6. Phonon Modes Localised at a Step in the Surface, Detected with the $a_{\text{line}}$ Criterion

The number of ions in the surface unit cell of a fifteen layer slab of MgO and KBr is $N = 30$, i.e. the number of non-trivial normal modes in these calculations is $3N - 6 = 84$ for each k-point. The number of ions in the step unit cell is 448, so the number of non-trivial normal modes is 1338.

Due to this vastly increased number of normal modes, a visual inspection of all normal modes becomes prohibitive in step calculations and an automated algorithm for detection of localised modes is a necessary ingredient to the detection of normal modes localised at steps (called step modes in the following).

3.3.6.1. Step Modes of the MgO(001) Surface

Fig. 3.24 shows histograms of (a) the surface localisation criterion function $a_{\text{surf}}$ and (b) the step localisation criterion function $a_{\text{line}}$ calculated with an MgO supercell with a step (for details see section 3.2.1). It can be seen that both densities are centred at lower values than for a flat surface (fig. 3.15c). For the measurement of surface localisation, this is due to the fact that in comparison to a flat surface, half of the ions at the surface (which would have received large weights) have been removed. For the step criterion, this is due to the fact that the cylinders with radius R around the steps do not cover the entire supercell (fig. 3.5).

Fig. 3.25 shows the dispersion spectrum of an MgO slab with a step (the wave vector is parallel to the step). It can be seen that $a_{\text{line}}$ values above 0.4 occur resonantly around 16 THz and between $k = (0, 0, 0)$ and $k = (0, 0, 2, 0)$ and below the main band around 5 THz near $k = (0, 0.5, 0)$.

Below the main band, more step localised modes are identified at smaller k vectors if the threshold value is relaxed to 0.33. Additional resonant step modes are then
identified around 10 THz at low \( k \) values and above 16 THz at high \( k \) values.

The normal mode at the \( \Gamma \)-point at 10.6 THz consists mainly of a longitudinal optical motion of the step edge ions. Modes of this kind at \( k \neq 0 \) (including the modes marked adjacent in fig. 3.25) may serve to transport an excitation along the step edge. Note that this normal mode, however, is not localised enough to satisfy the higher cutoff value of 0.4, i.e. energy transport is likely to be subject to considerable dissipation into the bulk of the crystal. Following the spots marking this type of step mode through the Brillouin zone, it can be seen that localisation is diminished towards the right in fig. 3.25. This means that bulk participation and hence dissipation is likely to be greater for larger \( k \)-vectors. The second class of step mode that can be found at the \( \Gamma \)-point at the higher frequency of 16.4 THz is illustrated in fig. 3.26b.

Out of the two planes in the supercell, only the sublattice in the paper plane is involved in the motion. There are several of these modes involving different sublattices and step nearest neighbour ion movement in different directions relative to the step ions.

This normal mode involves motion perpendicular to the step edge and around the step by adjacent ions. As it involves motion of step neighbour ions around the step, such a mode may play a role in funnelling vibrational energy to the step. This type of mode retains its character throughout the Brillouin zone and is detected at the right end of the dispersion spectrum, fig. 3.25, when the 0.33 cutoff is used. In between, it is less localised.

At the lower right end of fig. 3.25, step modes split from the bulk spectrum can be seen. These have the character of acoustic surface modes but are dominated by the motion of the ions at the step edge due to their lower coordination. These normal modes are, however, quite extended and with the small distance between two periodic images of the step (about 17 A), the corresponding degree of localisation for a real step cannot be predicted unambiguously.

### 3.3.6.2. Step Modes of the KBr(001) Surface

Fig. 3.27 shows histograms of (a) the surface localisation criterion function \( a_{\text{surf}} \) and (b) the step localisation criterion function \( a_{\text{line}} \). The step localisation function has a somewhat longer tail than in MgO, indicating that step modes exist whose localisation is stronger than that seen in MgO.

Fig. 3.28 shows the dispersion spectrum of a calculation of a KBr slab with a step. The band gap around 2.8 THz in the vibrational spectrum that was seen previously (in fig. 3.19) remains intact in the system with a step; a lagoon between 2.13 THz and 2.3 THz can be seen from \( k = (0, 0.4, 0) \) to \( k = (0, 0.5, 0) \).

At the upper end of both gaps, step localised normal modes are detected at a cutoff value of 0.5, some of which are even above 0.6, i.e. more strongly localised than the step localised modes in MgO, where values just above 0.4 were reached. Accordingly, many more step modes are identified in KBr if the cutoff value of 0.4 is used (fig. 3.28).

A strongly localised (\( a_{\text{line}} \geq 0.6 \)) resonant step mode exists at the \( \Gamma \)-point at 3.4 THz.
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Figure 3.28.: Dispersion spectrum of the KBr model system involving a step. Normal modes localised at the step satisfying different cutoff values of the $a_{\text{line}}$ criterion function are marked by dots.

KBr 15 layer dispersion

Figure 3.29.: Illustration of some step modes in the KBr(001) surface. (a) Optical mode localised at the step edge. Note that the localisation is much stronger than in any MgO step mode and that the ion below the step has the strongest participation, a characteristic not seen in MgO. (b) KBr step mode at a somewhat relaxed cutoff of 0.4 (here 0.49) comparable to the values achieved by MgO step modes. Here too, the ions next to the very step are involved most strongly. It consists mainly of a longitudinal optical motion of the step edge ions.

This is analogous to the mode identified in MgO that is a candidate for energy transport along the step edge. The lowest frequency step mode seen at $k = (0, 0.5, 0)$ is of the same character.

The second class of step mode that can be found at the $\Gamma$-point at the higher frequency of 3.6 THz is illustrated in fig. 3.29a. This mode is an example for the stronger localisation in KBr compared to MgO. Other than in MgO, where the lower coordination of the ions at the step leads to localised modes involving most prominently these ions, the step mode shown in fig. 3.29a demonstrates predominant motion of ions just below the step. A step mode with comparable degree of localisation to that found in MgO is shown in fig. 3.29b. It also involves the substep ion, as well as the higher terrace neighbour of the ion at the step.

3.3.6.3. Step Modes of the CaF$_2$ (111) Surface

Fig. 3.30 shows histograms of (a) the surface localisation criterion function $a_{\text{surf}}$ and (b) the step localisation criterion function $a_{\text{line}}$.

The measure of localisation, fig. 3.30b, has a single peak between 0.075 and 0.10. The upper tail of the histogram is around 0.25. This means that step localisation is greatly reduced compared to KBr, and even MgO.

Fig. 3.31 shows the dispersion spectrum of a calculation of a CaF$_2$ slab with a step. In the previous sections, a normal mode was considered localised at the step only if its $a_{\text{surf}}$ value exceeded 0.4. The maximum value of 0.265 reached in CaF$_2$ is far below this. An inspection of the displacements of the normal modes with this maximum $a_{\text{line}}$ value reveals that the displacements of the ions at the step are not significantly larger than in the rest of the supercell. This means that no step modes in CaF$_2$ are predicted with the present model.


3.3.7. Phonon Modes Localised at a Corner in MgO

3.3.7.1. Model

A simple continuation of the periodic approach used so far leads to a unit cell with periodically repeated kinks. As this requires an equal number of ions in both lateral directions along the surface, this dramatically increases the number of atoms in the unit cell, compared to step calculations. Conversely, in order to keep the calculation computationally viable, the lateral dimensions of the unit cell would have to be reduced compared to the step calculations. A surface unit cell such as that shown in fig. 3.32a results.

With steps only three lattice spacings long, which is also the distance between kinks, this clearly is not a good model for isolated kinks and thus would not produce useful results. Kinks at a surface step therefore have to be simulated by the corners of a non-periodic $8 \times 8 \times 8$ MgO cube, as shown in fig. 3.32b.

This means that, unlike at a surface, the corners of the cube are not neighbours to a surface terrace as they would be at a kink. The ions below a surface kink are more constrained than they are in the cube model. I will try to take this into account when interpreting the cube results and extrapolate some properties of normal modes localised at a surface kink.

3.3.7.2. Results

Fig. 3.33a shows a histogram of the one-dimensional criterion function $a_{\text{point}}$ for localisation around the eight corners of a $8 \times 8 \times 8$ MgO cube. The distance is measured from the corners of the cube. A maximum distance is defined so that the spheres around the corners up to this cutoff distance do not overlap. This maximum distance plays the role of the parameter $b$ in the criterion function (see section 2.3.4).

A large part inside the cube is then not covered by these spheres which explains why the histogram is centred around 0.075 rather than the mean value of the criterion function of 0.35. It can be seen that the histogram has a gap at 0.3 which makes for a canonical choice for a cutoff value of the criterion function.

As the cube consists of 512 ions, 1530 non-trivial normal modes exist in this system. Since the system is aperiodic and the defect considered is one-dimensional, the system was simulated only at the $\Gamma$-point and the frequencies of the normal modes localised at the corners ("corner modes") are presented in the framework of the phonon density of states (DOS) rather than a dispersion diagram as before. Fig. 3.33b shows the DOS with the frequencies of normal modes exceeding an $a_{\text{point}}$ value of 0.3 marked by dashed lines.

The lower-frequency normal modes at $f = 2.97$ THz and $f = 3.28$ THz are triply and doubly degenerate, respectively. All are transverse acoustic modes. The higher corner modes distort the cube into a trapezium-shape in all directions. The lower frequency corner modes play the role of the generalised Rayleigh modes at a corner.

More normal modes of this type are detected at lower criterion cutoff values but they are already quite extended so that they should not be regarded as corner modes. Fig. 3.34a shows a displacement diagram of one of the triply degenerate corner modes exemplifying such a generalised Rayleigh corner mode.

The isolated corner mode at $f = 7.11$ THz, whose displacement diagram is shown in fig. 3.34b, involves collective rotational motion of the three magnesium ions surrounding each corner oxygen around the axis of $C_3$ symmetry. The oxygen ions at the corners themselves are not involved in the motion. This is an example for
Figure 3.34: Displacement diagrams of normal modes localised at the corners of an MgO cube. (a) Generalised Rayleigh-type corner mode $f = 2.97$ THz, $\text{a point} = 0.32$ (similar ones exist at $f = 3.28$ THz and $\text{a point} = 0.31$, (b) corner mode at $f = 7.11$ THz and $\text{a point} = 0.32$ involving mostly the corner-neighbour magnesium ions in a rotational motion around the $C_3$ axes, (c) longitudinal optical corner mode involving mostly the corner ions. Of the latter, two different varieties exist localised mostly at the oxygen and the magnesium corners. Their respective frequencies and criterion function values are: Magnesium corner $- f = 18.4$ THz, $\text{a point} = 0.45$; oxygen $- f = 19.2$ THz, $\text{a point} = 0.31$. Note that the magnesium corner mode localisation exceeds the localisation of all other corner modes by more than 0.12.

what could be termed a “sub-corner mode”. The next diagonal layers of magnesium ions are also involved but only to a small degree; their rotation is in the opposite direction to the corner neighbour magnesium ion (not shown in the displacement diagram).

An analogue to this mode at magnesium corners is not detected at cutoff values down to 0.24. This is understandable, as the oxygen ions are not involved in the motion of this mode at all and hence the properties of the mode would change dramatically if the roles of magnesium and oxygen were exchanged. This is due to the considerable polarisability of the oxygen ions in MgO which affects (effectively damps) the motion of oxygen against the magnesium sublattice. This appears to decrease the localisation of such a mode, if it exists.* Finally, two high-frequency corner modes exist that involve optical motion of corner ions against their neighbours. This type of mode is shown by the displacement diagram in fig. 3.34c. Two forms of this mode exist, one each at oxygen and magnesium corners of the cube. The corner mode at the magnesium corners is of lower frequency but at $\text{a point} = 0.45$ significantly more localised than the other corner modes whose $\text{a point}$ values do not exceed 0.32. At present, however, it cannot be ascertained whether this mode corresponds to a kink localised mode or is only due to the tetrahedral symmetry of the simulated cube.

3.3.7.3. Kinks in Surface Steps

At kinks in surface steps, the ions below the higher terrace are constrained and their displacements diminished with respect to the MgO cube model. The corner modes presented in the previous section then transform into kink modes whose ionic displacements are limited to the atoms in the higher terrace. I will attempt in this section to extrapolate the results from the previous section to kinks in surface steps of MgO.

Fig. 3.35a illustrates what the displacement diagram of a generalised Rayleigh-type kink mode may look like. The corner modes presented in figs. 3.34b and (c) would also transform into corresponding kink modes, with diminished motion of the subsurface ions.

Fig. 3.35b shows a double kink which is a typical defect in steps at ionic surfaces. Generalised Rayleigh type modes can then only extend in one dimension along the step, with strongest displacement at the kink. An optical double kink mode corresponding to the optical corner modes presented in the previous section is illustrated in fig. 3.35b.

As indicated above, some of the modes predicted in this section may not exist, as the modes they are based on are predicted only due to the symmetry of the cube. A larger, non-symmetric calculation would have to be performed to answer this question, which is outside the scope of this work. The extent to which the ions immediately below the kink are displaced in a kink mode cannot be predicted reliably in analogy to the corner calculation. This can become important for kink modes, as exemplified by the step mode presented in fig. 3.29a, where motion of the ions below the step dominates.

3.4. Discussion

3.4.1. Surface Phonons

Table 3.6 shows the frequency range of the compounds discussed with the frequencies and k-points of their highest-frequency surface modes. It can be seen that in the ionic crystals studied the surface modes never occupy the highest-frequency parts of the vibrational spectra.

Lattice dynamics provide information about the frequencies and spatial extent (localisation) of normal modes. However, as these considerations are based on the
harmonic approximation, no specific statements about the coupling between normal
modes, i.e. vibrational energy dissipation, can be made. Speculations about dissipation
from molecules adsorbed on the surface can be obtained only from the spectral
properties and the localisation of the normal modes.

If a molecule adsorbed on a surface has molecular normal modes of vibration at
frequencies where the crystal possesses surface-localised modes, vibrational coupling
is likely to be enhanced. Similarly, if the surface-localisation of a lattice mode is
particularly high, the amplitude of ionic motion at the surface at a given temperature
will be particularly high.

As expected from the comparison of the bulk densities of state of the three com-
ounds with the surface DoS (sections 3.3.1, 3.3.4.1 to 3.3.4.3), surface-localised
modes are resonant with the bulk spectrum in MgO and resonant or in the vibra-
tional gap in KBr. Of these, the gap modes are the most strongly localised, also in
line with expectation. In CaF$_2$, the most surface-localised modes are dominated by
the fluoride sublattice, analogous to the bulk, where the cations are excluded from
TO modes due to symmetry reasons. Calcium ions participate in the TO surface
modes to a small degree, however, as the surface breaks the bulk symmetry.

All crystals feature generalised Rayleigh modes at the bottom of the dispersion
spectrum which are, however, not necessarily localised very strongly. This may,
however, be an artifact of the thin film model. The surface-localised modes in CaF$_2$
exist at isolated spots in the dispersion spectrum (fig. 3.22), similarly to MgO. The
difference between the two crystals lies in the preference for anion participation in
CaF$_2$ that appears to stem from the strictly symmetry-forbidden participation of
the anions in the CaF$_2$ TO modes.

Some of the MgO surface modes are found in lagoons (upper panel of fig. 3.16).
One surface mode between 10 THz and 15 THz almost spans the entire dispersion
spectrum. In KBr, the dispersion spectrum (upper panel of fig. 3.19) two surface
modes span the whole boundary of the irreducible part of the SBZ, while some more
lagoon and resonant surface modes exist at lower density around the k-point $X$.

Speculation About Dissipation Lifetimes of Adsorbed Molecules

On the basis of the above, it can be speculated that enhanced dissipation into surface
modes is likely for molecules adsorbed on the surfaces if they feature molecular
vibrations up the frequencies shown in table 3.6. Depending on the crystal, these
may be very low (i.e. easy to avoid). This consideration corresponds to step 2
in fig. 2.2 on p. 45. Of the three crystals, KBr has the most pronounced surface
localisation, hence admolecule vibrations would dissipate most quickly into surface
modes on this crystal.

On the other hand, surface modes are more likely to give up their vibrational
energy to the bulk if they are resonant (step 3 in fig. 2.2). So it can be speculated
that the crystal offering longer dissipation lifetimes for dissipation step 2 would have
shorter dissipation lifetimes for dissipation step 3.

### 3.4.2. Special Step Modes

The special character of the ionic displacements of the step modes in MgO and KBr
that involve motion along the step and around it (presented in sections 3.3.6.1 and
3.3.6.2) invites speculation about the possibility of funnelling and steering of the
vibrational energy of an incoming vibrational wave at a step.

Such a fictitious process is illustrated in fig. 3.36. An incoming vibrational wave
packet consisting of an infinite number of normal modes (on the top left) that may
originate from the vibrational photoexcitation of a defect site outside the image
reaches the step and leaves three classes of waves due to overlap or collisions with
the respective normal modes:

1. A transmitted wave packet,
2. a reflected wave packet and
3. vibrational motion along and around the step.

The last point is of main interest in this discussion. It means that the energy of
the initially free wave packet is funnelled to the step. This will have immediate
repercussions for the amount of energy reaching a molecule adsorbed on a step.

A particular case of funnelled energy transport along the step is illustrated in
fig. 3.37. The direct vibrational or electronic excitation of a photosensitive molecule
causes it to vibrate (1). This vibration will sooner or later involve a vibrational
normal mode mode along the step, either immediately during the excitation due
to an overlap with the step mode or later due to dissipation (2). The vibrational
excitation can then reach another molecule adsorbed on the step (3), which was not
excited in step (1). The vibrational energy transmitted could then be measured by
IR spectroscopy or dissociation/desorption of the second molecule.

This particular process presents a viable candidate for simulation using molecular
dynamics within the shell model. However, it requires a very large unit cell and is
therefore computationally quite demanding. It is also not the task of this thesis and
is therefore left as an idea for the future.

---

Table 3.6.: Maximum frequencies and maximum surface mode frequencies of crystals discussed.
The column on the right lists the k-points of the highest-frequency surface modes. The lowest
frequencies are zero, i.e. the frequency of the generalised Rayleigh mode at the $\Gamma$-point. Frequencies
in THz.

<table>
<thead>
<tr>
<th>material</th>
<th>top frequency (THz)</th>
<th>top surface frequency (THz)</th>
<th>k-point</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>21.5</td>
<td>18.3</td>
<td>(0.5,0.5,0)</td>
</tr>
<tr>
<td>KBr</td>
<td>6.0</td>
<td>4.1</td>
<td>(0.5,0.5,0)</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>11.5</td>
<td>10.0</td>
<td>(0,0,0)</td>
</tr>
</tbody>
</table>

3.4.3. Anharmonicity

In order to quantify how harmonic the crystals considered in this chapter are, the dimensionless anharmonicity parameter $\xi$ of the interatomic potentials $V(r)$ can be calculated, where $r$ is the interatomic distance. It is defined as

$$\xi = \frac{\hbar}{2Mr^2}\frac{V''(r) - \frac{1}{2}\left(V'(r)\right)^2}{V'(r)}$$  \hspace{1cm} (3.5)

where $M$ is the reduced mass of the two-body system and $\omega$ the harmonic frequency at the equilibrium distance $r_0$. The last factor corresponds to the modulus squared of the ratio between the third and the second order coefficients of the Taylor-series expansion of the potential. This definition is chosen so as to reproduce the anharmonicity of the Morse potential, whose definition is based on the non-linear terms of the energy levels, as discussed where it is applied below (in section 6.1.1.3).

The parameters for $V(r)$ can be found in tables 3.1 and 3.2. Note that the total potential must be used, i.e. the Buckingham pair potential $b(r) = A e^{-\beta r} - \frac{C}{r}$ plus the Coulomb potential $q(r) = \frac{Z_1 Z_2 e^2}{4\pi \epsilon_0 r}$ due to the ion charges $Q_1$ and $Q_2$.

Table 3.7 presents the anharmonicity parameters $\xi$ of the pair potentials between nearest neighbours of the crystals considered, calculated according to eq. (3.5). This will be used as indication for the anharmonicity in the crystal. Of course, the potentials felt by the normal modes of the crystals are not predicted accurately by the interatomic potentials but they are certainly an indication of their character. Longitudinal optical modes, for example, are dominated by approach and retraction of nearest neighbour ions.

On the other hand, it may be argued that in a lattice, the third-order terms of interionic potentials acting on a specific ion cancel each other out due to the neighbours on different sides. However, this is not the case at the surface and it is the anharmonicity of surface modes that is most important for the choice of a substrate for a reactive centre.

It can be seen that MgO has the least anharmonic pair potential of the three, followed by KBr. Since coupling between normal mode coordinates exists due to anharmonicity sampled by the system, the crystal with the lowest anharmonicity can be expected to display the lowest coupling between modes and hence the slowest dissipation from a specific normal mode chosen.

Other evidence supporting the view that MgO is an exceptionally harmonic crystal are a classical molecular dynamics study by Gavartin where the deviation of the

<table>
<thead>
<tr>
<th>Ion</th>
<th>Anharmonicity $\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.0020</td>
</tr>
<tr>
<td>K</td>
<td>0.0040</td>
</tr>
<tr>
<td>Ca</td>
<td>0.0072</td>
</tr>
</tbody>
</table>

Table 3.7: Anharmonicity parameters $\xi$ of the pair potentials between nearest neighbours of the crystals considered, calculated according to eq. (3.5). It can be seen that MgO is the least anharmonic of the three.
Mean Square Displacement (MSD) from the classical harmonic expectation is less than 5% at a range of temperatures and a study by Gavartin and Shluger124 where the approximately Gaussian shape of the MSD distribution was ascribed to the fluctuation of the interatomic potential acting on each ion. As a reaction involving coherent dynamics of the reactive species relies on low dissipation, which is mediated by anharmonicity, the substrate with the best prospects for this purpose is MgO.

### 3.4.4. Example System for Coherent Control

Although MgO features very high vibrational frequencies up to 21.5 THz and surface mode frequencies up to 18.3 THz, it should therefore be selected as substrate for the adsorption of an admolecule to be controlled, as the lower anharmonicity aids prolonged coherence lifetimes for the vibrations of an admolecule. Dissipation will then be unlikely to quench a prospective coherent control reaction.

Another way to quench vibrational coupling between the admolecule and the substrate is spectral separation. Using the knowledge about surface modes of MgO gained in this chapter it is clear that to fulfil this condition, the reaction coordinate should have a frequency well beyond 18.3 THz. This is done most easily by involving a light atom such as hydrogen. With these considerations, the selection of HCl adsorbed on the MgO(001) surface as an example system for the theoretical study of coherent control of an admolecule at a crystal surface can be rationalised, as it satisfies these conditions and a theoretical study is technically possible.

### 3.5. Conclusion

I have used shell model lattice dynamics to predict the normal mode structure in the (001) surfaces of MgO and KBr and the (111) surface of CaF\textsubscript{2} with and without steps in the surface (modelled by enlarged supercells). One-dimensional surface defects were modelled by the corners of a large finite cube of MgO.

The localisation of modes can be quantified by the $\alpha_{\text{surf}}$, $\alpha_{\text{line}}$, and $\alpha_{\text{point}}$ attenuation parameters. If these measures for localisation lie beyond a certain threshold value, the mode is said to be localised at that location. The threshold values can be based on a histogrammatic evaluation of the criterion functions over all normal modes. Using this criterion, vibrational modes localised at the surfaces and at steps of MgO, KBr and CaF\textsubscript{2} are identified among the modes resulting from shell model lattice dynamics calculations.

The surface phonon calculations we have performed qualitatively reproduce earlier results that were obtained with other methods. The fact that some surface mode branches have been overlooked by some previous theoretical studies is assigned to the weaker localisation of these surface modes, as quantified by the surface attenuation parameter. Additionally to this, we present here the first quantitative study of the surface localisation of different modes, making it possible to analyse normal mode localisation reproducibly.

KBr displays the strongest surface localisation of the three compounds. Four classes of modes are found that consistently exceed an $\alpha_{\text{surf}}$ value of 0.8 over all sampled k-points. At the same cutoff value, the normal modes identified as surface modes in MgO are scattered as short branches over the dispersion spectrum. This means that, for most modes, the property of being a surface mode only depends on the symmetry of the mode in KBr, whereas in MgO and CaF\textsubscript{2} it is strongly dependent on the wave vector as well.

When the criterion cutoff is relaxed to 0.6, more weakly localised normal modes are picked up which, for example in the case of the generalised Rayleigh modes in MgO and CaF\textsubscript{2}, now appear at all sampled k-points. Additional branches of surface-localised modes are detected as well, such as those starting at medium frequencies around the $\Gamma$ point. These surface modes show up in the experimental data but were not predicted in some previous theoretical studies of KBr (fig. 3.2). The problems in these studies can now be ascribed to the low degree of localisation of these modes. One surface mode is detected in MgO at the lower end of a lagoon, which runs counter to the notion that surface-localised modes in ionic crystals generally appear with lowered frequency, i.e. at the upper end of lagoons in the dispersion spectrum. This surprising fact necessitates further analysis.

The $\alpha_{\text{surf}}$ criterion was used to detect step localised modes in the three ionic crystals. Normal modes of vibration localised at steps in surfaces of MgO, KBr and CaF\textsubscript{2} were predicted from shell model calculations for the first time. The step modes in KBr were most strongly localised, with $\alpha_{\text{surf}}$ values exceeding 0.6. These were found almost exclusively at the upper end of phonon band gaps/lagoons in the dispersion spectrum (with the exception of one resonant step mode at the $\Gamma$-point). A corresponding number of modes localised at a step in MgO could be detected only at a cutoff value of 0.4. This tendency can be seen with the naked eye in the displacement diagrams. (However the decision which modes to select necessitated an automated criterion, as otherwise 1338 normal modes would need to be analysed by hand.) The $\alpha_{\text{surf}}$ attenuation parameter does not reach 0.27 in the CaF\textsubscript{2} step simulation supercell. This means that no step modes in CaF\textsubscript{2} are predicted by the present model.

Unlike in MgO, the ions at the step immediately below the upper terrace can participate very strongly in certain step modes of KBr. In MgO, the largest displacements are reserved for the ions at the boundary of the upper terrace. Step localised modes were found in MgO and KBr that involve vibration along the step. Their counterparts are step modes that involve motion around the step. This invites speculation that these are candidates for energy transport along the step and funnelling of a vibrational excitation to the step. A process involving energy exchange between

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two admolecules along the step is proposed and may be considered with a molecular dynamics simulation in the future.

The low anharmonicity and spectral separation between admolecule and substrate justify the selection of the proton desorption in HCl adsorbed on the MgO(001) surface as example reaction for the study of coherent control of a molecule adsorbed on an insulator surface.

Chapter 4. DFT Calculations of HCl Adsorbed on the MgO(001) Surface

Aims: The chemical nature of the adsorption of HCl on the MgO(001) surface is studied, particularly the questions of whether the molecule chemisorbs or physisorbs, dissociates at the surface and whether diffusion of the adsorbed species is thermally feasible.

Methods: To simulate the chemical properties of the system, Density Functional Theory (DFT) methods at the GGA level (section 2.1) are used with two different approaches: a Γ-point plane-wave model with periodic boundary conditions (PW-DFT) and an embedded cluster model with LCAO basis sets (EC-DFT).

In the PW-DFT calculations, a periodic slab models the surface. These calculations are performed with the Perdew-Wang’91 density functional as implemented in the program VASP. EC-DFT calculations are performed with the program GUESS using the B3LYP density functional as implemented in the program GAUSSIAN98.

The dipole-dipole interaction energy in the periodic boundary approach is estimated by calculating it in an approximately equivalent point charge system. A dipole-dipole interaction correction is applied when necessary.

Results: Both methods predict dissociative chemisorption of HCl on the MgO(001) surface due to the formation of an OH− molecule by the adsorbed proton and a surface O2−. OH− represents an electronic hole in the surface as it is in the lattice position of an O2− ion. The remaining Cl− ion is ionically bound to OH−. Hydrogen diffusion from the OH− molecule formed is not thermally feasible.

The chlorine ion is free to rotate around OH−. Chlorine diffusion away from the adsorption site is possible but energetically unfavourable. A simulated adiabatic retraction of the chlorine ion off the surface demonstrates that desorption of a charged Cl− ion is favoured.
4.1. Introduction

Crystal surfaces are meeting places for adsorbed molecules. At a given molecule density, the collision probability between reactants is much lower in the gas phase than at a surface because of the surface’s lower dimensionality. It is therefore desirable to produce reactive species such as free radicals on a crystal surface to greatly enhance the rate of a reaction involving such species. This can be done, for example, by a dissociation reaction at the surface during which part of the adsorbate is desorbed.

I am interested in systems with weak vibrational coupling to a crystal that offer the possibility to control a dissociation reaction by light. The HCl molecule on the MgO(001) surface as example system is a likely candidate to satisfy these conditions: The vibrational modes involving hydrogen are likely to be of much higher frequency than the rest of the system, i.e. they are localised spectrally (see chapter 3). A diatomic molecule with a dipole moment gradient is also likely to respond to the electric field of a laser pulse.

The reaction of hydrogen chloride molecules with magnesium oxide surfaces also serves as a general example for the reaction of a diatomic polar molecule with an ionic surface.

4.1.1. HCl on the MgO(001) Surface Terrace as Model System

MgO is an ionic crystal which forms a face-centred cubic (rocksalt structure) lattice. Its lattice constant is 4.21 Å at room temperature and pressure.

A freshly cleaved MgO surface can be quite rough on the mesoscopic scale. However, Barth and Henry have demonstrated by atomic scale AFM imaging that cleaving MgO in UHV with a well-controlled cleaving angle (to within less than 1°) and subsequent annealing yields clearly visible terraces (fig. 4.1a). The arrow points to a change in the AFM tip, which is not the subject of this project.

Since MgO(001) surface terraces can be prepared, adsorption of HCl to this surface is experimentally feasible. Fig. 4.1b illustrates HCl bonded to the MgO surface. It will turn out below that this is one of the configurations in which the adsorbed molecule is predicted to exist.

Rather than simulating HCl adsorption to special sites such as steps or kinks at the surface, I have used Density Functional Theory (DFT) methods to simulate HCl adsorbed on the MgO(001) surface terrace only. This makes it computationally viable to consider the system with different methodological approaches (discussed in section 4.2) whose results can be compared to gauge their accuracy. It will turn out that the results are such that qualitative statements can be made on the adsorption behaviour at steps and kinks (in section 4.5.4).

4.1.2. Questions to be Answered by this Chapter

The first questions important for this project are whether HCl physisorbs or chemisorbs and whether it adsorbs associatively or dissociatively, as these questions could not be unambiguously answered in previous experimental studies.

In order to get a rounded picture of the binding behaviour of HCl on MgO, the theoretical model has to deliver properties such as:

1. the binding energy for different geometries,
2. barriers for the diffusion of the molecule along the surface, and
3. the change of binding behaviour with increased coverage.

4.2. Computer Simulations of a Molecule Adsorbed on a Crystal Surface

Finding the binding energy for a molecule on the surface requires a model of the crystal with and without the admolecule. This includes a total energy expression (Hamiltonian), boundary conditions imposed on the wave function and a wave function representation (basis set).

Throughout this chapter, the Born-Oppenheimer approximation is applied, i.e. the electronic structure is calculated according to static nuclear coordinates. The electrons are subject to an external potential provided by the nuclear-electronic interaction.

4.2.1. Hamiltonian – The DFT Method

Density Functional Theory (DFT) is based on two theorems by Hohenberg and Kohn: (1) The non-degenerate electronic ground state energy of a system is a unique functional $E(\rho)$ of the electron density. (2) The ground state energy is the variational minimum over all electron densities of this density functional.
The functional $E(\rho)$ can be divided into kinetic, external potential and electron interaction terms. The latter consist of electrostatic, exchange and correlation. The last two of these are generally combined to the exchange-correlation term $E_{xc}$. Its exact form is unknown, so that approximations are employed in the construction of functionals usable for practical purposes.

The Local Density Approximation (LDA) $E_{xc}$ depends only on the local value of the electron density. This approach is exact in the case of a uniform electron gas but a strong approximation in many other situations. In spite of this, the LDA is quite successful at predicting geometries and ground state electronic properties of many structures. However, it neglects effects of fast-changing electron densities. This means that interatomic distances are systematically underestimated. The LDA method was therefore improved by extending it to functionals that also depend on the gradient of the electron density. This approach is called Generalised Gradient Approximation (GGA).

In this chapter, I present results obtained with the GGA functionals PW'91 and B3LYP that have been used in many recent materials science studies.

4.2.2. Boundary Conditions – Different Models for the Adsorption of a Molecule to a Crystal Surface

Two different models to which DFT methods can be applied are often used in computer simulations of point defects in solids (such as an admolecule adsorbed on the surface): the periodic model and the finite cluster model. They differ by the boundary conditions imposed on the electronic wave function (and on the nuclear coordinates).

The periodic model was first introduced for the calculation of perfect crystal lattices, while the cluster model derives from molecular calculations. Both can be tweaked to allow modelling of point defects in solids but neither should be relied upon alone, as each has its own weaknesses. These are, however, complementary so that a complete picture of the system can be constructed from a careful analysis of the results gained from both models.

4.2.2.1. Setup of the Periodic Model System

In a periodic setup, the wave function is subject to periodic boundary conditions; the charge density is the same in every unit cell and matches at the boundaries. A surface with or without an admolecule can be represented by a large unit cell, also called supercell, which can be imagined as periodically translated to build a series of infinite slabs with vacuum gaps between them (fig. 4.2a). This is called periodic slab model. The supercell employed for this project is usually four crystallographic planes thick with a planar size of four by four ions (fig. 4.2b+c).

Figure 4.2: Geometrical setup of periodic boundary calculations of HCl on MgO(001). (a) Periodicity of the supercell, (b) cross-section through the supercell, (c) three-dimensional representation of the supercell.

The distance between slabs is set to twice the thickness of the slab in order to diminish interaction between slabs. The translational vector of the supercell normal to the surface is then three times as long as the translational vectors parallel to the surface. I also did calculations with a halved vacuum gap between slabs to estimate the error introduced by slab-slab interactions. This error is within the accuracy of the method, so I conclude that the calculations are converged with respect to the vacuum gap.

I will present the results from the calculations with the larger vacuum gap to allow for geometries with the molecule removed considerably from the surface without approaching the next image of the slab. The two layers of MgO not facing the admolecule were fixed to the bulk structure for the purpose of periodic calculations while the two other layers were free to move to allow for surface relaxation. An HCl molecule was added at different initial geometries near the surface and then relaxed to find the stable configurations of the adsorbed molecule.

Most computer codes implement the periodic model using the plane wave basis set to represent the electronic wave function. This basis set can be converged with respect to a single parameter – the cutoff energy – which allows to compare the system with and without a defect (here an admolecule) on an equal footing.

Due to the implied periodicity, the system modelled is a surface with a periodic coverage of molecules rather than an isolated molecule adsorbed on the surface. Depending on the surface lattice vectors of the supercell, different coverages are modelled. This can be an advantage when such periodic coverages are considered but is a disadvantage if one is interested in the adsorption of isolated molecules.

A method to deal with this problem is discussed later in this chapter. Briefly, the dipole of the unit cell is determined and the dipole-dipole interaction energy calculated and used as a correction term for the total energy. This approach relies on the assumptions that (1) the uncorrected calculation yields a qualitatively correct geometry and charge density and (2) the dipole-dipole interaction is the leading term in the inter-cell multipole interaction energy.

A related problem is that the defect-induced distortion of the host lattice can only
be taken into account within the unit cell. If these distortions range beyond the unit cell boundaries, this may lead to inaccurate results.

In the following, I will use the term plane-wave DFT (PW-DFT) to label the method described in this section, implying the use of the supercell model with periodic boundary conditions and the plane wave basis set.

4.2.2.2. Setup of the Embedded Cluster Model System

Another method for simulating a point defect in a crystal lattice (e.g. the admolecule at the crystal surface) consists of modelling the point defect and its immediate environment as a large hypothetical molecule called a cluster. For this model to yield physically relevant results, the atomic and electronic structure of the crystal needs to be correctly reproduced and the defect-induced perturbations must be essentially localised within the cluster boundaries.

One advantage of the cluster approach is the large number of available quantum-chemical methods for electronic structure calculations. Particularly, Linear Combinations of Atomic Orbitals (LCAO) can be used as basis sets. These allow physical intuition to play a role in the optimisation of the basis set to speed up the calculations.

However, using LCAO basis sets implies the addition of basis functions due to adsorption of a molecule. The calculations with and without an admolecule are then not strictly comparable, as the additional basis functions can be populated by electrons from the surface lattice. LCAO bases are also generally non-orthogonal. This increases the analytical and numerical effort required for these methods and makes it non-trivial to assign charges to different atoms from a charge density result given in terms of LCAO functions.

The numerical effort of many post-Hartree-Fock methods is of the order \( O(n^3) \) or higher, where \( n \) is the number of basis functions. Besides the computational expense, the cluster method has the following problems: (1) The polarisability of the ions at the boundary of the cluster is enhanced (although the boundary is artificial). This causes problems if \( O^2^- \) ions are placed at the boundary of the cluster.\(^{130}\) This results in incorrect energies and possibly in an altogether incorrect electronic structure if the boundary atoms dominate the cluster. (2) The electrostatic potential of the infinite or semi-infinite crystal lattice (Madelung potential) is not adequately modelled by the finite cluster. As a result, orbital energies can be wrong. (3) As indicated above, the lattice response to the defect can be underestimated due to an insufficient cluster size.

The boundary of the cluster should be along a minimum charge density surface in order to allow an accurate description of the charge density by the quantum-mechanical cluster calculation. In an ionic crystal such as MgO, the cut can be made through cations that are modelled by special “pseudo-atoms” called effective core potential (ECP) atoms (also called “pseudopotential” atoms\(^{32}\)). This prevents leakage of charge density to the positive point charges. In MgO, these are Mg\(^{2+}\) cations whose valence electrons are simulated quantum mechanically but whose core electrons are taken into account only by a core potential. If these atoms are almost fully cationic due to the Madelung field in the ionic crystal, i.e. stripped of valence electrons, the use of ECP atoms guarantees a small charge density at the boundary, solving the first problem.

The other two problems can be compensated for by modelling the interaction of the quantum mechanically modelled cluster with the rest of the host lattice, the perturbation of the lattice itself by the defect (admolecule) and the effect of the lattice response on the defect itself. This is done by constructing an external potential (called embedding potential) in which the cluster is embedded. Several approaches to do this exist.\(^{132-135}\) We have used an approach by Sushko and Shluger\(^{136}\) which also takes the change in external potential due to the defect (admolecule) into account. This consists of the following elements:

1. Point masses of the appropriate charge are placed at the lattice sites outside the quantum cluster to model the Madelung potential. These interact with each other via electrostatic and short-range pair potentials.
2. The ECP cations at the cluster boundary are coupled to the point charge lattice by short-range potentials and electrostatic interaction.\(^{137}\)
3. The defect-induced lattice relaxation is taken into account by allowing a sufficiently large subset of the point charges to get polarised and change their positions to minimise the total energy of the system. This is done in such a way as to account for the effect of the lattice response on the cluster electronic structure. The interaction between the defect and the lattice is thus modelled self-consistently.

The resulting model system is illustrated in fig. 4.3a. Figs. 4.3b and (c) show the atoms in the quantum cluster used for simulating the adsorption of HCl on the MgO(001) surface.

**Figure 4.3.** Setup of HCl on MgO(001) embedded cluster calculations. A cluster of size Mg\(_{13}\)O\(_{29}\) was used, with five of the Mg atom treated fully and the rest as ECP atoms. (a) Schematic for embedding of the quantum cluster into a lattice of shell model ions. (b) Cross-section through the quantum cluster. (c) Three-dimensional representation of the quantum cluster. Note how the ECP magnesium ions surround the cluster oxygen ions at the interface to the shell model lattice to avoid leakage of the charge density onto shell model cations.
4.2.3. Implementations of PW-DFT and EC-DFT

As already indicated in the sections above, certain basis sets are best suited to the respective boundary conditions. The choice of basis set has repercussions on the way the calculation has to be performed but also limits the choice of density functionals available. The following two sections describe the particular methods used for the calculations presented in this chapter and the reasons for their selection in more detail.

4.2.3.1. Implementation of the PW-DFT Model

According to Bloch’s theorem, the eigenstates of a periodic potential are plane waves modulated by periodic functions. The modulated periodic functions can in turn be transformed into a set of Fourier coefficients.

This means that the natural choice of basis set for calculations in periodic boundary conditions is a set consisting of plane waves, since these can be chosen to satisfy the periodic boundary conditions by construction. This basis set is very useful because (1) it is orthogonal, (2) a product of two plane waves is also a plane wave and (3) the derivative operator is a multiplication in k-space.

To avoid the requirement for plane waves with very large frequencies needed to model the electron density near the nuclei, the plane-wave basis is used together with the pseudopotential method.139,140

With efficient computational methods exploiting properties (1) - (3), the reduced number of electrons due to the use of pseudopotentials and the periodicity of the model, the number of atoms that can be included in a supercell is generally a few times larger than the number of atoms in cluster calculations of comparable accuracy.

The decisive parameters for the quality of a plane-wave basis set are the k-point sampling and the energy cutoff. The k-point sampling determines how many wave vectors from the Brillouin zone are used in constructing the plane waves. The wavelengths of the periodic functions used to represent the electronic wave function correspond to their kinetic energy. The maximum for this parameter is set by the energy cutoff. Since the supercell used here is comparatively large, sampling the Γ-point (the origin of reciprocal space) alone corresponds to sampling the most relevant k-points from the Brillouin zone of the primitive crystal unit cell. This allows a twofold increase in calculation speed by constraining the Fourier coefficients to real values.

The extended character of the plane waves is a disadvantage when essentially local interactions are to be described. In particular, the PW basis is not well suited for the calculation of exact exchange, which is why this is currently not implemented in the plane-wave program package used. Therefore, the PW basis is used in conjunction with the semilocal GGA density approximation. The self-interaction error present in this approximation may lead to qualitatively incorrect predictions in systems where electronic interaction leads to the formation of localised states.124,141-143

The PW-DFT method is implemented in the VASP144,145 package with ultrasoft non-local pseudopotentials (Vanderbilt,139 as supplied by Kresse and Hafner140). The parameter-free density functional PW 91 by Perdew and Wang227 was used. It is a GGA level functional suitable for use with plane-wave bases. Note that in particular it does not involve exact exchange calculations.

For the calculation of HCl on the MgO(001) surface, the energy cutoff was set to 396 eV in consistency with the pseudopotential set. This cutoff is sufficient to converge the energy to an accuracy of 0.05 eV and the forces to an accuracy of 0.05 eV Å⁻¹.

4.2.3.2. Implementation of the EC-DFT Model

The localised nature of the LCAO basis functions allows to better represent the electronic wave function close to the atomic cores. All-electron calculations can therefore be performed. Perhaps the most advanced approach computationally is to use Gaussian type functions for the radial part of the AO and exploit their

mathematical simplicity. The computer program package GAUSSIAN98 uses the standard radial Gaussian atomic basis functions with spherical harmonics in the angular part.

LCAO basis functions allow to readily calculate the Hartree-Fock type exchange functional (which is computationally disadvantageous and hard to implement for plane-wave basis sets). A Hartree-Fock exchange contribution can then be admixed to a density functional in order to partially remedy the self-interaction error of LDA and GGA, including systematically underestimated single particle band gaps and an overall tendency to delocalise the electron density and overestimate binding energies.

Such an approach was taken in the construction of the B3LYP functional which I have used in the present EC-DFT calculations. The ratio of admixture between Hartree-Fock and DFT type exchange is determined by three parameters that were fitted by Becke to reproduce the energies of a set of benchmark molecules.

Although this construction implies particular suitability of this functional to molecular systems, it has also been successful in the prediction of geometric and energetic properties of crystalline systems. B3LYP is currently not available for plane-wave basis sets because the calculation of Hartree-Fock exchange is hindered by that choice of basis. This means that the calculations presented in this chapter were performed using different Hamiltonians as well as different boundary conditions and basis sets. It is therefore unfortunately not possible to ascribe any disagreements between the PW-DFT and the EC-DFT results to a particular one of these factors. However, a good qualitative agreement of the predictions made by the two methods in spite of the great differences will provide confidence in their physical relevance.

A self-consistent embedding procedure as described in section 4.2.2.2 above has been implemented in the computer program GUESS. GUESS uses GAUSSIAN98 to calculate the electronic structure of the quantum cluster and self-consistently relaxes the system according to the total forces acting on the ions, including mutual interactions between the cluster and its environment.

### 4.3. Previous Studies of HCl Adsorbed on Oxide Surfaces

#### 4.3.1. Previous Studies of Clean MgO(001) Surfaces

Before endeavouring to study the adsorption of HCl on the MgO(001) surface, the theoretical description of the surface itself has to be subjected to a comparison with previous results. The most prominent feature of the MgO(001) surface is the relaxation of the surface ions with respect to their bulk lattice positions, which leads to a small protrusion of the surface anions from the surface layer, called rumpling.

Surface relaxation and rumpling can be expressed in percentages of the lattice spacing.

\[
\delta d_{12} = \frac{d_{12} - d}{d} \times 100\%\ 
\Delta_1 = \frac{z^{\text{anion}}_{12} - z^{\text{cation}}_1}{d} \times 100\%
\]

#### Table 4.1. Comparison of surface relaxation parameters derived from experimental results

<table>
<thead>
<tr>
<th>(\delta d_{12}) (error) [%]</th>
<th>(\Delta_1) (error) [%]</th>
<th>Technique</th>
<th>Cleaved in</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.0 (3.0)</td>
<td>+3.0 (3.0)</td>
<td>LEED(^a)</td>
<td>vacuum</td>
</tr>
<tr>
<td>+0.4 (0.4)</td>
<td>+2.0 (2.0)</td>
<td>LEED</td>
<td>air</td>
</tr>
<tr>
<td>+1.25 (1.25)</td>
<td>+0.3 (0.9)</td>
<td>ICISS(^b)</td>
<td>air</td>
</tr>
<tr>
<td>+1.50 (1.5)</td>
<td>+0.5 (1.0)</td>
<td>MEIS(^b)</td>
<td>vacuum</td>
</tr>
<tr>
<td>+0.63 (0.4)</td>
<td>+1.1 (0.5)</td>
<td>GIXS(^f)</td>
<td>vacuum</td>
</tr>
<tr>
<td>+0.83 (3.4)</td>
<td>PW-DFT [this project]</td>
<td>PW-DFT</td>
<td>simulation</td>
</tr>
<tr>
<td>+0.05</td>
<td>+2.9</td>
<td>EC-DFT [this project]</td>
<td>simulation</td>
</tr>
</tbody>
</table>

\(\Delta_1\) agrees well with the experimental data, as does the PW-DFT value for \(\delta d_{12}\). Note that the parameter \(\delta d_{12}\) is very sensitive to changes of the assumed bulk lattice spacing (which is based on a non-ab initio model in EC-DFT) so that discrepancies in this parameter should not be overrated.

\(^a\)Low Energy Electron Diffraction, \(^b\)Reflected High Energy Electron Diffraction, \(^c\)Impact Collision Ion Scattering Spectroscopy, \(^d\)Extended Energy Loss Fine Structure, \(^e\)Medium Energy Ion Scattering, \(^f\)Grazing Incidence X-ray Scattering.
4.3.3. HCl Adsorbed on Polar Surfaces - Previous Experimental Work

Wittig et al.\textsuperscript{150,151} conducted HCl scattering experiments at the MgO(001) surface. A mixture of 1-2\% HCl diluted in He, Ne and H\textsubscript{2} molecules were supersonically expanded to form molecular beams at HCl kinetic energies of 0.11 eV, 0.54 eV and 0.90 eV. Vibrational and rotational states of incident and scattered beams were measured by pump-probe spectroscopy.

Scattering angles of HCl from the crystal surface were observed mainly at the specular angle for the higher energies but equally distributed over all possible angles for the lower incident energy of 0.11 eV. The observed distribution of rotational energy of the desorbed molecules was Boltzmann-like with characteristic temperatures that rise with the surface temperature. These findings were interpreted as indicative of an enhanced interaction with the surface of the 0.11 eV incidence energy molecules.

From time-of-flight (TOF) spectra of molecules of incident energy 0.11 eV scattered at an angle of 15° from the surface normal, an activation energy for desorption of $E_{\text{des}} = 0.3$ eV was estimated using the Arrhenius equation

$$k = A \cdot e^{-\frac{E}{RT}}$$

where $k$ is the reaction rate (here: desorption rate), $A$ a frequency factor, $E$ the activation energy, $k_B$ the gas constant and $T$ the temperature.

Wittig et al.\textsuperscript{150,151} interpreted their results citing the theoretical results from ref. 77. The latter models a dense coverage with HCl admolecules, which is not the case in the experiments presented in refs. 150, 151. At the end of this chapter I will therefore attempt to re-interpret the experimental evidence according to the predictions for low coverage presented in this chapter.

The adsorption of HCl on the MgO surface is being considered for industrial application as a means of separating HCl from flue gas produced in the combustion.
of coal in power plants. This is a necessary step before desulphurisation and separation of nitrogen oxides using activated coke because the ammonia used in this step reacts preferably with HCl to ammonium chloride, which then plugs the pores of the coke, destroying the catalyst.

The capacity for HCl adsorption to ionic surfaces at temperatures ranging from 160 K to 390 K (120°C) was studied with time-resolved techniques. It was observed that the adsorption rate of HCl varies widely with temperature, making it necessary to heat the crystal to 450°C before it was fully cleaned of adsorbed HCl molecules. The high adsorption rate at 120°C and the high temperature needed to clean the surface suggest a comparatively high adsorption energy, so that physisorption appears to be unlikely as the dominant adsorption mechanism.

A Fourier Transform Infrared (FTIR) spectroscopy study of HCl adsorption to γ-Al₂O₃ by Peri yielded appearance of a band attributed to hydroxyl (OH⁻) groups at 3500 cm⁻¹ (104.9 THz). At the same time, no band assignable to HCl was detected. This is indicative of dissociation of HCl due to adsorption. Subsequent FTIR experiments by Tanaka and Ogasawara confirmed Peri’s results. These authors also compared the hydroxyl bands forming due to HCl and water adsorption. The band appearing due to water adsorption is less pronounced and covers a wider range of frequencies. Tanaka and Ogasawara concluded that the OH⁻ signature seen in the adsorption of HCl is not due to formation of water at the surface. In later experimental work, Kyōkivī and Lindblad concluded that the OH⁻ groups formed at the surface are mainly acidic due to OH···Cl interaction.

A study of HCl adsorption on α-Al₂O₃ (by Elam et al.) yielded observation of a large range of desorption temperatures (300 K - 500 K). The authors interpreted this as the signature of adsorption at sites of different binding energies (e.g. terrace sites and defect sites) without the possibility for diffusion along the surface. The magnitude of the temperatures is a sign of strong binding. A constant peak desorption temperature from the Al₂O₃ surface at different levels of coverage was interpreted in this paper to be the signature of associative adsorption but, contradictively, the presence of OH⁻ signals was interpreted as a sign for dissociative adsorption.

It must be said that the experimental evidence involving HCl adsorption on alumina can only be seen as indication towards the possible adsorption behaviour of HCl to MgO(001). Besides being polar, alumina is of course different from MgO in many respects, most prominently in different ionic coordination and larger corrugation at the surface.

4.4. Results

The first step in exploring the PES of the molecule-surface system is finding the geometries and energies of stable configurations of the molecule adsorbed on the surface and comparing them with that of a “free” system, which consists of a free molecule in the vacuum and a clean surface without adsorbate.

The first property to compare is energy. Let $E_{\text{surf}}$ be the energy of the model system with a clean surface (not to be confused with the surface formation energy), $E_{\text{mol}}$ the energy of the free molecule and $E_{\text{conf}}$ the energy of a stable configuration with the molecule adsorbed at the surface, then the binding energy of the molecule at the surface can be defined as:

$$E_{\text{bind}}(\text{conf}) = E_{\text{mol}} + E_{\text{surf}} - E_{\text{conf}}.$$  

This means that if the system can lower its energy by adsorbing the molecule to the surface then $E_{\text{mol}} + E_{\text{surf}} > E_{\text{conf}}$ and hence $E_{\text{bind}}(\text{conf}) > 0$. After stable configurations are found, they can be analysed. Further calculations can then be done to ascertain the influence of coverage and dissociation/diffusion of the molecule at the surface.

In this, as in all following sections discussing periodic calculations, binding energy has to be understood as the binding energy per adsorbed molecule. This becomes particularly important when the coverage is changed by either increasing the unit cell size or adding several molecules to the unit cell.

### 4.4.1. PW-DFT Results

#### 4.4.1.1. MgO(001) Surface and HCl Molecule at Infinite Separation

As the two atomic layers not facing the admolecule adsorption site are fixed at the bulk geometry, the spacing of these layers is used as the reference value for $d$. Table 4.3 shows the relaxation parameters of the clean surface from the present PW-DFT calculations. The values of $\Delta d_{12} = +0.81\%$ and $\Delta \gamma = +3.6\%$ are comparable to some earlier LDA calculations and LEED experiments on vacuum cleaved samples referenced in section 4.3.1.

The bulk lattice constant was determined by relaxation of a supercell with the same atomic geometry but no interlayer gap. This ensures a comparable k-point sampling. The bulk lattice constant is 4.209 Å.

The energy of the clean surface (without admolecule) per unit cell is $E_{\text{surf}} = -378.86$ eV.

This is the total energy of the electrons and nuclei in the simulation and therefore
not to be confused with the surface formation energy.

For the PW-DFT calculation of the free HCl molecule I have used a relatively large unit cell size of 17 Å along all Cartesian coordinates in order to minimize interactions between periodic images of the same molecule. The energy of the free molecule thus calculated is

\[ E_{\text{mol}} = -6.08 \text{ eV}. \]

The distance between H and Cl in this calculation is 1.28 Å. The energy of the free system with one unit cell of the surface and one molecule at infinite separation is therefore

\[ E_{\text{surf}} + E_{\text{mol}} = -384.94 \text{ eV}. \]

### 4.4.1.2. HCl Binding to the MgO(001) Surface – Binding Energies and Geometric Configurations

The periodic setup used throughout most of the following sections is that discussed in section 4.2.2.1, i.e. a \( 4 \times 4 \times 4 \) surface slab unit cell for MgO to which one HCl molecule per unit cell can be adsorbed. The resulting system simulates a corresponding periodic coverage of the surface with HCl molecules. The coverage can be changed by using a different unit cell size or by adding more HCl molecules.

The final, relaxed geometry of the simulation unit cell is dependent on the initial geometry from which the relaxation is started. As HCl is polar, with a positive charge on hydrogen and a negative charge on chlorine, two stable adsorption sites may play a role:

1. Surface magnesium ions, due to their electrostatic attraction to the negative end (chlorine) of HCl and
2. Surface oxygen ions, due to their attraction to the positive end (proton) of HCl.

Several initial geometries where the molecule is near a surface magnesium ion with its negatively charged end (the chlorine ion) relaxed to a desorbed HCl molecule, i.e. surface magnesium ions can be excluded as adsorption sites.

Adsorption to a surface oxygen, however, is predicted. Upon adsorption, the molecule’s positively charged end (hydrogen) is associated with the adsorption site surface oxygen ion. Several final configurations (abbreviated “conf.”) are found to be stable or metastable and will be discussed in the following:

- **Conf. (1):** The HCl molecule stands upright over the adsorption site oxygen.
- **Conf. (2):** Chlorine is tilted in the (100) direction of the crystal (towards a neighbouring magnesium ion).
- **Conf. (3):** Chlorine is tilted in the (110) direction (diagonally between two neighbouring magnesium ions).

#### DFT Calculations of HCl Adsorbed on the MgO(001) Surface

<table>
<thead>
<tr>
<th>conf.</th>
<th>(1) upright</th>
<th>(2) tilted(100)</th>
<th>(3) tilted(110)</th>
<th>(4) dissoci. on Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{\text{conf}} )</td>
<td>-385.74</td>
<td>-385.98</td>
<td>-385.92</td>
<td>-385.42</td>
</tr>
<tr>
<td>( E_{\text{bind}} )</td>
<td>0.8</td>
<td>1.0</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>( E_{\text{corr}} )</td>
<td>1.25</td>
<td>1.3</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>( E_{6 \times 6 \times 4} )</td>
<td>-</td>
<td>1.4</td>
<td>-</td>
<td>0.8</td>
</tr>
</tbody>
</table>

| \( \alpha(\text{OH}) \) | 90° | 68.9° | 75.3° | 90.1° |
| \( \beta(\text{OCl}) \) | 90° | 53.7° | 59.8° | 88.3° |
| \( |r_0 - r_H| \) | 1.08 | 1.01 | 1.03 | 0.98 |
| \( |r_H - r_{Cl}| \) | 1.70 | 1.99 | 1.86 | 4.85 |
| \( |r_{O} - r_{Cl}| \) | 3.55 | 2.46 | 2.98 | 2.36 |

**Table 4.4:** Stable geometries of an adsorbed HCl molecule at the MgO terrace from PW-DFT calculations. Only the atoms surrounding the adsorption site are shown for clarity. Note that the calculations were in fact done on a unit cell of the size shown in Fig. 4.2. Configuration energies \( E_{\text{conf}} \), binding energies \( E_{\text{bind}} \) (where positive values indicate bound geometries), corrected binding energies \( E_{\text{corr}} \), energies from \( 6 \times 6 \times 4 \) unit cell and geometrical details: angles and distances between atoms, \( E_{6 \times 6 \times 4} \) are discussed in sections 4.4.1.11 and 4.4.1.5 below.

<table>
<thead>
<tr>
<th>initial geometry</th>
<th>relaxes to</th>
<th>Cl over Mg, H-Cl normal to surface</th>
<th>(0)</th>
<th>Cl over Mg, H-Cl parallel to surface</th>
<th>(2)</th>
<th>Cl over Mg, H over O</th>
<th>(2)</th>
<th>upright between two nearest neighbour O-</th>
<th>(0)</th>
<th>- H nearest to surface</th>
<th>(0)</th>
<th>- same as above, Cl nearest to surface</th>
<th>(0)</th>
</tr>
</thead>
</table>

**Table 4.5:** Some initial geometries and results of their relaxation in the periodic boundary model. (0) denotes desorption from the surface.

- **Conf. (4):** HCl is dissociated at the crystal surface with the proton sitting on top of an oxygen and the chlorine on top of a next-nearest neighbour magnesium (one lattice spacing to the side and half a lattice spacing forward from the adsorption site oxygen).

Geometric details, binding energies per unit cell and sketches of these configurations are shown in table 4.4.

Other initial geometries, listed in table 4.5, did not yield any adsorption sites distinct from the aforementioned (1) to (4). Instead, the system relaxes towards geometry (2) or towards a desorbed configuration, denoted (0). Relaxation towards a desorbed state means that the initial geometry is unstable; no adsorption of the molecule from this configuration can take place.

The distance between proton and chlorine in the associated adsorption geometries (1)-(3) is, at between 1.7 and 2.0 Å, considerably larger than in the free molecule, where it is 1.3 Å. The distance between the proton and the surface oxygen at the adsorption site is only 1.0 Å, nearly the same as in the free \( \text{OH}^+ \) molecule, where it is 0.96 Å. The small distances of the proton to the surface oxygen and the large
magnitude of the binding energies of around 1 eV suggest chemisorption rather than physisorption as the dominating adsorption mechanism.

The angle of 90.1° in the last column may have been expected to be 90.0° or below. The deviation from 90.0° is due to the different height-coordinates of the surface oxygen and magnesium ions (not just due to rumpling as for the clean surface but also electrostatic interaction with H⁺ and Cl⁻).

The proton always points away from the surface in order to minimise the repulsion with the magnesium ions surrounding the adsorption site oxygen. In confs. (2) and (3), the molecule is tilted with respect to the surface normal, i.e. the H–Cl axis is bent towards the nearest neighbour Mg for (2), or towards the point between the two nearest neighbour Mg ions for (3). In configurations (2) to (4), Cl⁻ hovers 2.4 to 2.5 Å above the surface. In configuration (1), this distance is 2.5 Å. Conf. (1) represents a barrier configuration between two equivalent geometries of the form (2) or (3), for a process in which the chlorine ion moves across the adsorption site. The barrier energy for this process, due to the Coulombic attraction of Cl⁻ to Mg²⁺, is 0.2 eV.

The barrier for a rotation of the Cl⁻ around the adsorption site is effectively zero. A calculation of a configuration with a projected surface angle between Mg–O lattice vector and HCl of 22.5°, i.e. geometrically between (2) and (3), has an energy of about 0.05 eV higher than configuration (3). However, this energy is not the result of a constrained optimisation but at a test geometry approximating the barrier between (2) and (3). The barrier energy may therefore be somewhat smaller than 0.05 eV. Since the accuracy of the DFT methods that this analysis is based on is at the same order of magnitude, I did not perform a constrained optimisation calculation and just state that the estimate for the rotation barrier is smaller or equal 0.05 eV.

A calculation with Cl⁻ between nearest and next-nearest neighbour Mg²⁺ ions (i.e. between configurations 2 and 4) yielded a total energy of −385.36 eV, i.e. less than 0.1 eV above the energy of conf. (4). A transition from conf. (3) to conf. (4) on a direct line is not viable because of the electrostatic repulsion between Cl⁻ and the surface oxygen O²⁻. It is therefore energetically more favourable to go via conf. (2). Table 4.6 shows an overview of the barrier energies.

**4.4.1.3. Geometric Response of the Surface Atoms to Adsorption of HCl**

One geometric aspect of the adsorption not discussed in the preceding section is the change of nuclear geometry in the surface lattice due to the admolecule. Fig. 4.4 shows the response of the MgO surface due to adsorption of a tilted HCl molecule in PW-DFT. The length of the arrows is exaggerated tenfold for clarity.

The angle of 90.1° in the last column may have been expected to be 90.0° or below. The deviation from 90.0° is due to the different height-coordinates of the surface oxygen and magnesium ions (not just due to rumpling as for the clean surface but also electrostatic interaction with H⁺ and Cl⁻).

The proton always points away from the surface in order to minimise the repulsion with the magnesium ions surrounding the adsorption site oxygen. In confs. (2) and (3), the molecule is tilted with respect to the surface normal, i.e. the H–Cl axis is bent towards the nearest neighbour Mg for (2), or towards the point between the two nearest neighbour Mg ions for (3). In configurations (2) to (4), Cl⁻ hovers 2.4 to 2.5 Å above the surface. In configuration (1), this distance is 2.5 Å. Conf. (1) represents a barrier configuration between two equivalent geometries of the form (2) or (3), for a process in which the chlorine ion moves across the adsorption site. The barrier energy for this process, due to the Coulombic attraction of Cl⁻ to Mg²⁺, is 0.2 eV.

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4.4.1.4. Electronic Density of States

After the binding energies and the nuclear coordinates of the system have been discussed, attention should be given to the electronic structure. A comparison of
Comparison of Plane-Wave Electronic Density of States for Clean Surface and with Adsorbed Molecule

Comparison of Plane-Wave Electronic Density of States for Clean Surface and with Adsorbed Molecule, "shifted"

Clean MgO(001) surf.

HCl on MgO(001)

HCl on MgO(001), shifted by .35eV

Figure 4.5.: Comparison of electronic densities of state (energies in eV) from PW-DFT with and without an adsorbed molecule. (a) comparison, (b) shifted to match valence bands. Note that the lower edges of the conduction bands match as well.

The electronic densities of state (DsOS) of a PW-DFT calculation with and without HCl is shown in fig. 4.5a. The band gap, at 2.6 eV, is greatly underestimated, as the experimental value is 7.8 eV. This is an artifact typical for PW-DFT calculations.

The solid line, showing the band structure for the molecule tilted in (100) direction, conf. (2), is shifted towards lower energies with respect to the result for the clean surface. This can be attributed to the repulsive nature of the dipole-dipole interaction present in this calculation which for the clean surface is negligible.

Fig. 4.5b shows a comparison of the band structures after correcting for the dipole-dipole interaction, i.e. after shifting the DOS with a molecule by 0.35 eV to the right. The conduction bands match, i.e. no states are introduced to the conduction band by the addition of the molecule. Note that the lower edges of the conduction bands match as well. The conduction band consists of several peaks. This is due to the low number of sampling k-points (only those due to the size of the supercell) and thus an artifact of the method employed.

New low-lying states are introduced by the molecule at ~8 eV and ~14 eV. An attempt to excite one of these, however, would result in an excitation of many valence band states into higher conduction band states at the same time.

For the purpose of controlling the dynamics of the adsorbed species via a laser pulse, a pump-dump scheme involving electronic excitation of a specific state will therefore not be the best route to pursue. Instead, I will in the following chapters concentrate on control of HCl on the MgO(001) surface via vibrational excitation.

4.4.1.5. Electronic Charge Assignment and Dipole

The electronic charge density, which is internally represented as linear combination of plane waves, is output by VASP on a grid (here 84×84×250 points, i.e. 0.1 Å grid spacing), to allow further analysis.

The simplest way to estimate the charge to be assigned to an atom is to consider the maximal non-overlapping spheres around each ion, integrate the charge density over each sphere and add this charge to the core charge. In this approach, the ratio between the spheres unassigned, i.e. the sum of these charge estimates is usually more positive than the total charge of the system.

A more sophisticated way of assigning charges is the Bader analysis, where the surface with zero charge density gradient around each ion is located and the charge density enclosed by it is assigned to the ion inside. An implementation of this method, however, is quite difficult and not within the scope of this project.

An inspection of isosurface plots of the difference in charge density between a calculation with an admolecule and one without shall suffice to make qualitative conclusions about the response of the charge density to the adsorption of HCl. Such a charge density difference plot for conf. (2) is presented in fig. 4.6a.

It can be seen that one of the main effects is a large amount of charge density that is donated from the surface oxygen to the proton. I will therefore refer to a covalently bonded OH− molecule from here on.

In the free HCl molecule, valence electron density is shared between hydrogen and chlorine. Adsorption of HCl to the MgO(001) surface adds no such density to the naked surface, as can be seen from the charge density difference plots. This means that the covalent bond between H and Cl is effectively broken. Instead, the proton shares charge density only with the adsorption site surface oxygen.

Since OH− sits at the lattice position of an O2− ion, it is positively charged (i.e. a
The discrepancy between this value and the difference between the energies of confs. (2) and (4) shown in table 4.4 (1.0 eV – 0.5 eV = 0.5 eV) can be attributed to (a) the increased electrostatic interaction in conf. (4) and (b) the increased polarisation of the oxygen ions surrounding the adsorption site in conf. (4). The effect (b) can be rationalised as follows:

Revisiting fig. 4.6a it can be seen which oxygen ions are polarised by the associated OH– and Cl– system. They are mainly the four oxygen ions surrounding the magnesium ion over which Cl– hovers, one of which is part of OH–. Note that the polarised oxygen ion at the far end of the picture is, due to PBC, a nearest neighbour of the Cl– adsorption site (in the neighbouring unit cell image).

Another oxygen ion that is apparently polarised in fig. 4.6a is the one two lattice sites behind OH–. In this configuration, it cannot be ascertained whether its polarisation is due to OH– or Cl–, as the two are too close together.

Conf. (4), whose density difference plot is shown in fig. 4.6b, shows a pronounced change in polarisation of the underlying oxygen crystal sublattice. As Cl– is now well separated from the OH– hole, its charge can now cause stronger polarisation of the surrounding oxygen ions.

The proton also has a more pronounced impact on the polarisation of its partner oxygen. The latter is no longer polarised laterally by chlorine, as the Cl– charge is effectively screened by the chlorine neighbour polarisation.

The polarisation of the oxygen ion two lattice sites behind OH– has remained the same as in conf. (2), so its polarisation can be ascribed to OH– rather than Cl–. This oxygen ion is a next-nearest neighbour of the adsorption site in two ways – into and out of the plane of the paper in fig. 4.6b (note PBC). For symmetry reasons this means that only the vertical component of the OH– hole charge polarises this oxygen ion. This is different in a $6 \times 6 \times 4$ unit cell, as in this case the discussed oxygen is a next-nearest neighbour of only one OH– molecule rather than several periodic images. The oxygen ion at the far end of the picture is now not a nearest neighbour of the Cl– adsorption site but still polarised slightly. This is because it is, due to PBC, a nearest neighbour of OH–.

In conclusion of this section it can be said that the differences between conf. (4) and conf. (2) concerning polarisation of the surface are:

1. More surface oxygen ions are polarised since the separated species have a larger aggregate number of nearest neighbour oxygen ions.
2. Each of the isolated oxygen ions is polarised more strongly in conf. (4), since in conf. (2) the hole on OH– and the negative charge on Cl– partially screen each other due to their small distance.

Since polarisation of the surface considerably lowers the total energy of the system and in conf. (4) the surface is polarised considerably more than in conf. (2), the

Figure 4.7: One-dimensional charge density plot of an upright HCl molecule adsorbed on the Mg(O001) surface and surface atoms below it along the line Cl–H–O–Mg–O. Note the large overlap between H and O and, compared to that, the small overlap between H and Cl.

**4.4.1.6. Polarisation of the Crystal due to Adsorption**

The difference in energy between confs. (2) and (4), whose charge density difference plots are shown in fig. 4.6a and (b), is made up of two parts:

1. The difference in electrostatic potential due to the attraction between the negative chlorine ion and the (in the context of the MgO lattice) positive OH– ion.
2. The energy lowering due to polarisation of surface oxygen ions due to adsorbed species.

The energy difference due to point 1 alone would be 2.88 eV. This number is based on the approximation that the distances between a full negative charge on Cl– and a full hole on OH– are 2.5 Å in conf. (2) and 5 Å in conf. (4). (See table 4.4 to compare with the distances between H and Cl and note that the centre of the hole on OH– is not on H but sits between O and H.) Below I will present the results of EC-DFT charge density analysis which predicts that these charges are somewhat reduced, which brings this estimate down to 2.4±0.4 eV.

<table>
<thead>
<tr>
<th>Distance (Å)</th>
<th>Charge (e Å⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.031 e Å⁻³</td>
</tr>
<tr>
<td>5.0</td>
<td>0.103 e Å⁻³</td>
</tr>
</tbody>
</table>
difference in energy between the two configurations is so much smaller than expected from a purely electrostatic estimate (0.5 eV versus 2.88 eV).

4.4.1.7. Different Coverages of the Surface

Up to this point, adsorption of HCl to MgO(001) has been discussed at the surface coverage corresponding to the $4 \times 4 \times 4$ unit cell chosen for its relatively large size and computational viability. As only the oxygen sites are adsorption sites for HCl on MgO, the PW-DFT calculations with one molecule per unit cell correspond to a coverage of one eighth monolayer. The dependence of the properties discussed in the previous sections on the surface coverage can be gauged by simulating different coverages. These can be performed

(a) with an enlarged unit cell for decreased coverage or
(b) by adding molecules to the unit cell for increased coverage. In comparison with a decreased unit cell size, this has the advantage of not imposing strict periodicity of the admolecules.

4.4.1.7.1. Decreased Coverage – Enlarged Unit Cell

To gauge the effect of decreased coverage, I have calculated confs. (2) and (4) with a unit cell consisting of $6 \times 6 \times 4$ MgO ions plus the molecule. A calculation of this size is, with current computer equipment, extremely demanding and could therefore not be performed for all configurations discussed in the previous sections.

The $4 \times 4 \times 4$ unit cell used up to here corresponds to one eighth monolayer, i.e. 12.5% coverage. The $6 \times 6 \times 4$ unit cell corresponds to one 18th monolayer, i.e. 5.6% coverage.

The corresponding binding energy values have been presented as $E_{6,6,4}$ in table 4.4 on p. 119. While for conf. (4) the $4 \times 4 \times 4$ unit cell calculation predicts an adsorption energy of 0.5 eV per unit cell, the $6 \times 6 \times 4$ unit cell yields 0.8 eV. For conf. (2), the corresponding values are 1.0 eV vs. 1.4 eV. The difference between these two values is due to electrostatic interaction between images of the unit cell.

The larger unit cell more closely approximates an isolated admolecule than the smaller one. This helps to recognise which of the displacements seen in fig. 4.4 are due to periodicity, as the enlarged unit cell represents an isolated adsorption more closely. Fig. 4.8 shows the response of the MgO ion positions (magnified tenfold) to the adsorption of a tilted HCl molecule calculated with the $6 \times 6 \times 4$ unit cell.

It can be seen that the displacements of the next-nearest neighbour surface oxygen ion (two atoms to the right of the adsorption site in the cross-section view) has a magnitude smaller than the nearest neighbour ion away from the slab – towards the adsorbed chlorine – in fig. 4.4 is an artifact of the periodic repetition of the dipole. In the larger unit cell, all magnesium ions surrounding the OH$^-$ centre move away from it, including the subsurface one, which behaved differently in the smaller unit cell. Consequently, this rise of the subsurface magnesium ion in the $4 \times 4 \times 4$ unit cell also has to be ascribed to the denser coverage.

It can be seen in fig. 4.8 that the surface oxygen and magnesium ions at the adsorption site relax away from the slab, towards the molecule. This can be rationalised by considering the polarity of the adsorbed species: OH$^-$ is formed, which represents a hole at the O$^{2-}$ lattice site; consequently OH$^-$ is pushed away from the surface. On the other hand, the remaining Cl$^-$ ion (bound ionically to the proton adsorption site) attracts the magnesium ion lying underneath it. In the calculation with the $4 \times 4 \times 4$ unit cell, the adsorption site oxygen and magnesium ions relax into the surface due to the denser coverage with dipoles.

It must be noted, however, that the relaxation discussed here is of very small magnitude (much smaller than suggested by the tenfold exaggerated diagrams). In fact, I will demonstrate below that almost all of the energy difference of 0.4 eV between the $6 \times 6 \times 4$ and the $4 \times 4 \times 4$ calculations can be ascribed to dipole-dipole repulsion between different images of the OH$^-$/Cl$^-$ complex. With respect to the
Table 4.7.: Binding energies per HCl molecule for different coverages of the MgO surface terrace in eV.

<table>
<thead>
<tr>
<th>Coverage</th>
<th>Binding Energy per HCl</th>
<th>1/16</th>
<th>1/8</th>
<th>1/4</th>
<th>1/2</th>
<th>1/8 on top of 1/2</th>
<th>Unstable</th>
<th>0.3</th>
</tr>
</thead>
</table>

Qualitative binding behaviour of HCl on the MgO(001) surface the two different unit cells agree. The 4 × 4 × 4 unit cell can therefore be regarded as a qualitatively correct model for the isolated molecule.

### 4.4.1.7.2. Increased Coverage – Additional Admolecules

In order to allow lowering of the total energy through symmetry breaking, I have used the 4 × 4 × 4 unit cell to calculate the energies of MgO terraces with one quarter and one half monolayer HCl coverage. The above section demonstrated that the dipole-dipole interaction between the images of the unit cell means a decrease in binding energy per molecule in the 4 × 4 × 4 unit cell compared to the 6 × 6 × 4 unit cell.

The results, shown in Table 4.7., are in accordance with the expectation that with lowering of the distance between molecules the dipole-dipole repulsion rises, further lowering the binding energy per molecule.

A coverage of one quarter monolayer corresponds to the coverage modelled by Chacon-Taylor and McCarthy. However, in my calculations symmetry breaking is allowed to lower the energy. The adsorption energy per HCl molecule of 0.83 eV compares well with the result of 0.48 eV from ref. 77 when taking into account that Hartree-Fock methods (in which electron correlation is absent) generally tend towards lower binding energies than DFT.

Covering every surface oxygen with an HCl molecule resulted in an unstable system, i.e., upon relaxation the molecules migrated into the vacuum. However, an HCl molecule can be added on top of a half monolayer of HCl with a binding energy of 0.3 eV. The additional HCl molecule is oriented with its positive (i.e., hydrogen) end towards the underlying HCl molecule, binding by electrostatic attraction. As the lowest proton is bonded chemically to a surface oxygen, it is ambiguous which chlorine ion the proton in the next layer binds to. This situation is typical of a hydrogen bond between the first and second admolecule layer (illustrated in Fig. 4.9).

### 4.4.1.8. Diffusion of HCl as a Whole Along the Surface

The previous sections have given a good overview of the minimum energy configurations of HCl adsorbed on the MgO(001) surface at different coverages and barriers between them. Aim of the simulations whose results are presented in this chapter is, however, to gather enough information on the potential energy surface of the system to perform dynamical simulations.

What is still missing is an answer to the question whether the HCl molecule as a whole can migrate along the surface. In order to find activation energies for diffusion of the adsorbed molecule as a whole along the surface, I have performed several PW-DFT calculations to model barrier configurations of molecular diffusion along the surface.

The activation energy for diffusion of an isolated molecule is the difference between the barrier energy and the energy of the stable configuration:

\[
E_{\text{act}} = E_{\text{barrier}} - E_{\text{conf}}. \tag{4.4}
\]

Let \(E_n(x)\) be the energy of configuration \(x\) in a periodic surface supercell of \(n \times n\) ions and \(E^0_n(x), E^m_n(x)\) . . . the corresponding dipole-dipole, dipole-quadrupole and higher order electrostatic interaction energies (neglecting interactions perpendicular to the surface as they are weak due to the large vacuum gap). Then the energy of the periodic system is the energy of the isolated defect (here admolecule) plus the electrostatic interaction energies

\[
E_n(x) = E_n + E^0_n(x) + E^m_n(x) + \ldots. \tag{4.5}
\]

Conversely,

\[
E_n = E_n(x) - E^0_n(x) - E^m_n(x) - \ldots. \tag{4.6}
\]

Fig. 4.10 illustrates electrostatic interaction between images of the unit cell.

It may be argued that dissociation processes have different activation energies at different surface coverages. However, inserting eq. (4.6) into eq. (4.4) for our 4 × 4 × 4 unit cell yields

\[
E_{\text{act}} = [E^0_{\text{barrier}}(4) + E^m_{\text{barrier}}(4) + E^m_{\text{conf}}(4) - \ldots] - [E^0_{\text{conf}}(4) + E^m_{\text{conf}}(4) + E^m_{\text{barrier}}(4) + \ldots]. \tag{4.7}
\]

As hydrogen and chlorine are both present at the surface during diffusion, it is reasonable to assume that

\[
E^m_{\text{barrier}}(4) \approx E^m_{\text{conf}}(4) \tag{4.8}
\]
In order to avoid a relaxation into one of the stable states already known, constrained optimisation was used in two different ways:

1. Starting from certain initial configurations, geometry relaxations were performed where chlorine was fixed and the proton was allowed to relax perpendicularly to the surface only. This forces the molecule to find a lowest energy configuration for each chlorine distance from the surface.

2. Both proton and chlorine were allowed to relax perpendicularly to the surface only to get an impression of the surface potential acting on the molecule as a whole at certain lateral coordinates and initial conditions.

A sideways drift of the centre of mass of the slab to form one of the configurations (1)–(4) is excluded due to the fixed layers in the MgO slab.

All periodic boundary calculations modelling transition states with a fixed chlorine arrive at an energy at or above the energy of the free system (clean surface plus a free HCl molecule). When both chlorine and hydrogen were allowed to relax perpendicularly to the surface, HCl relaxed towards the middle position between two periodic images of the MgO slab. This means that diffusion of HCl as a whole along the surface is only possible after desorption, i.e. molecules cannot diffuse as a whole and remain trapped at the surface at the same time.

Hence the activation energy for diffusion is the same as for desorption which, at 1.2–1.4 eV, is too high for thermal activation at an appreciable rate. For the purpose of femtosecond nuclear dynamics, diffusion can therefore be neglected.

### 4.4.1.9. Dissociation at the Surface

Although the molecule cannot move along the surface as a whole, I have already shown above that conf. (4), in which chlorine is situated above a next-nearest neighbour magnesium ion of OH$^-$ is stable. For dynamics, an isolated molecule will be assumed, so results from the 6 × 6 × 4 unit cell will be discussed in this section, as they approximate this situation.

As discussed in section 4.4.1.6, the energy difference between associated adsorption in conf. (2) and dissociated adsorption in conf. (4) is dominated by the Coulomb attraction between hydrogen and chlorine and energy lowering due to polarisation of surface oxygen ions.

The barrier between the two geometries (2) and (4) is about 0.05 eV above the energy of geometry (4) (see table 4.6). Due to the energy difference between confs. (2) and (4), however, the barrier energy is about 0.65 eV relative to the energy of conf. (2). In vibrational terms, this is a very high energy, so that spontaneous dissociation of the associated OH$^-$–Cl$^-$ system from conf. (2) is very unlikely to occur on the femtosecond timescale.

---

Table 4.8.: Diagrams for starting configuration, transition states and end configuration for three different transition pathways from adsorption at one surface oxygen to another.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diagram</td>
<td></td>
<td><img src="image1" alt="Diagram" /></td>
<td><img src="image2" alt="Diagram" /></td>
<td><img src="image3" alt="Diagram" /></td>
<td><img src="image4" alt="Diagram" /></td>
</tr>
</tbody>
</table>

---

From conf. (4), the chlorine ion may move to a further magnesium ion (with a certain barrier energy) and so forth. None of these configurations can be calculated with the unit cell used in this project, since removing Cl$^-$ further from OH$^-$ in one unit cell means approaching the adsorption site in a neighbouring unit cell.

Eventually, when the chlorine ion is far enough from OH$^-$, the differences between neighbouring local energy minima will level off. Unfortunately, the asymptotic value cannot be calculated with the PW-DFT method, as calculating isolated H$^+$ or Cl$^-$ ions adsorbed on the neutral MgO surface would mean an infinitely repeated charge, leading to a divergent energy. The possibility to compensate the charge by a continuous charge background exists but results of such calculations are not comparable to results without background charge (as used for the clean surface). The energy differences, interpreted as adsorption energies, would then be incorrect.

In comparison, it is straightforward to calculate the adsorption energy of charged systems with the EC-DFT method. I have therefore abstained from performing periodic calculations with charged unit cells and instead present adsorption energies of charged species calculated with the EC-DFT method in section 4.4.2 below.

4.4.1.10. Removal of Chlorine from the Surface

Besides leaving the adsorption site by moving along the surface, chlorine can also move into the vacuum. Starting from the upright configuration (1), I have performed a series of calculations in which chlorine is moved from the surface up to a retraction by 0.7 Å, i.e. an H-Cl distance of 2.4 Å (compare also table 4.4). At this distance, chlorine still interacts strongly with the adsorption site. At each distance, the rest of the system is relaxed to find the corresponding local minimum configuration for the total energy. Rather than obtaining the asymptotic dissociation energy (which is unavailable due to the limited distance between slabs) the response of the system to the retraction is analysed. Note that particularly the proton is relaxed, so this series of calculations can be seen as a test for the strength of the H-Cl interaction.

The distance of the proton from the adsorption site oxygen responds to removal of chlorine by approaching the adsorption site oxygen, assuming a distance of 0.96 Å as in the free OH$^-$ molecule. This reinforces the notion of dissociation of the free HCl molecule due to adsorption.

The electron density of the system also remains largely unaffected: OH$^-$ and chlorine retain their charge state. It is therefore energetically favourable to remove chlorine as an anion rather than as a neutral radical at small distances up to 2.4 Å.

Fig. 4.11 shows the energy dependence on chlorine retraction. As the many calculations presented a challenging computational task, the nuclear coordinates were not relaxed as well as the configurations presented in the previous sections, so that an error bar corresponding to a further energy minimisation by 0.1 eV has to be allowed for the calculations away from the minimum coordinate. It can be seen how the total energy rises with retraction \( r \) of chlorine from the minimum energy position. The grey line is a Morse potential

\[
m(r) = D \left( e^{-\beta(r-r_0)} - 1 \right)^2 - 1
\]

with \( r_0 = 0 \), \( D = 1.7 \) eV and \( \beta = 1.01 \) Å$^{-1}$. The choice of \( D \) is motivated by the Cl$^-$ dissociation energy calculated with EC-DFT (presented below).

4.4.1.11. Correction of the Dipole-Dipole Interaction

Up to now, the properties of an MgO(001) surface with a periodic coverage of HCl molecules have been considered. For the purpose of comparability with EC-DFT and those experimental results where low coverages are used, the properties of an isolated adsorbate have to be extrapolated from these results.

The negatively charged chlorine ion and the effectively positively charged (in the context of the crystal lattice) OH$^-$ ion form a dipole at the surface. The energies of the periodic system and the isolated system differ by the electrostatic interaction energy (eq. 4.6). If the dipole-dipole interaction dominates all higher order interactions, eq. (4.6) can be approximated by

\[
E_n \approx E_n(n) - E_n^e(n).
\]

The surface rumpling of the clean surface and the polarisation of the surface oxygen ions also give rise to small dipoles normal to the surface. Their interaction energies are, however, much smaller, physical and present in the clean surface unit cell as well as that with an adsorbed molecule, so that they cancel approximately in the calculation of the adsorption energy.

The interaction between adjacent molecules is, due to the large vacuum gap, mainly along the surface as opposed to between slabs. Since the adsolecules stick out from the surface, their interaction is subject to only small and uniform screening.
such that the dielectric constant in the calculation of the dipole-dipole interaction energy can be approximated by the vacuum value.

After these considerations and seeing that eq. (4.10) is only correct if higher order interactions are negligible, it is apparent that the calculated correction should be regarded as an estimate only.

A description of the method used to calculate the dipole-dipole interaction energy between rectangular unit cells can be found in Appendix C.1. It is based on an extension of Ewald summation.

This method can be used on different sets of point charges approximating the overall charge density in the unit cell. The simplest approach is to use an empirical point charge representation of the ions in the unit cell. For this, the lattice ions were represented by points carrying ±2 electron charges, while the adsorption site molecule formed due to adsorption was represented by the charges used by Saul and Catlow to parameterise a free OH molecule. Chlorine was assigned a full electron charge, i.e. represented as Cl⁻.

Oxygen polarisation at the adsorption site is thus accounted for by the ionic charges of OH⁻, while polarisation of the other lattice ions was not taken into account, as the plane-wave charge density cannot be straightforwardly used to quantify it. It is clear that the chosen charge parameters do not model the system very accurately but capture the situation qualitatively. Table 4.9 summarises the charge values used for this method. These charge values will reappear in chapter 5 in the shell model representation of the system.

After representing the system with these point charges, the dipole of the unit cell can be calculated from the charge centre of mass and the dipole-dipole interaction can be determined using the technique reviewed in Appendix C.1. Table 4.10 shows the binding energies with the corrections calculated with this method. The dipole-dipole energy \( E_{\text{dipole}} \) is shown, including that of the clean surface (second column) because it defines the zero point for the correction.

\[ \Delta E_{\text{dipole}} \] denotes the difference between the dipole-dipole energies of the respective configuration and the clean surface. These are the estimates for the interaction energy that have to be added to the binding energy \( E_{\text{bind}} \) to obtain the corrected binding energies \( E_{\text{corr}} \) which have already been presented in the overview of the configurations, table 4.4 (p. 119).

In the cases where the molecule is adsorbed associatively, i.e. the chlorine-hydrogen distance is between 1.7 and 2.0 Å, the surface normal component of the dipole dominates the interaction and the molecules repel. Hence the binding energy of the isolated molecule is slightly higher than the periodic boundary result. The signs of the corrections for confs. (1) through (3) reflect this.

An estimate of the correction is complicated in the dissociated configuration (4) by the size of the unit cell. As illustrated in fig. 4.12, the choice of dipole orientation becomes ambiguous. Each proton has two nearest neighbour chlorine ions among the periodic images of the unit cell. This immediately means that the quadrupole formed by the alternation of Cl⁻, OH⁻ (hole), Cl⁻ is non-negligible and the electrostatic interaction energy is not dominated by the dipole-dipole term.

As the dipole-dipole correction of conf. (1) is greater than that of confs. (2) and (3), the barrier energies of the processes where Cl⁻ travels across OH⁻ have to be corrected downward to about to 0.05 eV. As the dipole-dipole interaction correction of confs. (2) and (3) is similar, it can be safely assumed that it is the same for the barrier configuration between them, as it is characterised only by a different lateral angle to the lattice. The barrier energy between confs. (2) and (3) therefore does not need to be corrected. The corrected barrier energies are presented alongside the barrier energies with the corrections calculated with this method. The dipole-dipole interaction energy that have to be added to the binding energy \( E_{\text{bind}} \) to obtain the corrected binding energies \( E_{\text{corr}} \) have already been presented in the overview of the configurations, table 4.4 (p. 119).

For the barrier between confs. (2) and (4), the 6 × 6 × 4 unit cell energies \( E_{6\times6\times4} \) have to be used as approximation for adsorption of an isolated molecule because the higher order electrostatic interactions play a role in conf. (4). The change in energy due to the larger unit cell is 0.1 eV larger for conf. (2) than for conf. (4). As another 6 × 6 × 4 unit cell calculation merely for the sake of determining the barrier energy is too expensive computationally, I can only estimate that the barrier energy would be corrected by the average between the two, i.e. it is lowered relative to conf. (4) by about 0.05 eV.

The dipole-dipole correction procedure can also be applied to the unit cell used by Chacon-Taylor and McCarthy. In ref. 77, calculations were done with a periodic supercell of 2 × 2 surface unit cells, i.e. 4 + 4 MgO ions in the surface layer. Such a unit cell with an upright HCl molecule yields a dipole-dipole interaction energy of 1.4 eV, which is of the same order as the binding energy itself. This explains...
why an entirely different binding behaviour with binding energies between 0.35 eV to 0.48 eV could be predicted in ref. 77, as there the electrostatic interaction energy competes effectively against the adsorption energy per molecule.

The increased supercell with $6 \times 6 \times 4$ atoms, i.e. $3\sqrt{2} \times 3\sqrt{2}$ surface unit cells, on the other hand, yields a dipole-dipole interaction of only 0.05 eV, which is of the order of the accuracy of the DFT method used. This means that electrostatic interaction between unit cells of this size is negligible and accordingly confirms that the results of these calculations can be regarded as a good approximation to an isolated adsorbate.

Using this larger unit cell, the binding energy of the tilted molecule, configuration (2), is calculated as 1.4 eV and the binding energy of the dissociated configuration (4) is calculated as 0.8 eV. The first is in good agreement with the dipole-corrected binding energy of the $4 \times 4 \times 4$ unit cell, i.e. $2\sqrt{2} \times 2\sqrt{2}$ surface unit cells, while the latter is the first realistic result for the isolated adsorption in the dissociated configuration (4).

The representation of the unit cell charge density by an empirical rigid ion model is, of course, quite a crude approximation. I have therefore attempted to improve the correction energies presented in this section using the core charges together with the calculated electron density, which was represented on a grid of $84 \times 84 \times 250$ points in the VASP output.

When calculating the dipole of the unit cell from this data, the flux of charge density through the unit cell boundary has to be taken into account. No standard computer implementation for this procedure exist. It is also not one of the central tasks of this project, so that this approach was abandoned.

Another attempt to obtain higher quality correction values by reducing the electron density to a smaller number of point charges by integrating over parts of the unit cell and calculating the Madelung potential from this data was also unsuccessful, as computational accessibility forces an unphysically crude representation of the system. A similar approach employing the charge density differences (as presented in fig. 4.6) lead to similarly unsuccessful results.

An empirical representation of the system remains the only useful approach to calculate the correction energies to date. A future correction scheme based on the more accurate description of the simulation unit cell due to the electron density will have to take into account the charge density flux through the unit cell boundary.

### 4.4.2. EC-DFT Results

As discussed in section 4.2, the PW-DFT results alone cannot be relied upon to accurately predict the binding behaviour of the admolecule. The electrostatic interaction between unit cells discussed in the preceding sections is one source of error that has to be accounted for. Other approximations are the basis set, the ultrasoft pseudopotentials employed and the density functional itself, which in the plane-wave method used currently does not contain exact exchange contributions.

Contrasting the PW-DFT results with EC-DFT results is therefore desirable to gauge the accuracy of both methods. If they coincide, either one can be used to produce reliable predictions for properties that are difficult to obtain with the other. Such properties are:

- The adsorption energies of charged species (leads to convergence problems in PW-DFT but is unproblematic in EC-DFT).
- Charge density assignment to nuclei in the simulation region (not implemented in PW-DFT code used but in EC-DFT code).
- Vibrational frequencies of adsorbed species (computationally demanding in PW-DFT but can be calculated specifically for a few atoms in EC-DFT code, saving computational time).
- Dependence on coverage (straightforward in PW-DFT but virtually impossible in EC-DFT).

The following sections will thus serve to complete the picture gained from PW-DFT.

#### 4.4.2.1. Basis Set Dependence of Results

Before launching into a large number of calculations corresponding to different geometric configurations, the convergence of the results with respect to the basis set has to be ascertained using a small cluster. This has already been done by Sushko and Shluger, whose results I present in this section. Although completion of LCAO bases is not straightforward, standard Gaussian-type basis sets offer a path to extend the basis set until satisfactory results are achieved.

The basis set used has to be sufficient to represent the electronic ground state at the desired level of accuracy. Table 4.12 shows a comparison of the HOMO, LUMO and total energies from calculations with a number of basis sets of an embedded MgClO$_4$ cluster representing part of the MgO(100) surface terrace.

---

Figure 4.12: Ambiguity of dipole choice in the unit cell for the dissociated molecule due to equal distances of each proton to two nearest neighbour chlorine ions.

---

Table 4.12: Comparison of basis sets for an embedded Mg$_{17}$O$_5$ surface cluster in the ideal lattice configuration. All energy values in eV; total energy values compared to 6-31G* basis. HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied MO. Data and figure reproduced with permission from Shluger and Sushko.

Table 4.13: Relaxation of the MgO surface in the EC-DFT calculations. PW-DFT results from table 4.3 shown in brackets for comparison.

Note that basis sets which are too extended can produce unphysical artifacts. For example, Sushko and Shluger found that the LUMO in calculations with the 6-311+G* basis set is delocalised outside the cluster. This is unphysical and has to be avoided, so I did not use diffuse basis functions in the EC-DFT calculations presented.

For the treatment of HCl on MgO I have used standard basis sets up to 6-311G* for oxygen and 6-31G for Mg. These provide polarisation basis functions on the oxygen ions which are important for predicting polarisation of surface atoms by the molecule correctly.

4.4.2.2. MgO(001) Surface and HCl Molecule at Infinite Separation

A large number of point charges outside the quantum cluster and surrounding the relaxed shell model region is fixed, modelling the bulk geometry. It therefore seems appropriate to choose the spacing between these fixed ions as the reference value for the distance $d$ between two ions.

Table 4.13 shows the relaxation parameters of the clean surface in the EC-DFT calculations. The value of $\Delta_1 = +2.9\%$ is comparable to the PW-DFT results in section 4.4.1.1 hence also to some earlier LDA calculations and LEED experiments on vacuum cleaved samples.

The value $\beta_{d_{12}} = +0.05\%$, on the other hand, is lower than that predicted in PW-DFT. This value is, due to its definition (relative deviation of $d_{12}$ from $d$, eq. (3.1)), very sensitive to changes in the assumed bulk lattice spacing $d$.

However, the shell model parameters that I have used to model the semi-infinite crystal environment in the EC-DFT calculations are chosen such that they are approximately compatible with the quantum cluster. This approximation causes the oxygen ions at the centre of the cluster to protrude from the surface further than those at the boundary of the cluster.

The mismatch between the relative rumpling determined with the PW-DFT and

DFT Calculations of HCl Adsorbed on the MgO(001) Surface

<table>
<thead>
<tr>
<th>conf.</th>
<th>(1) upright</th>
<th>(2) tilted(100)</th>
<th>(3) tilted(110)</th>
<th>(4) dissoci. on Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{surf}}$</td>
<td>$-84016.496$</td>
<td>$-84016.621$</td>
<td>$-84016.538$</td>
<td>$-84015.945$</td>
</tr>
<tr>
<td>$E_{\text{bind}}$</td>
<td>$1.41$</td>
<td>$1.54$</td>
<td>$1.46$</td>
<td>$0.86$</td>
</tr>
<tr>
<td>$E_{\text{corr}}$</td>
<td>$1.25$</td>
<td>$1.3$</td>
<td>$1.0$</td>
<td>$0.5$</td>
</tr>
<tr>
<td>$E_{q=4\times4}$</td>
<td>$0.8$</td>
<td>$1.0$</td>
<td>$1.0$</td>
<td>$0.8$</td>
</tr>
</tbody>
</table>

Table 4.14: Stable geometries of an adsorbed HCl molecule at the MgO terrace according to EC-DFT calculations. Only a few atoms of the MgO crystal are shown for clarity, note that the calculations were done on supercells illustrated in fig. 4.2 and on embedded clusters of the size shown in fig. 4.3, respectively. Configuration energies, binding energies and geometric details: angles and distances between atoms [with results from PW-DFT calculation, table 4.4, in square brackets].

EC-DFT methods is therefore largely due to the mismatch between quantum cluster and shell model. It is advisable to only use the innermost atoms of the quantum cluster to determine the relaxation parameters which is how we obtained the numbers discussed here.

The energy of the clean surface determined with the EC-DFT method is

$E_{\text{surf}} = -71475.268$ eV.

As before, this is merely the energy of the simulation system and not to be confused with the surface formation energy. The modulus of this value is larger than for the periodic calculation, as the model is larger (with ions represented either quantum-mechanically or using the shell model) and, most importantly, the quantum region is treated by an all-electron calculation.

The energy of the free HCl molecule was determined with a GAUSSIAN98 cluster calculation as

$E_{\text{mol}} = -12539.815$ eV.

The distance between H and Cl in these calculations is 1.29 Å (1.28 Å in the corresponding PW-DFT calculation). The energy of the free system is therefore

$E_{\text{surf}} + E_{\text{mol}} = -84015.083$ eV.

4.4.2.3. Binding Energies of HCl to the MgO(001) Surface

The relaxed geometries of configurations (1) - (4) and their binding energies according to EC-DFT (presented in table 4.14) agree well with PW-DFT results with corrections for the electrostatic interaction. The barrier energies correspond to the dipole-dipole corrected PW-DFT barrier energies presented in table 4.6 and are

DFT Calculations of HCl Adsorbed on the MgO(001) Surface

The key distances (O–H and H–Cl) agree very well with the PW-DFT results. However, there are considerable differences in the angles of the molecule with respect to the surface. The energy dependence on the angles is weak, as the system is mainly ionic (with the exception of the OH bond). This means they are very sensitive to the Hamiltonian used for energy minimisation. Having realised this and taking the limited accuracy of the method into account, the qualitative agreement of the angles is a satisfactory result.

The binding energies from PW-DFT with the 4×4 unit cell without \(E(4 \times 4)\) and with \(E_{\text{corr}}\) dipole-dipole correction and from \(6 \times 6 \times 4\) PW-DFT calculations \(E(6 \times 6)\) are shown alongside the EC-DFT binding energies \(E_{\text{bind}}\) for comparison.

There is a slight tendency in the EC-DFT results towards higher binding energies compared to the corrected and \(6 \times 6 \times 4\) periodic boundary results. However, the dipole-dipole correction is always towards the EC-DFT results, not away from them. For conf. (4), no dipole-dipole correction was performed (as discussed in section 4.4.1.11) and the value \(E(6 \times 6)\) must be referred to instead.

### 4.4.2.4. Electronic Density of States

Since the quantum cluster contains 13 oxygen and 5 magnesium ions and at most one proton and one chlorine ion, the LCAO orbitals can be assigned easily using the aufbau principle due to the number of orbitals in each band if the bands are separated, as shown in the upper part of table 4.15 for the clean MgO(001) surface.

![Comparison of Plane-Wave Electronic Density of States for Clean Surface and with Adsorbed Molecule](image)

**Figure 4.13.** (a) Comparison of electronic densities of state from EC-DFT calculations with and without an adsorbed molecule. (b) Repetition of the PW-DFT result (fig. 4.5b) for comparison.

Particularly, the oxygen 2p orbitals can be identified as crystal valence band (VB). The band gap between valence and conduction band (CB) is 6.32 eV. The size of the cluster effectively confines the electrons, so the energy of the unoccupied orbitals is increased with respect to the de-localised limit. The value of 6 eV compared to the experimental value of 7.8 eV\(^{159}\) is a reassurance that this error is not too large and the cluster not too small to reflect crystalline properties of the electronic structure. It is, however, considerably larger than the gap in the periodic-boundary results (2.6 eV). This difference is largely due to the use of the B3LYP functional in EC-DFT that contains an admixture of Hartree-Fock exchange.

The introduction of HCl onto the surface of MgO introduces new levels, as shown in the lower part of table 4.15 for conf. (2), one of the lowest energy configurations. Some low-lying molecular states can be distinguished. The highest occupied states introduced by the presence of the molecule are resonant with the oxygen states of the valence band.

The stick spectra presented in table 4.15 can also be presented as density of states by histogrammatically collecting them in a number of bins. The result of this process is shown in fig. 4.13a. The graphical comparison of the densities of state with and without adsorbed molecule shows that the valence band widens only slightly at the top end, while no clearly separated new states are introduced in the band gap by the presence of the molecule.

Although I have not calculated matrix elements of certain transitions, it can be said that this makes the possibility of control through selective electronic excitation of the HCl molecule unlikely, as the highest molecular states are effectively resonant with the surface oxygen valence band states.

**Table 4.15.** Upper table: Occupied orbitals in the EC-DFT calculation of a clean MgO(001) surface. Lower table: Occupied orbitals in the EC-DFT calculation of a HCl molecule adsorbed in configuration (2) at the MgO(001) surface.

<table>
<thead>
<tr>
<th>1</th>
<th>5</th>
<th>13</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>15</th>
<th>13</th>
<th>39</th>
</tr>
</thead>
<tbody>
<tr>
<td>min. energy [eV]</td>
<td>-1271.34</td>
<td>-516.86</td>
<td>-81.88</td>
<td>-47.77</td>
<td>-22.73</td>
<td>-8.61</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>max. energy [eV]</td>
<td>-1270.67</td>
<td>-516.44</td>
<td>-81.17</td>
<td>-46.95</td>
<td>-21.55</td>
<td>-5.86</td>
<td>-0.64</td>
<td></td>
</tr>
<tr>
<td>assignment</td>
<td>Mg1s</td>
<td>O1s</td>
<td>Mg2s</td>
<td>Mg2p</td>
<td>O2s</td>
<td>O2p</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

**Remark:** VB CB

Note that the energies of the states introduced into the VB by HCl adsorption are embedded in the oxygen valence states.

Table 4.16: Comparison of charge assignments from spherical integration of periodic boundary results and NPA of EC-DFT results for the tilted geometry, configuration (2). Charges are given in multiples of the positive unit charge.

<table>
<thead>
<tr>
<th>ion type</th>
<th>Cl</th>
<th>H in HCl</th>
<th>O in OH−</th>
<th>other O</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>plane-wave, spherical integration</td>
<td>-0.9</td>
<td>-1.14</td>
<td>-1.79</td>
<td>0.5</td>
<td>-1.8</td>
</tr>
<tr>
<td>embedded cluster, Mulliken</td>
<td>-0.75</td>
<td>-1.10</td>
<td>-1.55</td>
<td>1.31</td>
<td>-0.85</td>
</tr>
<tr>
<td>embedded cluster, NPA</td>
<td>-0.85</td>
<td>-1.42</td>
<td>-1.79</td>
<td>1.71</td>
<td>-1.42</td>
</tr>
</tbody>
</table>

4.4.2.5. Electronic Charge Assignment

When using a basis set of linear combinations of atomic orbitals (LCAO), as is the case in the EC-DFT calculations, one can use the fact that each basis function is assigned to a specific atom (or ion) to assign the resulting charge density to the atoms. This approach is complicated by the fact that the basis functions are not mutually orthogonal and so the overlap populations have to be split between centres. Several methods to do this exist, among them the Mulliken Analysis, and the Natural Population Analysis (NPA) NPA is the preferred method because it is designed to be much less basis-set dependent than the Mulliken analysis and does not suffer from drawbacks such as the occurrence of negative populations. The two methods are compared in more detail in appendix C.2.

With the GAUSSIAN98 program package, Mulliken Analysis and NPA can be performed routinely. The results of these analyses are contrasted with the crude charge-in-sphere analysis (introduced on p. 122) of the PW-DFT charge density in table 4.16.

As discussed in section 4.4.1.5, the touching spheres which form the integration areas for the plane-wave charge density do not cover the whole space, i.e. the charge integrated over all spheres is smaller than the number of electrons in the system. Hence the error always tends towards positive charges for this method.

It can be seen that, compared to NPA, Mulliken analysis systematically underestimates the absolute charges of the species. This is expected, as overlap populations are split equally between the partaking atoms. However, Mulliken analysis captures the qualitative situation fairly well. As the result of Mulliken analysis depends on the basis set, this is an indication that the basis set used is comparatively well balanced for the system considered.

Keeping in mind that the error of the charge-in-sphere estimates is always on the side of positive charge compared to the charges that would be assigned due to the more accurate Bader analysis (introduced on p. 123), it can be said that they support the NPA charge assignment. The charge densities in the PW-DFT and EC-DFT calculations are similar, particularly the chemical character of the binding of the molecule to the surface is in agreement with the PW-DFT results.

The charges assigned to the components of the free HCl molecule due to NPA are H+0.25 and Cl−0.85. Adsorbed on the surface, chlorine has an NPA charge of Cl−0.85. This means that the charge density on the proton (NPA charge +0.53 at the surface) is donated mostly by the adsorption site oxygen ion.

The chlorine charge of −0.85 means that the estimate for the next-nearest neighbour dissociation energy from the Coulomb potential alone used in section 4.4.1.6 must be somewhat reduced. The estimate for CI− was 2.88 eV, while the estimate according to Cl−0.85 is 2.08 eV. In fact, the NPA charge of chlorine in conf. (4) is already −0.92, so the real Coulomb energy is between these two values, i.e. 2.5 eV±0.4 eV. The difference between this value and the 0.6 eV to 0.7 eV energy difference predicted by PW-DFT and EC-DFT, respectively, is due to the different extent of surface oxygen polarisation, as detailed in section 4.4.1.6.

4.4.2.6. Geometric Response of the Surface Atoms to Adsorption of HCl in EC-DFT

Fig. 4.14 shows the tenfold exaggerated response of the MgO ions to the adsorption of HCl. The relaxation was calculated by subtracting the coordinates of the ions before addition of the molecule from the coordinates after. This can be done because there is a large number of fixed point charges around the cluster, forming a reference frame disallowing displacement of the cluster as a whole during relaxation.

The magnesium ions surrounding the adsorption site all move away from it. The reason for this is the hole on OH−. The displacements of the Mg ions are biased towards the direction of the H−Cl dipole. This result agrees well with that predicted by PW-DFT with the 6 × 6 × 4 unit cell. A quantitative discussion of this agreement can be found in section 4.5 below.

The magnitude of the relaxation falls off rapidly with distance from the hydrogen adsorption site, so that it is negligible at its boundary. This means that the quantum cluster is large enough to represent realistically the geometric response of the surface to adsorption of HCl. Note that, even if this were not the case, the lattice response would be represented by the part of the surrounding shell model lattice that is free to relax due to the adsorption. This would, however, not include the response of the electronic charge density to adsorption.


DFT Calculations of HCl Adsorbed on the MgO(001) Surface
4.4.2.7. Vibrational Frequencies of OH\(^-\) Modes

The embedded cluster program package GUESS allows to calculate the vibrational frequencies of a few selected atoms with respect to the forces exerted on them by the whole simulated system.

Table 4.17 shows an overview of the modes found and their frequencies. It can be seen that the non-translational modes have frequencies which are well-separated from the top of the MgO surface slab vibrational band which is at 22 THz. This means they are unlikely to couple strongly to the normal modes of the MgO substrate.

Experimental results for the stretch mode of OH\(^-\) formed due to HCl adsorption to the \(\gamma\)-\(\text{Al}_2\text{O}_3\) surface,\(^{155-157}\) yielded a band centred around 3500 cm\(^{-1}\), i.e. 104.9 THz. However, this band is quite extended (as far as 2000 cm\(^{-1}\)) and \(\gamma\)-\(\text{Al}_2\text{O}_3\) offers a variety of mutually surface oxygen ions of different coordination as adsorption sites, so the agreement with the predicted frequency of 92.4 THz for OH\(^-\) formed at the MgO(001) surface is satisfactory.

4.4.2.8. Dissociation at the surface

Unlike the PW-DFT method, the EC-DFT technique allows to calculate charged systems. I calculated an MgO protonation energy of 12.3 eV and a Cl\(^-\) adsorption energy of 1.7 eV.

The protonation energy of MgO has been determined previously by embedded cluster Hartree-Fock (HF) calculations\(^{167}\) at 10.4 eV and by flame-ion mass spectrometry experiments\(^{168}\) at around 10 eV. The difference between the EC-DFT and the HF result can be attributed to the tendency of Hartree-Fock to underestimate binding energies and of DFT to overestimate them slightly.

The dissociation energy for HCl into charged ions at the surface is 1.8 eV compared to corresponding value for the free molecule of 14.4 eV (determined by a GAUSSIAN98 calculation). The latter can be rationalised by remembering that the dissociation energy consists of the protonation energy of H\(^+\)0 (H\(^+\) has a protonation energy of 13.6 eV) and the Coulomb potential between the charged species.

This means that the dissociation energy at the surface is higher than the adsorption energy (which is 1.4-1.5 eV). However, desorption and dissociation at the surface are orthogonal coordinates – desorption from the dissociated configuration corresponds to desorption of the isolated species (14 eV), so the dissociated configuration at the surface is stable. The alternative to dissociating the adsorbed molecule into charged ions is to dissociate it into neutral atoms. The binding energies of H\(^+\) and Cl\(^-\) to the MgO surface are 0.3 eV and 1.5 eV, respectively. This result agrees very well with the PW-DFT results of 0.2 eV and 1.5 eV, another sign that the electrostatic interaction due to periodicity in PW-DFT is dominating the discrepancy between the two methods.

4.5. Discussion

4.5.1. Agreement Between PW-DFT and EC-DFT Results

Table 4.14 on p. 139 demonstrated the good agreement of the stable geometries and their energies of an isolated HCl molecule adsorbed on the MgO(001) surface calculated with EC-DFT and PW-DFT with dipole-dipole correction. As demonstrated in the side-by-side comparison of the electron densities of state (fig. 4.13) and the atomic charge assignments presented in table 4.16, the electronic states predicted are also comparable.

Section 4.4.2.6 demonstrated the good qualitative agreement between the 6 \(\times\) 6 \(\times\) 4 PW-DFT and the EC-DFT calculations even in a property as subtle as the surface relaxation due to adsorption. Note that these results are obtained with different models and different density functionals. This presents a strong case for the physical relevance of both the PW-DFT and the EC-DFT results presented.
It is possible to quantify the degree of agreement between the lattice responses to HCl adsorption predicted with EC-DFT and PW-DFT. This allows to rationalise the assertion that the displacements shown in fig. 4.8 on p. 127 for the larger surface supercell of 6\times6 ions are less affected by periodicity artefacts than the displacements shown in fig. 4.4 on p. 121 for the smaller surface supercell of 4\times4 ions.

To this end, the displacements of \( n \) ions of interest are accumulated in 3-dimensional vectors, \( \mathbf{d}_L \) for the EC-DFT and \( \mathbf{d}_P \) for PW-DFT. In case of perfect agreement, the overlap normalised with respect to \( \mathbf{d}_P \)

\[
\sigma = \frac{\mathbf{d}_L \cdot \mathbf{d}_P}{|\mathbf{d}_P|^2}
\]

should be equal to unity.

The Mg and O ions immediately involved in the adsorption, binding chemically to the proton and electrostatically to chlorine, respond more strongly to adsorption of HCl than the other crystal atoms. I will therefore consider them separately. The overlap between the relaxation vectors of the 6 \times 6 \times 4 unit cell and the embedded cluster is

\[
\sigma^{6\times6\times4}_{\text{MgO}} = 1.165.
\]

This means that the EC-DFT calculation predicts a slightly larger response to adsorption of HCl than the 6 \times 6 \times 4 PW-DFT calculation. The Mg ions surrounding the adsorption site, including the Mg ion below the adsorption site oxygen but excluding the Mg ion already considered (because the magnitude of its displacement dominates the others’), yields

\[
\sigma^{4\times4\times4}_{\text{Mg}_6} = 0.982.
\]

This speaks for very good agreement. In comparison to these values close to unity, the corresponding values for the smaller 4 \times 4 \times 4 unit cell are

\[
\sigma^{4\times4\times4}_{\text{MgO}} = 0.27 \text{ and } \sigma^{4\times4\times4}_{\text{Mg}_6(4)} = -0.12.
\]

This means that the relaxation of the surface in the 4 \times 4 \times 4 PW-DFT calculation is almost orthogonal to the relaxation predicted by the EC-DFT method.

A fifty percent increase of both the unit cell width and breadth when going from the 4 \times 4 \times 4 to the 6 \times 6 \times 4 unit cell had to be paid for by computing 2.25 times as many atoms, consequently spending 11.4 times the computational effort. (The PW-DFT code used scales with the cube of the number of atoms in the unit cell.) This is a very high expense for the reproduction of a property as subtle as the surface relaxation. It is, however, reassuring to know that in principle the results of EC-DFT and PW-DFT can be made to agree. Both of the two approaches can therefore be regarded as physically relevant.

The central properties of interest, such as binding energies and stable geometries are, however, already sufficiently accurate in the 4\times4\times4 unit cell when dipole-dipole corrections are applied. Results of either method can therefore be used interchangeably to construct a full picture of the physical system. This is useful particularly for those properties that are difficult to obtain from one of the methods.

**4.5.2. Overview of Reactions Involving HCl at the MgO(001) Surface**

A diagram with all the processes discussed in the previous paragraphs and their energies is shown in fig. 4.15. The total energy of a closed loop in the diagram is always zero (keeping in mind that the energy values have to be reversed when considering a reaction proceeding against the direction of an arrow). This diagram can also be used to make statements about processes not discussed up to here.

For example, removal of chlorine as a charged ion from the associated molecule costs 1.8 eV to dissociate OH\(^-\) and Cl\(^-\) at the surface plus 1.7 eV to remove the isolated Cl\(^-\) from the surface, i.e. 3.5 eV in total. In comparison, removing Cl\(^{2-}\) from the adsorbed molecule as neutral atom costs 3.5 eV alone for dissociation at the surface plus 1.5 eV for desorption of Cl\(^{2-}\).

This means that removal of Cl\(^-\) as anion is preferred over the removal of Cl\(^{2-}\) as neutral atom. I have already considered this process with PW-DFT at finite separation in section 4.4.1.10. It was not clear from these calculations, however, which charge state would be preferred at *infinite separation*. It can now be said that the potential energy curves for removal of chlorine for the neutral over the charged state do not cross. This is in stark contrast to most molecular systems, for example the free HCl molecule, where neutral separation (at 3.9 eV) is favoured over charged separation (14.4 eV).

The dissociation energy at the surface into neutral species is 3.5 eV (4.9 eV in the vacuum). As dissociation into charged ions at the surface takes 1.8 eV, it is energetically favoured over dissociation into neutral species. However, both processes are due to their activation energy not accessible thermally at room temperature.
DFT Calculations of HCl Adsorbed on the MgO(001) Surface

McCarthy who predicted 0.48 eV binding energy. The adsorption energy per HCl molecule of 0.83 eV predicted by PW-DFT compares well with this result, as Hartree-Fock methods (which lack electron correlation) generally tend towards predicting lower binding energies than DFT at the GGA level without admixture of Hartree-Fock exchange. At this coverage, the adsorption energy per molecule is far from the adsorption energy of an isolated molecule (1.5 eV with HF admixture using EC-DFT, i.e. the B3LYP functional).

The prediction of simultaneous chemical dissociation and electrostatic association of HCl on the MgO(001) surface from the DFT calculations presented in this chapter demonstrates that signatures of OH\(^{-}\) vibrational modes as seen in HCl on \(\gamma - \text{Al}_2\text{O}_3\) \(^{156,157}\) and a constant peak desorption temperature from \(\text{Al}_2\text{O}_3\) at different levels of coverage (interpreted as signature of associative adsorption) do not necessarily contradict each other.

The experimental results discussed in the preceding paragraphs agree well with the theoretical predictions made in this chapter. Wittig et al.\(^{156}\) however, derived an activation energy of 0.3 eV by applying the Arrhenius equation (4.3) to the measured desorption rate.

As I have demonstrated that the adsorption energy per HCl molecule decreases with coverage, it may be supposed that the discrepancy between the adsorption energy of HCl predicted here (1.4–1.5 eV) to the desorption energy calculated due to experimental results by Wittig et al. is due to coverage. However, the experiment gives repeatable results for many molecular pulses,\(^{169}\) which indicates that the surface coverage remains low throughout the experiment. Due to the ratio of HCl in the molecular beam (1–2%) the surface coverage is estimated to be of the order of 10\(^{-3}\) monolayers HCl.\(^{169}\) Effects of HCl coverage can therefore be excluded as the reason for the discrepancy. It can, however, be due to one or several of the following factors:

1. HCl arrives at the surface diluted in a molecular beam with He, Ne and H\(_2\). As MgO is a highly polar crystal, rare gases can bind to it due to polarisation. This means that the surface coverage with foreign species in general may be much higher than the coverage with HCl molecules.

   a) This may affect the binding behaviour of HCl in ways not accounted for by the present theoretical investigation.

   b) The desorption behaviour may also be affected. The Arrhenius equation is based on the assumption that the reactive species are dilute, so its use may be inappropriate for the purpose of extracting the activation energy for HCl desorption in this experiment.

   c) There is experimental evidence\(^{170}\) that polar diatomic molecules in supersonic expansion experiments are in fact entrained with the other species. The dynamical processes considered then involve not just HCl but also

\[\text{Fig. 4.16.} \quad \text{A sketch of the potential surface of dissociation versus desorption coordinates. Starting from the adsorbed molecule at the potential minimum, the orthogonal dissociation and desorption coordinates are the channels indicated towards the left and right. Note that the potential along the dissociation coordinate is modulated due to the periodic surface potential.}\]

\[\text{Fig. 4.17.} \quad \text{Illustration of potential along Cl\(^{-}\) diffusion coordinate. The potential is modulated by the alternation of sites above magnesium ions and sites between magnesium ions.}\]

4.5.3. Comparison with Previous Work

A quarter monolayer coverage, i.e. two HCl molecules per 4 \(\times\) 4 \(\times\) 4 unit cell, corresponds to the coverage simulated with the unit cell used by Chacon-Taylor and
the solvent particles reaching the surface just before or after HCl. This may lead to a markedly different behaviour.

d) Solvent particles present at the surface may aid vibrational dissipation of HCl molecules adsorbed on the surface.

2. At the temperatures at which temporal profiles of HCl desorption were reported in refs. 150, 151 (up to 188 K), chemisorbed HCl molecules should remain at the surface. In Temperature Programmed Desorption (TPD) experiments of H2O from TiO2(110), for example, Brinkley et al.171 found a desorption peak at about 300 K which they attributed to the first monolayer of H2O adsorbed on the polar crystal surface. The adsorption energies of H2O to TiO2(110) and of HCl to MgO(001) should be comparable, as the systems are similar in their ionic character and the admolecules can donate protons to the surface oxygen ions.

From this I conclude that the desorbed molecules measured by Wittig et al.150,151 are those that underwent direct-scattering and trapping-desorption processes. These are distinct from chemisorption.172 In fact, the sticking coefficient measured in a similar scattering experiment by Gabbani et al.173 (where barium at 380 ms\(^{-1}\) was scattered off an MgO(001) surface at room temperature) is 0.76±0.05, i.e. about three quarters of the atoms reaching the surface never leave it. The activation energy extracted from the exponential decay of the temporal profiles measured is therefore not comparable to the binding energy of the chemisorbed HCl molecule.

3. In ref. 150, Wittig et al. presented scattering angle distributions for incident angles of 45° from the surface normal for the 0.11 eV beam and 30° for the 0.54 eV and 0.90 eV beams. Between the two latter beams, the higher energy beam showed the wider scattering angle distribution. This is not consistent with the supposed tendency towards specular scattering at higher incident energies.

4. The characteristic temperature \(T_{\text{rot}}\) of the rotational energy distribution of the scattered molecules was reported to rise with the incident energy in ref. 150. This is in accordance with the results of pair potential molecular dynamics simulations of the scattering of N\(_2\) off the Pt(111) surface by Blömer et al.174 The relatively small dependence on the incidence angle of \(T_{\text{rot}}\) for the 0.11 eV compared to the 0.54 eV and 0.90 eV beams was interpreted in ref. 150 as an indication of a longer residence time of the lower-energetic molecules at the surface. However, ref. 174 demonstrates how translational energy is converted to rotational energy for directly scattered molecules, i.e. the smaller dependence may equally be ascribed to the smaller amount of translational energy available.

Figure 4.18.: Illustration of proposed mechanism for trapping-desorption of HCl experiment. The coordinate shown is the stretch coordinate of the OH\(^-\) molecule. I propose that the bond formation energy after trapping (1) can be effectively stored in the OH\(^-\) vibrational modes without being dissipated into the crystal for several picoseconds (2). This means that desorption (3) occurs from the elevated energy level (2) rather than the vibrational ground state (0).

These points demonstrate that the dynamics experiments of refs. 150,151 can presently not be understood fully and that the microscopic mechanisms involved need to be studied further.

Theory can offer additional insight that can be used to interpret the experimental findings. The DFT calculations presented in this chapter predict the formation of OH\(^-\) at the surface, whose vibrational and librational frequencies are well separated from the bulk phonon density of states of MgO. The lifetimes of excitations along these modes are therefore likely to be comparatively large (of the order of picoseconds). In fact, I will describe in chapter 5 molecular dynamics simulations I have performed in which a vibrational excitation of the stretch mode survives for about 2 ps. Leaving aside the open question of interaction with He, Ne and H\(_2\) that are present in the beam, I propose the following mechanism for a trapping-desorption process of an isolated HCl molecule off the MgO(001) surface terrace, illustrated in fig. 4.18:

The potential for the relative coordinate between O and H is indicated by the strong line. As HCl approaches the surface (1), a chemical bond between the proton and a surface oxygen is formed. The smallest incident kinetic energy in the experiments of Wittig et al. corresponds to a velocity of 763.1 ms\(^{-1}\). At an incidence angle of 15°, this corresponds to an approach velocity perpendicular to the surface of 737.1 ms\(^{-1}\). Assuming an interaction region of 5 Å above the surface (a generous estimate, as the Madelung potential decays exponentially with the distance), the molecule has about 1.35 ps to dissipate its excess energy and get trapped. Considering the well-separated OH\(^-\) frequency, this is a very short time.

For those molecules that do get trapped at the surface, the bond formation energy is stored in the vibrational energy of OH\(^-\) and is dissipated very slowly due to the spectral localisation of the OH\(^-\) modes. The activation energy for desorption (3) is then the difference in energies between the vacuum level and level (2). This can be a lot smaller than the difference between the vacuum level and the vibrational ground
state energy. The latter difference is the binding energy minus the zero vibration energy, i.e. $1.4 \text{ eV} - \frac{0.65 \text{ eV}}{2} \approx 1.2 \text{ eV}$.

The adsorption energies extracted from the simulations presented here are related to the minimum of the potential shown in fig. 4.18, while the activation energy measured in the scattering experiment would relate to the difference between the vacuum level and the energy of the trapped molecule (2), which is much smaller. This is the case if dissipation due to solvent particles (point 1d above) is low, an assumption likely to be met, as the OH$^-$ stretch is spectrally localised (with about doubled frequency in the H$_2$ stretch and lower frequencies for all other modes involving solvent particles).

The illustration shown is related to the vibrational coordinate between hydrogen and oxygen (not hydrogen and chlorine). However, the survival of vibrational states of HCl observed in ref. 151 can be rationalised by observing that their vibrational energy can be stored in OH$^-$ vibrational quanta. As for the thermalised rotational distributions at all incident energies, the collision of randomly oriented diatomic molecules with a surface should lead to such a rotational distribution quite naturally. The dependence of the characteristic rotational temperature on the temperature of the crystal can be ascribed to events where molecules collide with oncoming surface atoms. Overall, this demonstrates that the experimental observations in refs. 150, 151, 155–157 are not contradictory to the theoretical predictions presented in this chapter.

### 4.5.4. Special Sites and Dynamics

It is computationally not viable to simulate special adsorption sites such as steps and kinks within the PW-DFT approach, since much larger unit cells would have to be used. As was seen in chapter 3, a finite cube of MgO(001) has vibrational normal modes localised at the corners, so that lattice dynamics and molecular dynamics (MD) calculations have to be performed in a periodic setup, where again special sites are difficult to treat. This is why this chapter has been limited to adsorption of HCl to the MgO(001) surface terrace.

The adsorption is strong enough at the surface terrace to effectively prevent diffusion already, so diffusion is unlikely to occur at special surface sites because there the adsorption energy of HCl should be even higher. This is due to the decreased coordination of the adsorption site oxygen and hence increased polarisability. The dynamics calculations discussed in the next chapter can then use a model for the adsorption site with a special oxygen ion to reproduce the OH$^-$ interatomic potential. The relative velocity of O and H can be recorded as the proton remains bound to the same surface oxygen ion throughout the simulation.

Due to stronger binding, the frequency of the stretch mode of OH$^-$ should be increased at special adsorption sites. This means that the OH$^-$ remains spectrally separated from the MgO band. The chlorine ion should still be associated with the hole on OH$^-$.

If a surface with a dense coverage of molecules were to be simulated dynamically, then the electrostatic interaction between neighbouring molecules would have to be taken into account, particularly if the molecules do not move in unison. This is clearly not desirable, as I want to simulate the smallest possible number of vibrational modes. Relatively isolated molecules adsorbed on the surface were therefore assumed for the dynamics calculations whose results are presented in the following chapters, necessitating usage of a comparatively large unit cell of $8 \times 8 \times 7 \text{ MgO}$ ions.

### 4.6. Conclusion

#### 4.6.1. Summary of Results

The DFT calculations presented in this chapter give new insights into the binding behaviour of HCl molecules on the (001) surface terrace of MgO. They predict binding of HCl to the MgO(001) surface to be caused primarily by a chemical bond between a surface oxygen and the molecular proton. The binding energy in the most stable configurations, (2) and (3), is between 1.4 eV and 1.5 eV.

The adsorption site surface oxygen ion donates about half an electron to the proton. Chlorine carries almost a full negative charge, i.e. the electronic charge density that is shared between chlorine and hydrogen in the free HCl molecule is pushed towards chlorine when the molecule approaches the surface. In unison with the breaking of the covalent bond between H and Cl, their distance increases to between 1.7 and 2.0 Å, compared to 1.3 Å in the free molecule. Chlorine is held in place by its electrostatic attraction to the OH$^-$ molecule, which represents a hole in the context of the crystal. Hence HCl at the surface is chemically dissociated but electrostatically associated.

Libration of chlorine across the adsorption site has a barrier of 0.05 eV or less and is therefore thermally accessible. The chlorine ion resides well inside the strongly attractive part of the Coulomb potential created by the hole on OH$^-$. Dissociation of Cl$^-$ to the adsorption site next-nearest neighbour Mg$^{2+}$ ion at the surface has a barrier of 0.65 eV. This makes it unlikely to occur at short timescales. Dissociation at the surface to infinite separation takes 1.8 eV. The dissociated system is stable with respect to desorption of the dissociated species.

Other configurations of HCl adsorbed on the MgO(001) surface terrace, such as a physical bond due to Coulomb attraction between a surface magnesium and the molecular chlorine (with hydrogen not taking part in the binding to the surface), are predicted to be unstable.
Although different functionals were used with the PW-DFT and the EC-DFT methods, their results agreed for isolated molecular adsorption when electrostatic interaction in PW-DFT was accounted for. The binding energy decreases with coverage. A simulation with one admolecule for each surface oxygen ion yielded desorbed molecules, i.e. this coverage is unstable. Additional HCl molecules can however be adsorbed on top of a 1/2 monolayer. The additional molecules are bound to the underlying layer of chlorine ions by hydrogen bonding.

The electronic levels introduced into the valence band by the molecule are resonant to the band structure of the MgO crystal and therefore may not be excited selectively. On the other hand, an OH$^-$ molecule is formed in the surface. The vibrational frequencies of OH$^-$ libration, rotation and vibration are well separated from the crystal (30-92 THz vs. 22 THz maximum of MgO). This provides an opportunity to excite OH$^-$ vibrations selectively by infrared radiation. This will be discussed in greater detail in the following chapters and eventually exploited to propose a coherent control scheme for the dynamics of the OH$^-$ stretch mode.

4.6.2. Proposed Experiments for Further Investigation

Experiments involving adsorption of slow HCl molecules, at low coverages, allowing sufficient time to dissipate energy from the adsorption process, should allow more time to dissipate the binding energy and thus lead to higher activation energies for desorption than reported in ref. 150. This may be done with a double vacuum chamber setup with separate pumps as used in ref. 173, where one chamber with low-pressure HCl gas is separated by a skimmer from the chamber where the scattering takes place. The velocity of the incoming molecules can be controlled by the pressure difference between the chambers. Low-kinetic energy trapping-desorption experiments involving H$^{35}$Cl and D$^{37}$Cl should illuminate whether HCl molecules dissociate and recombine (in mixed combinations) at the surface prior to desorption. This would yield an unambiguous answer to the question whether molecules dissociate and whether chlorine can diffuse at the surface at long time scales.

Chapter 5. Shell Model Dynamics of HCl on the MgO(001) Surface Terrace

Aims: The properties of HCl on the MgO(001) surface derived from the calculations described in the previous chapter are used to set up an appropriate shell model representation of this system. The system is subsequently studied using shell model lattice dynamics and molecular dynamics (MD).

The phonon modes from lattice dynamics calculations are analysed with respect to localisation at the adsorption site of HCl. The results of this analysis are then used to aid the analysis of equilibrium and non-equilibrium MD calculations. The non-equilibrium MD are initialised by a simulated sudden excitation of the stretch mode of OH$^-$.

Methods: The adsorption site attenuation parameter $a_{\text{point}}$ was applied to the lattice dynamics results (see section 2.3.4) to find normal modes localised at the adsorption site. Shell-model molecular dynamics (sections 2.2 and 5.2) as implemented in the program GULP were used to perform adiabatic MD simulations. The massless shells are fully relaxed after each core propagation step.

After equilibrium dynamics, a sudden excitation of the OH$^-$ stretch mode is applied to a snapshot of the equilibrium dynamics. This is done using custom velocity changes that take the parameters of the snapshot into account (section 5.2.4.1). This scheme makes sure that exactly the amount of kinetic energy specified is added to a certain normal mode and no energy is added to other normal modes. FROG analysis (section 5.6) and cross-correlation functions (section 5.7) are used to analyse the trajectories of some modes (velocities where available, compound kinetic energies otherwise).

Results: Normal modes associated with the admolecule are presented. The stretch mode frequency of OH$^-$ is well separated from the MgO slab spectrum while its rotational and librational modes are closer but still separated. No internal HCl modes exist, confirming the notion of dissociated adsorption of HCl.

Three classes of modes can be distinguished: Modes that are almost fully localised on the admolecule, modes that involve the admolecule to a high degree but also other atoms of the system and modes that are fully delocalised over the whole system. The OH$^-$ normal modes fall into the first class, while normal modes with large Cl$^-$ contributions fall into the second.

During the non-equilibrium MD, the excitation of the stretch mode of OH$^-$ stays at a constant level for 1.55 ps and only then starts to decay with a lifetime of 0.82 ps. This is suggestive of a mechanism in which symmetry breaking is involved, i.e. the dissipation is started by certain environmental conditions and, once started, proceeds independently.

The energy exchange between the OH$^-$ stretch mode and the surface proceeds exclusively via the OH$^-$ rotational and librational modes, whose orientations at each time step are readily derived from symmetry considerations. Due to its weak electrostatic bond to OH$^-$ as well as the surface, Cl$^-$ does not constitute a dissipation channel for OH$^-$, however, chlorine may play a role in initiating the dissipation process between the OH$^-$ stretch mode and OH$^-$ rotation/libration by providing an environment with a broken symmetry. A model is extracted for the dissipation of the OH$^-$ stretch energy for use with nuclear quantum dynamics.

### 5.1. Introduction

Lattice dynamics calculations yield the vibrational modes of a physical system. These do not interact in the harmonic approximation. According to perturbation theory, energy dissipation in a weakly anharmonic system proceeds via interactions between these modes.

In order to quantify this coupling, it is therefore necessary to go beyond the harmonic approximation by using the molecular dynamics (MD) method which means time-integrating the classical equations of motion. This allows to find the pathways along which vibrational energy is dissipated. MD is used with a shell model representation of the system of interest in order to avoid overestimating the frequencies of optical modes.

In the course of an MD simulation, ions are displaced from their equilibrium positions and therefore the normal modes are subject to anharmonic parts of the potential energy surface. These anharmonicities mediate the energy transfer between different modes.

The idea behind these calculations is to track the populations of the normal modes. Correlations between a decreasing population of one mode and an increasing population of another are then interpreted as a sign of coupling present between the two normal modes.

<table>
<thead>
<tr>
<th>ensemble</th>
<th>fixed quantities in MD</th>
<th>short</th>
</tr>
</thead>
<tbody>
<tr>
<td>microcanonical</td>
<td>number of atoms, volume, energy</td>
<td>NVE</td>
</tr>
<tr>
<td>canonical</td>
<td>number of atoms, volume, temperature</td>
<td>NVT</td>
</tr>
<tr>
<td>grand canonical</td>
<td>number of atoms, pressure, temperature, chemical potential, volume, temperature</td>
<td>NpT</td>
</tr>
</tbody>
</table>

Table 5.1.: Overview of thermodynamic ensembles. In order to be able to follow the flow of energy between normal modes, the microcanonical ensemble has been used for this project.

### 5.2. Molecular Dynamics Methods

#### 5.2.1. Introduction

Statistical properties like temperature and pressure can be extracted from the microscopic state of an atomic system. The collection of all microscopic states of a system that represent a certain combination of fixed statistical properties is called a thermodynamic ensemble. Table 5.1 shows an overview of different types of thermodynamic ensembles with the statistical quantities conserved in the type of molecular dynamics simulations that are used to simulate them. A special case is the canonical ensemble, which is simulated either by isochoric-isothermal or the isobaric-isothermal MD, depending on the problem considered. Note that the results of MD simulations may not reproduce the observable distribution functions of a particular ensemble but aspire to approximate them.

This approach relies on the assumption that observables can be extracted from a thermodynamic system by time-averaging. The relation between time averages and ensemble averages is the subject of the ergodic hypothesis:

**Ergodic hypothesis:** During a propagation in time, a system passes through all states in the ensemble, so that for any observable $O$ the time average equals the ensemble average

$$
\langle O \rangle_{\text{time}} = \langle O \rangle_{\text{ensemble}} \, .
$$

In practice, this is done by taking the time average over a finite simulation period, which, beside a possible non-ergodicity of the system, is an important source of error.

The objective of the MD simulations in this project is to analyse the transfer of vibrational energy between the HCl admolecule and the MgO(001) surface. Due to the finite accuracy of the methods for solving the atomic equations of motion, it may be assumed that it is beneficial to enforce constant temperature by renormalising the atomic velocities. This would, however, interfere with the very processes of energy exchange in which I am interested. Of the ensembles in table 5.1, the NVE or microcanonical ensemble is therefore best suited to answer the questions posed. Fluctuations in the normal mode populations of this ensemble are then entirely due to the energy exchange processes under consideration and not due to the procedures keeping temperature or pressure constant.
For consistency with lattice dynamics, I have used the GULP program package by Gale\(^3\) to perform molecular dynamics. This enabled me to easily transfer the lattice dynamics Hamiltonian to MD simulations. The normal modes from the lattice dynamics calculations are then compatible with the MD simulation and can thus be used to analyse it.

### 5.2.2. Shell Model MD

After imposing certain initial conditions (which are discussed below), the model system is propagated according to the Newtonian equations of motion. To do this, I have used the Leapfrog-Verlet method, which yielded satisfactory accuracy. This and an alternative propagation scheme are formally formulated in appendix B. I have used a time step of 0.5 fs to capture the high-frequency hydrogen dynamics. After each time step, the shells are relaxed with respect to the current core positions until the forces on them fall below \(10^{-10} \text{ eV Å}^{-1}\). The shell relaxation has to be performed at this high accuracy to enforce total energy and momentum conservation.

The total energy is conserved to within one hundredth of an electron volt during a simulation of several picoseconds, which is satisfactory. The MD runs were done at a temperature of 450 K (i.e. initial temperature at equilibrium geometry of 900 K), in order to achieve a higher ion collision rate compared to room temperature and hence faster equilibration. Satisfactory equilibration was achieved after a simulation period of 2 ps, which can be recognised by the levelling off of the temperature. Strictly speaking, equilibration of the normal mode population needs to be ascertained but normal mode analysis is non-trivial away from the equilibrium geometry of the system and so this is beyond the scope of this work.

### 5.2.3. Initialisation of Equilibrium MD

In the software used (GULP\(^3\)), molecular dynamics are initialised by positioning the atoms at their equilibrium positions (i.e. the potential energy is zero) and random velocities are assigned to them, satisfying the Maxwell-Boltzmann distribution corresponding to a certain starting temperature. Since at thermodynamic equilibrium the total energy is partitioned equally between potential and kinetic energy, the starting temperature must be set to twice the target temperature.

This approach means that the initial state may have non-zero total momentum. The total momentum is made zero in GULP by changing the velocity of two ions in the unit cell, such that the momentum from all other ions is counterbalanced. This disturbs the velocity distribution only marginally when the unit cell usually consists of many ions (which is the case in the simulations presented here).

This construction of initial conditions clearly does not represent thermodynamic equilibrium. Therefore molecular dynamics have to be run for a time long enough to allow a sufficient number of collisions between the ions, which due to anharmonicity equilibrate the populations of the vibrational modes. This part of the molecular dynamics simulation is called equilibration and is not used to extract any physical information, as it is ruled by the unphysical initial conditions. Only the dynamics after the equilibration period are used to produce results. This part of the dynamics is called production.

### 5.2.4. A Novel Initialisation Method for Non-Equilibrium Molecular Dynamics at Nonzero Temperature

#### 5.2.4.1. Excitation of the OH\(^-\) Stretch Mode

After a production MD run of 7.5 ps, I have altered the state of the system by a sudden excitation of the OH\(^-\) stretch mode whose dissipation will be observed. This section describes how this is done.

Dissipation dynamics may be performed at zero Kelvin, as was done for example by Moritsugu et al.\(^{175}\) on a protein molecule and, most recently, by Yamamoto et al.\(^{176,177}\) on complexes of small molecules. In these works non-equilibrium molecular dynamics were initialised by giving non-zero initial velocity to only one normal mode and leaving all other normal modes unpopulated. This does, however, not model the modes accepting population from the excited mode according to the elevated temperatures used in many experiments, e.g. room temperature.

Rather than using this approach, I have therefore performed dissipation dynamics that are initialised by altering the state at the end of the non-zero temperature equilibrium MD run only in the OH\(^-\) stretch mode. The MD run is stopped after the equilibrium production run and all position and velocity vectors are saved. The velocities are to be altered by excitation of the OH\(^-\) stretch mode. Consequently, the MD run is restarted using the saved positions and the altered velocities.

As this section describes the excitation step, I will refer to the state of the system as it comes out from the equilibrium run as “initial” positions and velocities. This “initial” state is determinate but uncontrolled, so a method is described to apply an excitation to any initial state. This method yields the change of the initial velocity vectors needed to effect the desired excitation. The proposed method can be extended to any mode whose excitation decay one might want to simulate. I present this generalisation in the following section (5.2.4.2).

Let \(m_O\) and \(m_H\) be the masses of the oxygen and hydrogen ions, \(\bar{v}_0\) and \(\bar{v}_H\) their initial velocities and \(\Delta E\) the amount of kinetic energy to be injected by adding the velocities \(\bar{v}_0\) and \(\bar{v}_H\) to them.

The kinetic energy after the excitation is

\[
E_k = \frac{m_O}{2} (\bar{v}_0 + \bar{v}_0)^2 + \frac{m_H}{2} (\bar{v}_H + \bar{v}_H)^2,
\]

while the initial kinetic energy was

\[ E_0 = \frac{\mu_O}{2} v_{\text{O}}^2 + \frac{\mu_H}{2} v_{\text{H}}^2. \]

Accordingly, the energy change is

\[ \Delta E = E_1 - E_0 = \frac{\mu_O}{2} (\vec{v}_0^2 + \vec{v}_O^2) + \frac{\mu_H}{2} (\vec{v}_H^2 + \vec{v}_H^2). \] (5.2)

Obviously the energy change does not just depend on the velocity changes \( \vec{v}_0 \) and \( \vec{v}_H \) but also on mixed terms with the initial velocities \( \vec{v}_O \) and \( \vec{v}_H \). This means that conversely the velocities that have to be added will depend on the initial velocities as well as \( \Delta E \).

The change of the total momentum must be zero, therefore

\[ \vec{v}_O = -\frac{\mu_O}{\mu_H} \vec{v}_O. \] (5.3)

Substituting (5.3) into (5.2) yields

\[ \frac{\mu_O}{2} \left(1 + \frac{\mu_O}{\mu_H}\right) v_{\text{O}}^2 + \mu_O (\vec{v}_O - \vec{v}_H) \vec{v}_O - \Delta E = 0. \] (5.4)

The stretch mode of OH\textsuperscript{−} is to be excited, for which our educated guess is that it is always collinear with the OH\textsuperscript{−} molecule. Then \( \vec{v}_O \) must be collinear with the normalised direction vector \( \vec{x} \) that points from the hydrogen ion to the oxygen ion (i.e. \( \vec{v}_O \) and \( \vec{v}_H \) depend on the initial positions as well)

\[ \vec{v}_O = a \vec{x}, \quad a \in \mathbb{R}, \quad \vec{x} \cdot \vec{x} = 1. \] (5.5)

Substituting this into (5.4) leads to a scalar quadratic equation for \( a \)

\[ \frac{\mu_O}{2} \left(1 + \frac{\mu_O}{\mu_H}\right) \cdot a^2 + \mu_O (\vec{v}_O - \vec{v}_H) \vec{x} - \Delta E = 0 \] (5.6)

which is readily solved by

\[ a_{1/2} = \frac{-(\vec{v}_O - \vec{v}_H) \vec{x} \pm \sqrt{((\vec{v}_O - \vec{v}_H) \vec{x})^2 + \frac{\Delta E}{\mu_o}}}{1 + \frac{\mu_O}{\mu_H}} \]

Substituting a solution of choice back into (5.5) and (5.3) yields velocity changes \( \vec{v}_O \) and \( \vec{v}_H \) necessary to bring about the kinetic energy change \( \Delta E \).

5.2.4.2. Generalisation of the Proposed Method to the Excitation of a General Vibrational Mode

This method of injecting kinetic energy can be generalised to modes with participation of more than two atoms. Since the system after an equilibrium MD simulation at non-zero temperature is generally not at the equilibrium geometry, the normal mode at this geometry has to be excited. For the OH\textsuperscript{−} stretch mode, the current stretch mode was readily guessed according to the direction vector from oxygen to the proton as done in eqs. (5.5) and (5.5). This is not the case for all modes.

However, in a purely crystalline system at moderate temperatures the order of the atoms does not change radically, so using the equilibrium normal modes can be a good approximation. For the OH\textsuperscript{−} ad molecule, this was not the case, as the orientation of the molecule can change.

Generally, non-equilibrium normal modes can be determined by assuming harmonic potentials in a similar fashion as reviewed in section 2.1. However, away from equilibrium the simplifying relation \( \frac{\partial \mu}{\partial v} = 0 \) does not hold and so the potential gradient has to be taken into account in the construction of the harmonic dependence of the potential on the ionic coordinates.

Non-equilibrium lattice dynamics are reviewed in ref. 83 but I will not present them here, as I have performed non-equilibrium MD exclusively for the OH\textsuperscript{−} stretch mode, where this is not necessary as the OH\textsuperscript{−} stretch mode is readily guessed at every initial configuration.

In analogy to eq. (5.2),

\[ \Delta E = \sum_{j=1}^{N} \sum_{\beta=1}^{3} \frac{\mu_j}{2} v_{j\beta} (2u_{j\beta} + v_{j\beta}) . \] (5.7)

Now I want to transform this equation into a scalar quadratic equation as above. To this end, I will use the components of the normal mode vector that is to be excited, as in eqs. (5.3) and (5.5).

Instead of keeping to a vector formulation as in eq. (5.4) and only subsequently extracting a scalar parameter by using the direction vector \( \vec{x} \), I will do this in one step (as there is no obvious three-dimensional direction vector in a general mode).

As mentioned in section 2.1, normal modes are given as mass weighted ratios \( p_{n(\beta)} \) with

\[ p_{n(\beta)} = \sqrt{\mu} x_{n(\beta)} \] with \( \sum_{n=1}^{3N} x_{n(\beta)}^2 = 1. \)

where \( n \) labels the number of a mode with \( N \) atoms in the unit cell \((n = 1, \ldots, 3N)\), \( j \) is the number of an ion, \( \mu_j \) its mass and \( \beta \) is a Cartesian direction, \( \beta = 1, 2, 3. \) The proportional displacement in the mode \( n \) of ion \( j \) in the direction \( \beta \) is then \( x_{n(\beta)} \).

As before, the velocities of the different Cartesian components of the participating atoms are changed at the same ratio as the Cartesian coordinates of the mode. Now choose one Cartesian component \( p_{n(\alpha)} \) such that \( |p_{n(\alpha)}| \gg 0 \), and express all other velocity components in terms of this one:

\[ \frac{v_{j\beta}}{v_{\alpha}} = \frac{x_{n(\beta)}}{x_{n(\alpha)}} = \sqrt{\frac{\mu_j}{\mu}} \frac{p_{j(\beta)}}{p_{j(\alpha)}} \] (5.8)

This can be related to the OH\textsuperscript{−} stretch mode excitation from the previous section as follows. For the OH\textsuperscript{−} stretch mode, eq. (5.8) reads

\[ p_{\text{O}H} = \Lambda x_{\text{O}}, \quad p_{\text{H}H} = -\Lambda x_{\text{H}} x_{\text{O}} \] (5.9)

where \( x_{\text{O}} \) are the Cartesian components of the direction vector \( \vec{x} \) of eq. (5.5) and \( \Lambda \) is a normalisation constant. Choosing a velocity component of oxygen as \( v_{\text{O}H} \) and plugging eq. (5.9) into eq. (5.8) yields eq. (5.3).

Now go back to the case of a general mode; substitution of eq. (5.8) into eq. (5.7)
yields
\[ \left( \sum_j \frac{\mu_j^2 p_{n(j)}}{2 \mu_j P_{n(\infty)}} \right) v_{m} + \left( \sum_j \frac{\mu_j^2 p_{n(j)}}{\sqrt{\mu_j P_{n(\infty)}}} \right) v_{n} - \Delta E = 0. \]

The solution of this scalar quadratic equation is
\[ (v_{n})_{1/2} = \left( \frac{\sum_j \mu_j^2 p_{n(j)} u_{j(j)}}{\sum_j \mu_j^2 P_{n(\infty)}} \pm \sqrt{\left( \frac{\sum_j \mu_j^2 p_{n(j)} u_{j(j)}}{\sum_j \mu_j^2 P_{n(\infty)}} \right)^2 + 2 \Delta E \left( \sum_j \mu_j^2 p_{n(j)} u_{j(j)} \right)} \right) \sqrt{\mu_j P_{n(\infty)}}. \tag{5.10} \]

Since \( p_{n(\infty)} \) appears as a factor, eq. (5.10) only adds energy if \( |p_{n(\infty)}| \neq 0 \), which is what was assumed. Thus, eq. (5.10) yields the velocity changes to apply to inject exactly \( \Delta E \) into the kinetic energy of mode \( n \).

### 5.2.5. Analysis of Dissipation Dynamics Results using the Cross-Correlation Function

I am interested in how energy progresses from one normal mode of the system to another. To this end, I will look at the functions giving the kinetic energies of the modes and see if I can observe vibrational energy decreasing in one and simultaneously increasing in the other. Another way to look at it is to find a time shift for one function where it overlaps most with the other. This can then be viewed as the time it takes for vibrational energy to reappear in the same mode.

A measure for the overlap between two complex functions \( f_1 \) and \( f_2 \) defined on the interval \( I \) at a time-shift \( \tau \) between them is the cross-correlation function

\[ r(\tau) = \frac{\int_I f_1(t) (t - \tau) f_2(t) dt}{\sqrt{\int_I [f_1(t)]^2 dt} \sqrt{\int_I [f_2(t)]^2 dt}} \]

where \( M_1 f_1 \) denotes the expectation value of the function \( f_1 \) over the interval \( I \) and \( \sqrt{\int_I [f_1(t)]^2 dt} \) is the standard deviation. \( r(\tau) \) has a modulus of one if the functions shifted relative to each other by \( \tau \) only differ by a phase factor and is zero if they have no overlap at all.

In the present case where the functions are real (kinetic energy) and are given only on the time-steps of the molecular dynamics calculation, \( I \), \( f_1 \) and \( f_2 \) can be evaluated only at \( t = t_0 + i \Delta t \), \( r \) can only be calculated at multiples of the time step, i.e. at \( \tau_j = j \Delta t \). The discretised formula

\[ r(\tau_j) = \frac{\sum_i (f_1(t_i) - M_1 f_1) (f_2(t_i - \tau_j) - M_2 f_2)}{\sqrt{\sum_i [f_1(t_i) - M_1 f_1]^2} \sqrt{\sum_i [f_2(t_i) - M_2 f_2]^2}} \tag{5.11} \]

is used.
order to reproduce the key properties of the OH$^-$ molecule.

For the hydroxyl group I started from the Morse potential parameterisation by Saul and Catlow$^{162}$ and altered the dissociation energy in order to approach the desorption energy found in the ab initio calculations of chapter 4:

The original Morse potential due to ref. 162 models the free hydroxyl molecule which at large intramolecular separation consists of an O$^-$ ion and a neutral H$^0$ atom. As was seen in the overview of ab initio adsorption energies (fig. 4.15), desorption of a neutral hydrogen atom can be represented as first removing chlorine along the surface away from the adsorption site (3.5 eV) and then removing the now isolated hydrogen from the surface (0.3 eV). The desorption energy of H$^0$ is therefore predicted to be 3.8 eV.

I have chosen a value of 5 eV for the Morse parameter $D$ (table 5.2), which is a compromise between this dissociation energy and vibrational frequency of OH$^-$. The model potential corresponds to a classical frequency of 109 THz (3638 cm$^{-1}$) which compares to a measured frequency of 111 THz (3700 cm$^{-1}$) in the free OH$^-$ molecule.$^{181}$ Another comparison can be made to the stretch mode of OH$^-$ formed due to HCl adsorption at the $\gamma$-Al$_2$O$_3$ surface,$^{155-157}$ which yielded a band centred around 3500 cm$^{-1}$, i.e. 104.9 THz. Note that the model for the hydroxyl group involves exclusion of the (explicit) electrostatic interaction between the involved oxygen ion and the proton, as that is implied in the Morse potential used.

I have furthermore parameterised a repulsive Buckingham potential for the interaction between H and Cl. It has no attractive part (i.e. the coefficient $C$ of the van der Waals $r^{-6}$ term is zero). This potential is needed to counter the Coulomb attraction between H$^+$ and Cl$^-$ at smaller distances (thereby modelling the charge density donated to hydrogen from the adsorption site surface oxygen). The remaining two parameters $A$ and $\rho$ of the potential were found by systematic searching. The parameters were chosen to reproduce the geometry of the adsorbed system and the energy change as the distance between H and Cl is decreased (i.e. where the repulsion dominates over the Coulomb attraction).

As full electron charges are used on OH$^-$ and Cl$^-$ and the corresponding chlorine charge from DFT calculations is lower, this repulsive force is overestimated compared to the DFT results. In the natural population analysis of the ab initio EC-DFT results, section 4.4.2.5, the charge on chlorine was seen to be between 0.85 and 0.92 electronic charges. This means that the attractive force between chlorine and the cationic species in the system is overestimated in the shell model, lowering the energy with respect to the ab initio result. However, the force field parametrisation used for chlorine is compatible only to the fully charged ion. Re-parameterising the interaction of chlorine with the other species of the system is outside the scope of this project, so the chlorine charge was left at one electron charge.
In order to gauge the quality of the force field fitted for the admolecule, the configurations (1) through (4) were simulated using this model. A comparison of the results of these calculations with the DFT results is shown in table 5.3, alongside diagrams illustrating the configurations.

The configurations were approximated in the shell model by constrained or full optimisation. Constrained optimisation was necessary for confs. (1), (3) and (4) because all these initial configurations converged to configuration (2).

This is mainly due to the energy minimiser of the shell-model lattice dynamics code GULP that always finds the global energy minimum even when starting from a saddle point. It is also indicative of the absence in the shell model of the small barriers between the configurations found with the ab initio methods. These are always of the order of 0.05 eV (compare table 4.6), so the transitions are easily accessible at room temperature. This means that the disappearance of the barriers should not introduce an important error to the molecular dynamics.

Conf. (1) was constrained by fixing the lateral coordinates of the proton and the chlorine ions. Both ions are free to relax perpendicularly to the surface and all other surface ions are free to relax in any direction. This means that the constrained optimisation of conf. (1) is exceptional in that this setup strictly conforms to the saddle point. In contrast, confs. (3) and (4) were constrained by fixing the lateral coordinates of chlorine and one magnesium ion at the centre of the slab. Thus, the local environment of the adsorption site is allowed to relax, however, chlorine is not allowed to relax laterally with respect to the whole crystal which introduces an additional error to the calculation.

The energy differences between the constrained optimisations of confs. (3), and (4) and conf. (2) are therefore upper bounds for the shell model energy differences of the local minima obtained with DFT.

Table 5.3 shows the energies relative to conf. (2) for the shell model and the EC-DFT and PW-DFT methods (see chapter 4). It can be seen that the relative energies of confs. (1) and (3) are enhanced in the shell model. This has to be attributed to the overestimate of the energy lowering in conf. (2) due to Coulomb attraction between chlorine and a surface magnesium ion. A signature of this effect can be found in the shorter equilibrium distance between chlorine and the surface ions in all configurations.

Unlike for confs. (1) and (3), the relative energy of conf. (4) is smaller in the shell model than in the ab initio results. This is likely to be due to the full charge on Cl\(^-\) in the shell model, which helps to lower the energy due to attraction to the adsorption site Mg\(^+\) ion and polarisation of the adjacent oxygen ions. Another feature worth mentioning is the increased surface angle of the OH\(^-\) axis in conf. (4). This is due to the repulsion between OH\(^-\) and its nearest neighbour cations, which lifts OH\(^-\) out of the surface in conf. (4). This effect is more pronounced in the shell

<table>
<thead>
<tr>
<th>conf.</th>
<th>(1) upright</th>
<th>(2) tilted(100)</th>
<th>(3) tilted(110)</th>
<th>(4) dissociating</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{conf}}$</td>
<td>-9116.606</td>
<td>-9116.998</td>
<td>-9116.853</td>
<td>-9116.405</td>
</tr>
<tr>
<td>$\Delta E_{\text{shell}}$</td>
<td>0.39</td>
<td>0</td>
<td>1.05</td>
<td>0.53</td>
</tr>
<tr>
<td>$\Delta E_{\text{EC}}$</td>
<td>0.13</td>
<td>0</td>
<td>0.08</td>
<td>0.68</td>
</tr>
<tr>
<td>$\Delta E_{\text{PWcorr}}$</td>
<td>0.05</td>
<td>0</td>
<td>-0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 5.3: Key geometries of an adsorbed HCl molecule at the MgO terrace as calculated with the shell model. Only a few atoms of the MgO crystal are shown for clarity; note that the calculations were done on a unit cell of $8 \times 8 \times 7$ MgO ions. Energies in eV relative to conf. (2) from shell model, EC-DFT, dipole-dipole corrected PW-DFT and large unit cell PW-DFT calculations. Geometric details: angles and distances between atoms. Results from EC-DFT calculation, table 4.14, in square brackets. See also table 4.4 for comparison with PW-DFT results.

5.4.2. Phonons Localised at the Adsorbed Molecule

Lattice dynamics calculations were performed at the $\Gamma$-point using the supercell described in section 5.3.2. The localisation criterion $\sigma_{\text{point}}$ reviewed in section 2.3.4, where the parameter that is weighted is the distance from the OH\(^-\) group.

An overview of the modes with the largest $\sigma_{\text{point}}$ values at the adsorption site is given in table 5.4. The participation function $P$ is shown alongside the ionic participations $p_O$, $p_H$, $p_{\text{Mg}}$ and $p_{\text{Cl}}$ of the adsorption site oxygen, the proton, the chlorine ion and the surface magnesium ion nearest to Cl\(^-\), plus the IR and Raman intensities of the respective mode. The participation functions of the modes above the double line are between 1.0 and 91, whereas the average over all modes of the participation function is 173 (450 ions in the supercell), a significant difference. Note that among the modes with low participation function are such normal modes as substrate modes, modes localised at the centre of the slab and extended surface modes, all of which are not localised at the admolecule. The participation therefore serves as additional information rather than to detect modes localised at the adsorption site.

Below the double line in table 5.4 the two most important OH\(^-\) compound modes
Shell Model Dynamics of HCl on the MgO(001) Surface Terrace

The most important modes localised at the HCl molecule adsorbed at the MgO surface, their frequency, participation of the surface oxygen at the adsorption site and the chlorine, participation function, infrared (IR) and Raman intensities.

\[ \text{Table 5.4:} \]

<table>
<thead>
<tr>
<th>Characterisation</th>
<th>( f [\text{THz}] )</th>
<th>( \alpha_{\text{point}} )</th>
<th>( P_{\text{O}} )</th>
<th>( P_{\text{H}} )</th>
<th>( P_{\text{Cl}} )</th>
<th>( P_{\text{R}} )</th>
<th>( P_{\text{IR}} )</th>
<th>( P_{\text{Raman}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cl}^- ) rotation(^a)</td>
<td>1.192</td>
<td>0.91</td>
<td>1.04</td>
<td>0.0049</td>
<td>0.0804</td>
<td>0.0001</td>
<td>0.0124</td>
<td>0.0000</td>
</tr>
<tr>
<td>( \text{Cl}^- ) libration(^b)</td>
<td>2.099</td>
<td>0.71</td>
<td>3.22</td>
<td>0.0373</td>
<td>0.0000</td>
<td>0.0551</td>
<td>0.0006</td>
<td>0.0465</td>
</tr>
<tr>
<td>( \text{Cl}^- ) libration(^c)</td>
<td>2.277</td>
<td>0.58</td>
<td>8.29</td>
<td>0.0308</td>
<td>0.0019</td>
<td>0.3440</td>
<td>0.0021</td>
<td>0.0291</td>
</tr>
<tr>
<td>( \text{Cl}^- ) normal(^d)</td>
<td>3.089</td>
<td>0.42</td>
<td>35.58</td>
<td>0.0293</td>
<td>0.0024</td>
<td>0.1341</td>
<td>0.0588</td>
<td>0.0227</td>
</tr>
<tr>
<td>( \text{Cl}^- ) normal(^e)</td>
<td>3.400</td>
<td>0.53</td>
<td>38.29</td>
<td>0.0119</td>
<td>0.0010</td>
<td>0.0652</td>
<td>0.0286</td>
<td>0.0106</td>
</tr>
<tr>
<td>( \text{Cl}^- ) normal(^f)</td>
<td>3.923</td>
<td>0.43</td>
<td>3.089</td>
<td>0.0363</td>
<td>0.0030</td>
<td>0.3031</td>
<td>0.1329</td>
<td>0.0361</td>
</tr>
<tr>
<td>( \text{OH}^- ) rotation(^g)</td>
<td>27.823</td>
<td>0.69</td>
<td>1.12</td>
<td>0.0485</td>
<td>0.9052</td>
<td>0.0013</td>
<td>0.0047</td>
<td>0.2719</td>
</tr>
<tr>
<td>( \text{OH}^- ) libration(^h)</td>
<td>29.631</td>
<td>0.71</td>
<td>9.31</td>
<td>0.0359</td>
<td>0.9271</td>
<td>0.0008</td>
<td>0.0155</td>
<td>0.2589</td>
</tr>
<tr>
<td>( \text{OH}^- ) stretch(^i)</td>
<td>86.957</td>
<td>0.71</td>
<td>1.13</td>
<td>0.0591</td>
<td>0.9407</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.4511</td>
</tr>
<tr>
<td>( \text{OH}^- ) compound(^j)</td>
<td>3.922</td>
<td>0.43</td>
<td>3.089</td>
<td>0.0363</td>
<td>0.0060</td>
<td>0.3031</td>
<td>0.1329</td>
<td>0.0364</td>
</tr>
<tr>
<td>( \text{OH}^- ) compound(^k)</td>
<td>14.344</td>
<td>0.29</td>
<td>92.27</td>
<td>0.0139</td>
<td>0.0025</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0241</td>
</tr>
</tbody>
</table>

\(^{a,b,c,d,e,f,g,h,i,j,k}\) rotation in a plane parallel to the surface around \( \text{OH}^- \), libration - towards and away from \( \text{OH}^- \), normal to the surface, rotation of \( H \) parallel to the surface around \( \text{O} \), libration in a plane perpendicular to the surface around \( \text{O} \), motion of \( \text{OH}^- \) molecule as a whole in a vibrational mode.

Fig. 5.1 illustrates the most important vibrational modes contributing to these normal modes. The normal modes involving chlorine are characterised by chlorine rotation around the adsorption site, chlorine libration (a motion of chlorine towards the adsorption site) and chlorine motion normal to the surface. \( \text{Cl}^- \) rotation and libration take place in a plane parallel to the surface. Both chlorine libration and surface-normal motion occur in several normal modes. The participation of chlorine in these modes is weak: at between 0.065 and 0.55, compared to a chlorine participation in the \( \text{Cl}^- \) rotational mode of 0.98. Together with the \( \alpha_{\text{point}} \) values, this demonstrates that the librational and surface-normal chlorine normal modes are not as strongly localised at the adsorption site as the rotational chlorine mode. The participations of \( O \) and \( H \) in the modes associated with \( \text{Cl}^- \) are very low, while those of the surface magnesium ion are comparatively high in the surface-normal modes. This indicates that the less-localised librational and surface-normal chlorine modes involve the surface lattice ions rather than \( \text{OH}^- \).

The other class of modes is made up of normal modes involving the hydroxyl \( \text{OH}^- \) group formed at the surface. These are characterised as rotation, libration and stretch. Note that, while the rotational mode of \( \text{OH}^- \) displaces the proton in a plane parallel to the surface, the librational mode of \( \text{OH}^- \) does not. Instead, it displaces the proton in the plane of the paper, spanned by the surface normal through the adsorption site oxygen and the \( O-H \) axis.

Additionally, Table 5.4 demonstrates that, among the modes localised at the adsorption site, there are no modes with simultaneous participation of hydrogen and chlorine. This underlines the notion of the breaking of the \( H-Cl \) bond upon adsorption.

The modes that involve the \( \text{Cl}^- \) ion have unusually low frequencies and therefore are good examples for the “soft modes” often associated with adsorption of a molecule to a surface. On the other hand, the \( \text{OH}^- \) modes are higher in frequency than the lattice (whose normal modes extend up to about 22 THz); particularly the \( \text{OH}^- \) stretch is far removed from the \( \text{MgO} \) band, at 86.1 THz. The deviation of the \( \text{OH}^- \) stretch frequency from the frequency corresponding to the second derivative at the minimum of the \( O-H \) Morse potential must be due to interaction with the surface. Fig. 5.2 shows the frequencies of the localised modes in comparison to the vibrational density of states (DOS) of the total \( \text{MgO} + \text{HCl} \) system.
Unlike the general surface modes in fig. 3.16 on p. 77, the modes localised at
the molecular adsorption site lie outside or at the fringes of the DOS of the MgO
slab. This is due to the modes involving the light proton and the hard (chemical)
potential it is subject to, resulting in modes of higher frequency than the MgO band
and, on the lower end of the spectrum, due to the high mass of chlorine and softer
(electrostatic) potential experienced by it.

Due to the central symmetry perturbation of the potential caused by the adsorbed
molecule, a breathing mode centred at the adsorption site is predicted to exist, i.e. a
normal mode involving point symmetric motion of the adsorption site neighbours
away from or towards it. It turns out that the OH\(^{-}\) stretch mode contains this
breathing motion. The OH\(^{-}\) stretch is dominated by oxygen and hydrogen motion
(compound participation 0.9998, see table 5.4). I only noticed the breathing motion
contained in the OH\(^{-}\) stretch after analysing the molecular dynamics simulation of
the system, so I will discuss it in more detail below.

The increased Raman intensities (table 5.4) in the normal modes involving surface-
normal Cl\(^{−}\) motion confirms that these modes involve the lattice, while the increased
IR intensities of the OH\(^{-}\) normal modes indicates that they are the best candidates
for vibrational excitation by IR laser pulses. The results of simulations of the latter
process are presented in chapter 6.

5.5. Results of MD Simulations

5.5.1. Equilibrium Dynamics Results

In order to establish the frequencies of the normal modes localised at the adsorption
site predicted by lattice dynamics, I have performed equilibrium molecular dynamics
simulations of the same model system. Following an equilibration run of 2 ps, after
which no oscillation of temperature was observed, a production run of 7.5 ps was
performed. The target temperature chosen for the system was 450 K, i.e. higher
than room temperature, in order to gain faster dynamical equilibration (and faster
dissipation, see below).

A frequency spectrum can be extracted from the production equilibrium MD
run by calculation of the power spectrum of the velocity autocorrelation function
averaged over all ionic coordinates. This is done by the maximum entropy method\(^{182}\)
rather than the Fourier transform method in order to control the accuracy more
easily.

Fig. 5.3 shows a comparison of the DsOS of the MgO(001) surface with an ad-
sorbed HCl molecule, as simulated with lattice dynamics (dark blue line) and molec-
ular dynamics (light red line). The DsOS cover the same frequency spectrum in the
region up to 22 THz and are distinct only in the linewidths – the MD lines are generally narrower. As the lattice dynamics DOS is based on a hypothetical
linewidth, the agreement is satisfactory in the region of the MgO band. The localised mode
frequencies are discussed in the next figure.

Figure 5.3.: DOS calculated with molecular dynamics of MgO(001) surface with adsorbed HCl
molecule (red line) compared to the corresponding lattice dynamics result (blue line). The DsOS
cover the same frequency spectrum in the region up to 25 THz and are distinct only in the linewidths – the MD lines are generally narrower. As the lattice dynamics DOS is based on a hypothetical
linewidth, the agreement is satisfactory.

Fig. 5.4a shows the low frequency region of the MD DOS. It can be seen that
the low-frequency modes are shifted to lower frequencies compared to the lattice
dynamics result. This can be attributed to the sampling of less inclined parts of the
potential energy surface.

The frequency spectrum in the range of the OH\(^{-}\) stretch mode in fig. 5.4b, while
that around the frequencies of the rotational and librational modes is shown in
fig. 5.4c. The shoulders or side-peaks at \(\omega_{0} \pm \Delta \omega\), where \(\omega_{0}\) is the main frequency
of one of the modes discussed, indicate interaction with a low-frequency mode at
\(\omega' = \Delta \omega'\).

Note, however, that the barriers between adjacent minima of the potential energy along the OH\textsuperscript{−} rotational and librational modes are vibrationally accessible at the simulated temperature (T = 450 K). Near the barriers, the dynamics are not described by the harmonic model, instead they move more slowly. This means that the shoulders and side peaks seen in fig. 5.4 may also be indicative of coupling between OH\textsuperscript{−} stretch mode and rotational/librational motion and mutual coupling between OH\textsuperscript{−} rotation and libration. The presence of such coupling is in fact supported by the analysis presented below.

While the rotational and librational frequencies of OH\textsuperscript{−} observed in the MD simulation are shifted down with respect to the lattice dynamics results as expected due to sampling of softer areas of the potential, the frequency of the OH\textsuperscript{−} stretch mode is shifted upward. This may be due to the constraint experienced by the adsorption site oxygen ion by its nearest neighbours in the surface.

5.5.2. Dissipation Dynamics

After a production run of \( T_{p} = 7.5 \) ps of the equilibrium dynamics, I halted the simulation and injected energy into the OH\textsuperscript{−} stretch mode. This was done according to the formula presented in section 5.2.4.1. The excitation energy chosen is the energy of a single vibrational quantum of the OH\textsuperscript{−} stretch in the harmonic approximation, which at the frequency of the stretch mode
\[
\omega = 2870 \text{ cm}^{-1} = 86.04 \text{ THz} \text{ results in }
\Delta E = h\omega = 0.356 \text{ eV}.
\]

In the following continuation of the MD – the dissipation dynamics run – the dissipation process was observed by tracking the kinetic energy in different sets of modes as it progressed away from the originally excited mode into the substrate, via the OH\textsuperscript{−} rotational and librational modes. Dissipation dynamics were performed for \( T_{D} = 6.3 \) ps.

The simulated excitation was applied to a snapshot of the MD simulation run at \( T = 450 \) K. Previous dissipation dynamics, for example by Moritsugu et al.\textsuperscript{175} and most recently Yamamoto et al.\textsuperscript{176,177} have been performed at zero temperature, i.e. in these studies all modes but the one to excite are initially unpopulated. In the simulation presented here, these modes are at a thermal equilibrium population.

During the analysis of the ensuing dynamics, a difficulty arises in attributing kinetic energy to a certain mode: When the atoms are removed from the minimum energy configuration, an application of the harmonic approximation will yield different results to lattice dynamics at equilibrium, as different force constants are sampled there. In theory, a new lattice dynamics calculation would have to be performed for each time-step of an MD run in order to properly attribute energy to certain normal modes.

Luckily in this case some modes of interest – the ones associated with the adsorbed molecule – can be guessed reasonably well by observing the nature of the modes (illustrated in fig. 5.1). Depending on the orientation of the OH\textsuperscript{−} molecule, rotation and libration are defined in a canonical way (see fig. 5.1). The same goes for the chlorine vibrational modes, depending on the orientation of the imaginary coordinate of the hydroxyl group \( \text{OH} \).

The projection of the OH\textsuperscript{−} rotation and libration. The presence of such coupling is in fact supported by the analysis presented below.

The velocities discussed below are then extracted by dot-product projecting the relative velocity of OH\textsuperscript{−} to these direction vectors:
\[
\begin{align*}
\mathbf{v}_{\text{OH}} &= \mathbf{v}_{\text{H}} - \mathbf{v}_{\text{O}}, \\
\mathbf{v}_{\text{str}} &= \mathbf{v}_{\text{OH}} \cdot \mathbf{x}_{\text{str}}, \\
\mathbf{v}_{\text{rot}} &= \mathbf{v}_{\text{OH}} \cdot \mathbf{x}_{\text{rot}}, \\
\mathbf{v}_{\text{lib}} &= \mathbf{v}_{\text{OH}} \cdot \mathbf{x}_{\text{lib}}.
\end{align*}
\]

Fig. 5.5 shows the kinetic energies of the OH\textsuperscript{−} modes in the system during the molecular dynamics simulation, along with their sum. The time scale is shifted to put the excitation of the stretch mode of OH\textsuperscript{−} at time \( t = 0 \). Rotational modes can be distinguished from the librational modes marked in the same colour by realising that they are the only modes that do not go to zero every half cycle.

It can be seen from the graph that the stretch excitation survives for a comparatively long time, about 1.55 ps, before dissipation starts to become visible. This time and all other times discussed in the following paragraphs are marked in the diagram by dotted lines in the graph.

Most of the excitation energy goes into the rotational and librational modes of OH\textsuperscript{−}, however the simultaneous onset of energy dissipation from all three modes into the crystal is evidenced by the apparent drop of the envelope of the compound OH\textsuperscript{−} kinetic energy, in the lowest panel of fig. 5.5.

The rotational and librational modes of OH\textsuperscript{−} maintain a high level of excitation for at least another 2 ps before dropping to noticeably lower levels themselves.

At 3.45 ps, the OH\textsuperscript{−} stretch mode starts regaining some of its kinetic energy. It
is unclear whether this energy comes solely from the OH\textsuperscript{−} rotational and librational modes or also from the crystal. The latter would represent a return of vibrational energy from the crystal. An indication for this is the rise in total energy of all OH\textsuperscript{−} modes which becomes apparent after the earlier time of 3.2 ps (marked in the graph). However, the crystal which is usually imagined as a semi-infinite body, is modelled here by a unit cell of relatively few atoms, so finite size effects cannot be excluded and it is difficult to ascertain whether the observed recurrence of vibrational energy is physical or not.

Most of the recurring energy appears to stem from the OH\textsuperscript{−} librational/rotational modes. Due to the remaining question of finite size, however, the recurrence data should not be considered for extraction of any quantitative statements.

It is remarkable that the energy of the stretch mode returns to a level far above the thermal equilibrium (at $t < 0$).

The time lag between the rise in total OH\textsuperscript{−} energy and that of the stretch mode indicates once more that coupling between the crystal modes and the stretch mode proceeds via the OH\textsuperscript{−} rotational and librational modes.

Fig. 5.6 demonstrates that the kinetic energy graphs of the modes associated with chlorine do not change significantly after excitation of the OH\textsuperscript{−} stretch mode. The Cl rotation (panel immediately below OH\textsuperscript{−} stretch) about the OH\textsuperscript{−} adsorption site shows a peak immediately after the excitation and throughout later times seems slightly more energetic on average than prior to the excitation. However, these energies are of the same order as immediately before excitation, so they do not represent a significant enough change to make any definitive statements on a relation between this mode and the OH\textsuperscript{−} stretch.

The chlorine ion in the vicinity of the OH\textsuperscript{−} molecule and bounded to it by Coulomb attraction therefore does not seem to interact vibrationally with OH\textsuperscript{−} to a relevant extent.

In order to discover more elements of the dissipation process that I hypothesised on in fig. 2.2 on p. 45, I would also like to look at the crystal ions. Since lattice dynamics away from the equilibrium are outside the scope of this project, I have not considered normal modes for these but instead resorted to simply adding the kinetic energies of certain sets of atoms and plotting the sums together with the OH\textsuperscript{−} mode energies.

For example, to observe dissipation step (2) from fig. 2.2, i.e. from the adsorption site to its nearest neighbour atoms in the crystal, I have plotted the sums of the kinetic energies of the nearest neighbour atoms (excluding the OH\textsuperscript{−} oxygen ion bound to the proton, as illustrated in fig. 5.7).

Fig. 5.8 shows them along with the OH\textsuperscript{−} mode energies. Although the data is very noisy, the following characteristics can be recognised: A clear break in character of the curves can be recognised at the excitation time, particularly for the magnesium ions that are the immediate neighbours of the adsorption site. Not only are the nearest neighbour atoms more vibrationally energetic after the OH\textsuperscript{−} excitation, there also seems to appear a high frequency component.

This will be seen more clearly during analysis with the FROG technique in section 5.6 below. The nearest neighbours immediately take part in the stretch motion of OH\textsuperscript{−}. In interpreting this fact, the distinction between normal modes and other...
general vibrational modes is important. As the compound participation of O and H in the OH\(^-\) stretch normal mode is slightly below unity (compare table 5.4), other ions take part in this normal mode as well. The stretch vibrational mode of the hydroxyl group\(^*\) is excited at the beginning of dissipation dynamics. This vibrational mode has a large overlap with the OH\(^-\) stretch normal mode but but it also has small overlaps with other normal modes. I will show in the following that the OH\(^-\) stretch normal mode involves motion of adsorption site nearest neighbours in the lattice. This means that the excitation of the OH\(^-\) stretch vibrational mode applied in this dissipation dynamics calculation immediately involves motion of the adsorption site nearest neighbour Mg ions. I will term this in the following as overlap between the OH\(^-\) stretch normal mode and the lattice vibrational modes. This can be contrasted to coupling by two factors: (1) Coupling is thought to occur between normal modes only, rather than any vibrational modes. (2) Changes in the vibrational population of vibrational modes due to overlap are sudden, while coupling between normal modes takes time.

The kinetic energy of the nearest neighbours declines simultaneously with that of the OH\(^-\) stretch mode, however not as much since they take part in other normal modes as well. The dip at 2.9 ps coincides with the minimum of vibrational activity in the OH\(^-\) stretch mode (and conversely with the maximum in the rotational and librational OH\(^-\) modes). A maximum around 3.45 ps which is particularly pronounced for the nearest neighbour oxygen ions coincides with the onset of recurrence of vibrational energy in the OH\(^-\) stretch mode. It is followed by a further decline of energy towards 4.2 ps.

Dissipation step (2) from fig. 2.2 goes from the nearest neighbours into the extended surface planes. I have plotted the sums of the kinetic energies of the atoms in the atomic surface layer (without the oxygen ion that is part of the OH\(^-\) molecule) and the atomic layer underneath. Fig. 5.9 shows them along with the OH\(^-\) mode energies. The kinetic energy in the surface planes shows no clear change after the excitation of OH\(^-\), so any coupling that may be present cannot be recognised by direct inspection of the kinetic energy curves.

\*This is not the hydroxyl stretch normal mode, as that involves nearest neighbour lattice ions of the adsorption site.

5.6. Analysis of MD Results using Frequency-Resolved Optical Gating (FROG)

5.6.1. FROG Analysis of the Dynamics Along Vibrational Modes Involving OH$^-$ and Cl$^-$

Rather than looking at the MD trajectory directly, as was done in the previous section, one may also analyze the result of the molecular dynamics calculations by looking at how the frequencies of certain properties (such as mode velocities and kinetic energies) develop over time. The method of choice for this is the simulated Frequency-Resolved Optical Gating (FROG). This method is reviewed in section 2.4.

I used the FROG technique with a Gaussian gate function $g$ with

$$ \sigma = \frac{1}{20} (T_f + T_0) = \frac{1}{40} (7.5 \text{ ps } + 6.3 \text{ ps}) = 345 \text{ fs}.$$ 

This setting yielded satisfactory detail in the resulting FROG traces.

Before looking at the results, I should consider what to expect from them. I have selected certain vibrational modes involving OH$^-$ and Cl$^-$ in the hope that they approximate normal modes and recorded their velocities. The only features that should be visible for a normal mode are its original frequency and some overtones and slight frequency shifts due to the sampling of anharmonicity. Due to coupling, the population of a normal mode can change and therefore frequency shift and overtones may appear and disappear according to how strongly any present anharmonicities are sampled.

When analysing the frequency spectrum of a certain vibrational mode, it has to be taken into account whether it is a normal mode or not. If it is not, frequencies other than that of a certain normal mode involving this mode need not be signs of coupling but instead of overlap with other normal modes.*

Fig. 5.10 shows FROG traces of the OH$^-$ modes. They may be compared to the densities of state shown in fig. 5.3 on p. 171. The kinetic energy of these modes was shown in fig. 5.6 – the relevant times discussed in the previous section are 1.55 ps after excitation (when the OH$^-$ stretch mode excitation starts to decline) and 3.45 ps (when it starts to recur). Note that these times mark the beginnings of decline and recurrence, respectively, which are extended processes centred around

*These normal modes are then found at the frequencies detected.
2 ps and 3.75 ps, respectively.

The FROG trace of the OH\(^-\) stretch mode, fig. 5.11a, shows that at the excitation time \( t = 0 \) the main frequency of the mode shifts down from 87 THz to about 80 THz and at the same time overtones of twice the main frequency appear. Both can be attributed to the sampling of anharmonic sections of the Morse potential by the excited mode. Around 2 ps, during the de-excitation of the stretch mode, these features disappear.

While in fig. 5.10a each line marks one tenth of the maximum intensity, fig. 5.10b shows the same FROG trace with a tenfold increased resolution. This means an increased density of lines at high intensity but also that ten more lines show up below the lowest line of fig. 5.10a.

It can now be seen that the frequency doubled overtones of the OH\(^-\) stretch reappear at 3.75 ps, when the mode population recovers, concurrently with a, this time less pronounced, frequency shift. This is in line with the expectation that the frequency shift and the overtones are due to a higher population of the OH\(^-\) stretch vibration.

During the whole simulation run, the FROG trace of the OH\(^-\) stretch mode shows little or no contributions that are not near the main frequency or its overtones. This is a sign that the OH\(^-\) stretch is a normal mode that couples to other modes only very weakly.

The FROG trace of the OH\(^-\) libration, figs. 5.10c and (d), shows overtones of the basic frequency (28 THz) at about 56 THz (and, to a lesser extent, at 84 THz, as seen in the higher resolution image). Note that the scale of the ordinate is longer in fig. 5.10d, as the low intensities found at higher frequencies show up in this image.

These are present through most of the MD run. However, I have chosen the excitation time \( t = 0 \) such that the librational and rotational modes of OH\(^-\) are barely populated at this time. This means that overtones are diminished from \( t = 0 \) up to \( t \approx 2 \) ps, when the dissipation from the stretch mode becomes noticeable and the librational mode becomes populated again.

Note that the 28 THz frequency that shows up in the FROG trace is slightly below the 29.6 THz predicted by lattice dynamics (section 5.4.2) which indicates that anharmonic sections of the potential are sampled. In fact, a close look at fig. 5.11c reveals that between 0 ps and 2 ps, when the mode is barely populated, the main frequency is shifted up to nearly 30 THz.

The spectrum is not as concentrated on the main frequency and its overtones as for the stretch mode (subfigure a) which demonstrates that treating the OH\(^-\) libration as a normal mode is a less valid approximation than for the stretch. This was visible already in the participation function values (and the participations of O and H) in table 5.4 on p. 168.

The rotational mode is special in that it does not need to return to zero during each period, as visible in fig. 5.5. This behaviour shows up in the FROG trace (fig. 5.11e) as a considerable zero frequency part. Apart from this characteristic, a downshift of the frequency can be seen after 3 ps, which is partly reversed after 4 ps, when the mode loses some of its population. These shifts are, as before, due to the sampling of anharmonicity when the mode is populated more highly (i.e. between 3 ps and 4 ps). Some admixture at other frequencies can be seen but not as much as for the libration.

Fig. 5.11 shows FROG trace of the surface normal, librational and rotational vibrational modes of Cl\(^-\).
To consider the motion of Cl$^-$ perpendicular to the surface as a normal mode is, as the coefficients in table 5.4 demonstrated, not such a good approximation. It is merely a vibrational mode convenient to separate from the rest of the system.

Accordingly, its FROG trace in fig. 5.11d is more or less the spectrum of the whole system — again with the frequency shift of the OH$^-$ stretch nicely visible — with the notable exception of the OH$^-$ rotation and libration between 25 and 30 THz. These OH$^-$ modes have their main components pointing parallel to the surface and therefore cannot overlap with the motion of Cl$^-$ perpendicular to the surface.

The FROG trace of the Cl$^-$ libration, fig. 5.11e, is too weak away from the main frequency (2 THz) to draw any conclusions apart from that contributions from the crystal up to 15 THz are present — an indication that the overlap is strongest with surface modes. The OH$^-$ stretch is not present because the OH$^-$ molecule is never pointing directly at the Cl$^-$ ion but at a more obtuse angle to the MgO surface and therefore does not overlap.

The FROG trace of the Cl$^-$ rotation, fig. 5.11f, shows the rotation-typical zero frequency contribution with some features in the bulk MgO band as well as some clear features just below 27 THz. This is in spite of the low participation function of the Cl$^-$ rotation in table 5.4. These are indications of contributions from the OH$^-$ rotation and libration which perturb the potential felt by Cl$^-$ in the plane parallel to the surface since OH$^-$ is polar. This means that in this changed environment the low participation in the chlorine rotational motion is not valid.

Rotation and libration of OH$^-$ contribute with the largest amplitude between nearest and furthest distance to Cl$^-$ and therefore overlap most prominently with the in-plane Cl$^-$ modes.

All in all, the different components of Cl$^-$ motion show considerable overlap with the OH$^-$ modes, each according to its direction relative to the axis of OH$^-$, but it has to be stressed that these overlaps are not indications of coupling between normal modes but only an expression of the non-normality of the modes chosen for Cl$^-$.

In conclusion, no direct evidence for coupling between the OH$^-$ modes and modes involving Cl$^-$ is found by analysis with the FROG method.

### 5.6.2. FROG Analysis of Vibrational Modes Involving Lattice Ions

I would also like to use the FROG technique to study the dissipation step (2) from fig. 2.2 on p. 45, i.e. from the adsorption site to its nearest neighbour atoms in the crystal. However, for this problem no straightforward direction vector exists whose velocity could be analysed. I will therefore use FROG to analyse the compound kinetic energies of some selections of ions.

Before launching into the analysis of the nearest neighbour and surface plane kinetic energies using FROG, it has to be stressed that, while the FROG traces of velocities were considered up to here, the kinetic energies are made up of linear combinations of velocities squared. The kinetic energy corresponding to a superposition of two harmonic oscillator velocities

\[ v = c_1 v_1 + c_2 v_2 = c_1 \cos(\omega_1 t) + c_2 \cos(\omega_2 t + \delta) \]

is proportional to

\[ E_{\text{kin}} \sim c^2 = (c_1 \cos(\omega_1 t) + c_2 \cos(\omega_2 t + \delta))^2 = c_1^2 \cos^2(\omega_1 t) + 2c_1c_2 \cos(\omega_1 t) \cos(\omega_2 t + \delta) + c_2^2 \cos^2(\omega_2 t + \delta). \]

After applying some trigonometric addition theorems, this transforms into

\[ E_{\text{kin}} \sim \frac{c_1^2}{2} (1 + \cos(2\omega_1 t)) + \frac{c_2^2}{2} (1 + \cos(2\omega_2 t)) + c_1c_2 \cos((\omega_1 + \omega_2) t + \delta) + \cos((\omega_1 - \omega_2) t - \delta). \]

(5.12)

This means that the frequencies entering the spectrum of the kinetic energy are a zero-frequency part, \( \omega_1 \), \( \omega_1 + \omega_2 \), \( \omega_1 - \omega_2 \) and \( 2\omega_2 \). If \( c_1 \gg c_2 \) then the intensities \( I(\omega) \) of certain frequencies in the FROG trace show up with decreasing order of intensity, i.e.

\[ c_1 \gg c_2 \quad \rightarrow \quad I(2\omega_1) \gg I(\omega_1 + \omega_2) = I(\omega_1 - \omega_2) \gg I(2\omega_2). \]

(5.13)

When looking for certain modes, one should therefore look first for signals at twice their frequency, then for sums or differences of their frequency with that of another mode.

Fig. 5.12 shows the FROG traces of the nearest neighbour magnesium and oxygen ions around the adsorption site, over two frequency intervals. Both contain zero-frequency contributions due to the constant terms in eq. 5.12. Further contributions can be seen up to 30 THz, less pronounced for the oxygen ions. As noticed before for Cl$^-$, surface modes have their strongest contributions below 15 THz and since the ions considered are in the atomic planes at the surface, the visible contributions are probably due to the doubled frequencies of surface modes.

The features at and below 55 THz can be attributed to the doubled rotational and librational OH$^-$ modes, while the single and the doubled frequencies of the OH$^-$ stretch are visible at above 80 THz and above 160 THz, respectively. Note that the feature at 160 THz is the stronger of the two as predicted by eq. 5.13. The well pronounced features of the OH$^-$ stretch in the fig. 5.12b clearly demonstrate the updrift of the frequency of the OH$^-$ stretch caused by a decaying impact of anharmonicity due to dissipation.

Fig. 5.13 shows the FROG traces of the surface and subsurface atomic planes. Both contain zero-frequency contributions as before and are furthermore dominated by low frequencies at and below 2 THz. These are modes that move all surface atoms and are therefore much stronger in the spectrum than any other mode. The first and second surface planes contain some of the nearest neighbour atoms of the...
Figure 5.12: FROG trace of the nearest neighbour Magnesium ions around the adsorption site. It can be seen that the OH\(^{-}\) stretch mode appears immediately at time \(t = 0\), speaking for overlap with the OH\(^{-}\) stretch mode rather than coupling.

Figure 5.13: FROG trace of the nearest neighbour Magnesium ions around the adsorption site. No structure due to OH\(^{-}\) stretch excitation at \(t = 0\) can be seen.

### Table 5.5

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-0.220377</td>
<td></td>
<td>-0.944533</td>
<td>-0.969901 towards ads. site O</td>
</tr>
<tr>
<td>ads. site O</td>
<td>+0.0546965</td>
<td></td>
<td>+0.236374</td>
<td>-0.243141 towards H</td>
</tr>
<tr>
<td>Cl</td>
<td>+0.003840</td>
<td></td>
<td></td>
<td>away from surf.</td>
</tr>
<tr>
<td>Mg under Cl</td>
<td>-0.0045</td>
<td></td>
<td>-0.003722</td>
<td>away from Cl</td>
</tr>
<tr>
<td>Mg opposite Cl</td>
<td>+0.0042</td>
<td></td>
<td></td>
<td>towards ads. site O</td>
</tr>
<tr>
<td>Mg perpendicular H-Cl</td>
<td>+0.005674</td>
<td></td>
<td></td>
<td>towards ads. site O</td>
</tr>
<tr>
<td>subsurf. Mg</td>
<td>+0.003296</td>
<td></td>
<td></td>
<td>towards ads. site O</td>
</tr>
<tr>
<td>O next to Cl</td>
<td>+0.007241</td>
<td>+0.001436</td>
<td>+0.001307</td>
<td>towards Cl</td>
</tr>
<tr>
<td>O opposite Cl</td>
<td>+0.001428</td>
<td>+0.001716</td>
<td>+0.000567</td>
<td>towards Cl</td>
</tr>
<tr>
<td>subsurf. under Cl</td>
<td>-0.000852</td>
<td></td>
<td></td>
<td>-0.001578 away from ads. site O</td>
</tr>
<tr>
<td>subsurf. opposite Cl</td>
<td>-0.001351</td>
<td></td>
<td></td>
<td>-0.001890 away from ads. site O</td>
</tr>
</tbody>
</table>

As discussed in the previous section, the excitation of the OH\(^{-}\) stretch mode introduces high frequency components to the dynamics of the Cl\(^-\) ion and the nearest neighbour ions of the adsorption site.

This is indicative of a participation of these ions in the OH\(^{-}\) modes, particularly the stretch mode. Table 5.5 shows the main components of the OH\(^{-}\) stretch mode.

It can be seen that the motion of the proton and the oxygen ion bound to it dominate the motion in the stretch mode completely, i.e. regarding it as motion of these species only is a good approximation.

Due to normalisation, the sum of all other mode components squared is 1.737 x 10\(^{-4}\). There are 450 ions in the system, hence 1500 normal modes. At equal partici-
pation of all Cartesian components in a mode, the components would each be about $1.3 \times 10^{-7}$.

The non-OH$^-$ components in table 5.5 are, at between $5 \times 10^{-4}$ and $5 \times 10^{-3}$, significantly larger than this. The mode vectors listed are therefore significant but obviously very small compared to the participations of O and H (which is the reason why this was not detected earlier).

As the adsorption site oxygen leaves the surface to approach the proton, the surrounding magnesium ions move towards the vacated oxygen site. At the same time, the nearest-neighbour oxygen ions move away from the adsorption site. This is characteristic of an optical breathing mode.

Chlorine also takes part in the motion by moving away from the surface. This distorts the motion of the surface ions near chlorine. All in all, the deeper analysis of this mode yields a resounding support for the hypothesis of the previous section where I stated that the OH$^-$ stretch mode overlaps with the motion of chlorine and the nearest neighbours of the adsorption site rather than coupling to them.

The librational and rotational modes of OH$^-$ also contain significant (compared to the rest of the system) contributions from the nearest neighbour atoms, at different symmetries. The breathing character of these modes could not be detected by the automated localisation criterion used, as the motion of OH$^-$ greatly dominates the modes. Only after performing dissipation dynamics and analysing the compound kinetic energy of the nearest neighbour ions did it become apparent that a more thorough analysis of the OH$^-$ modes yields the breathing modes sought.

It is reassuring that theoretically predicted breathing modes could be identified this way. However, I will not be specifically concerned with breathing modes in the following. Instead, suffice it to note that the stretch mode of OH$^-$ involves motion of Cl$^-$ perpendicular to the surface and an optical breathing mode of the nearest neighbour surface ions of the adsorption site.

### 5.7. Analysis of MD Results using Cross-Correlation Functions

Additionally to inspecting the trajectories of the MD simulation by plotting kinetic energy curves and FROG traces, cross-correlation functions can be used to assess the relations between normal modes. The cross-correlation function of two MD trajectories $f_1$ and $f_2$, as defined by equation (5.11), can be interpreted as the amount of overlap between the two functions, where $f_2$ is shifted backwards by $\tau$ with respect to $f_1$. For the purpose of finding connections between the modes, I am interested in the shifts at which maxima of the cross correlation function are assumed. These maxima are indications that there may be processes transferring energy between the modes considered and that the time it takes for the energy to be transferred from the first vibrational mode to the second is $|\tau|$. If $\tau$ is negative, the direction of energy flow is from $f_2$ to $f_1$.

For the purpose of calculating the cross-correlation, I used only the excitation MD results up to 3.2 ps after the excitation, as beyond this time no statement can be made whether the non-physical finite size distorts the results. The kinetic energy functions are thought of as continued by their expectation values on either side, i.e. towards $\tau = 3.2$ ps the cross-correlation function $r(\tau)$ goes to zero.

Fig. 5.14a shows the part from 0 ps to 3.2 ps of the OH$^-$ and Cl$^-$ kinetic energy functions that has been used to calculate the cross-correlation results shown in the other panels of this figure. Fig. 5.14b shows the cross-correlation between the rotational and librational normal modes of OH$^-$.

A peak of around 0.5 at $t = 0$ confirms...
the visual impression that these two modes show essentially analogue behaviour.

The following two panels, fig. 5.14c and (d), show the cross-correlation functions between OH⁻ rotation and libration, respectively, with the OH⁻ stretch mode. In interpreting these results, it has to be remembered that the functions are continued by their expectation values outside the time interval \( t = [0, 3.2\, \text{ps}] \) and therefore the cross-correlation function necessarily goes to zero towards the boundaries of this interval.

Taking these properties into account, interpretation of the graph in fig. 5.14d seems difficult but the rapid falloff of the cross-correlation in fig. 5.14c after 2 ps is indicative of a real maximum which is not just an artifact of the tendency to zero towards 3.2 ps. The peaks at negative times are merely an expression of the good correlation between the subintervals with small amplitude (and hence constant negative distance from the expectation value). They demonstrate a spurious maximum due to the finite length of the cross-correlation.

The falloff of fig. 5.14c after 2 ps is markedly stronger than this. This confirms the earlier visual assessment of the shift between the stretch and rotational/librational modes in section 5.5 and indicates energy transfer from the OH⁻ stretch to its rotational and vibrational modes after 2 ps.

Two of the modes associated with the Cl⁻ ion show maxima in the cross-correlation with the OH⁻ stretch (fig. 5.14e). However, these maxima are at the time shift zero and are thus merely expressions of the uniform character of the chlorine vibrations. Finally, fig. 5.14f shows the cross-correlation between the Cl⁻ modes and the rotational mode of OH⁻. The panels show pronounced maxima only at negative times. These would have to be interpreted as an indication of energy transfer from Cl⁻ vibrations to the OH⁻ rotation, which may be a side-effect of the excitation of the rotational OH⁻ mode but is not directly connected to the energy dissipation from the stretch mode.

However, the sudden onset of dissipation is indicative of a certain geometric environment necessary to start dissipation. This may be, for example, that during a stretch motion, the proton collides non-frontally with the chlorine ion such that it is deflected sideways, which adds population to the rotational or librational modes. Another mechanism could be that the chlorine's rotational motion proceeds at an integer fraction of the OH⁻ rotation, so that the first can inject energy into the latter. This may jumpstart the dissipation process, since, at higher rotational excitation, the OH⁻ stretch motion becomes subject to a faster changing environment and therefore more collisions.

I omit the corresponding graph for the OH⁻ libration since, as evidenced in fig. 5.14b, it is very similar to the one for the rotational OH⁻ mode.

The cross-correlations of nearest neighbour and surface plane kinetic energy functions with the OH⁻ stretch are shown in fig. 5.15.

![Figure 5.15: Kinetic energy cross-correlation functions of the OH⁻ stretch mode with the adsorption site nearest neighbour and surface plane atoms. Abscissa is propagation time in picoseconds.](image_url)
reasonable guesses approximating normal modes, they are not strictly orthogonal. Non-orthogonality expresses itself by an apparent parallel behaviour which is most noticeable for modes overlapping with the OH\textsuperscript{−} stretch. These show an excitation simultaneous to that of the OH\textsuperscript{−} stretch mode which is readily detected due to the considerable energy (0.356 eV) injected.

Modes coupling to the OH\textsuperscript{−} stretch, on the other hand, display a time lag between the OH\textsuperscript{−} stretch excitation and their own. The time lag therefore presents a way to distinguish modes that merely overlap with the OH\textsuperscript{−} stretch and those that show actual coupling. Only the latter are responsible for energy dissipation from the stretch mode.

It is difficult to extract any definitive statements on the nature of the coupling between OH\textsuperscript{−} and its nearest neighbours from visual inspection of the kinetic energy curves alone. The rise in rotational and librational population during the period when the OH\textsuperscript{−} stretch is depopulated appears to indicate coupling, however the recurrence of the OH\textsuperscript{−} stretch that coincides with a decline of the nearest neighbour motion (fig. 5.8) contradicts this assumption and hints at a direct link between nearest neighbours and OH\textsuperscript{−} stretch.

FROG analysis has demonstrated that the chlorine motion perpendicular to the surface as well as the motion of the adsorption site nearest neighbours in the surface overlap with the OH\textsuperscript{−} stretch. In conjunction with cross-correlation functions that have maxima at zero time shift this demonstrates overlap between the modes.

According to perturbation theory and due to symmetry, normal modes of the crystal substrate centred at the adsorption site are expected to exist. A more thorough analysis of the OH\textsuperscript{−} normal modes, exemplified by the stretch mode in table 5.5, reveals that these breathing modes are in fact found in the OH\textsuperscript{−} stretch mode.

The sudden onset of dissipation is indicative of a certain geometric environment necessary to start dissipation. This may be, for example, that during a stretch

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**Figure 5.16.** Kinetic energy cross-correlation functions of the OH\textsuperscript{−} rotational mode with the adsorption site nearest neighbour and surface plane atoms. Abscissa is propagation time in picoseconds. Peaks at negative time shifts are ascribed to overlap of breathing mode with OH\textsuperscript{−} stretch.

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### 5.8. Discussion

Repercussions of the dissociative nature of the adsorption of HCl onto the MgO(001) surface terrace are clearly visible throughout the shell model normal mode structure. While the proton and adsorption site oxygen dominate the normal modes of the highest frequencies, appreciable chlorine motion is found only in modes of very low frequency.

The three normal modes with appreciable contributions from OH\textsuperscript{−} are dominated strongly by the participation of the proton and surface oxygen. In contrast, the normal modes with contributions from chlorine are not entirely dominated by chlorine motion (with the exception of the rotational mode). Instead, a multitude of normal modes exists that chlorine participates in, a selection of which was presented in table 5.4.

In discussing the results of the MD simulations presented in this chapter, the distinction between overlap of two modes and coupling of two modes plays a paramount role. Since the vibrational modes considered are generally not normal modes but
motion, the proton collides non-frontally with the chlorine ion such that it is deflected sideways, which adds population to the rotational or librational modes. Another mechanism could be that the chlorine’s rotational motion proceeds at an integer fraction of the OH$^-$ rotation, so that the first can inject energy into the latter. This may jumpstart the dissipation process, since, at higher rotational excitation, the OH$^-$ stretch motion becomes subject to a faster changing environment and therefore more collisions. As it is bound to the adsorption site merely by Coulomb attraction, chlorine subsequently plays only a spectator role in the dissipation from the OH$^-$ stretch mode.

The notion of a jumpstarted dissipation process is supported by a second dissipation dynamics run I have performed starting from different initial conditions, in which the onset of dissipation lay at a different time. One should really do very many runs of dissipation dynamics in order to ascertain the probability distribution of the dissipation onset.

Since the MD run presented here alone required many hours on a cluster with 64 processors, such an undertaking would however be hugely demanding computationally.

After dissipation is set going, it proceeds exponentially, draining the stretch mode of all its energy. Although dissipation from the modes of OH$^-$ into the surface can be perceived, as shown by the falloff of the compound OH$^-$ kinetic energy (fig. 5.5 on p. 174), the coupling of the OH$^-$ stretch mode with its rotational and librational modes is the rate-determining step in the dissipation from the stretch mode.

The problem of the recurrence of compound OH$^-$ kinetic energy seen in the bottom panel of fig. 5.5 can be revisited by a simple consideration: Assume that all energy dissipated from the three OH$^-$ modes were dissipated exclusively into the surface (not the bulk) of the crystal and propagates as a circular wave from the adsorption site.

Due to the periodic boundary conditions, this wave will soon travel through the adsorption sites of neighbouring images of the unit cell. A diagram illustrating the outgoing wave is shown in fig. 5.17. The outgoing wave carrying vibrational energy travels through 64 ions at the perimeter of the diagram, out of which eight are adsorption sites. Conversely, each adsorption site is surrounded by eight other adsorption sites. Based on this picture, the surrounding adsorption sites should donate one eighth of the dissipated energy back to the central one.

Currently it is not possible to find out which of the two options dominates. The only way to solve this problem fully is repeating the calculation with a much larger unit cell and observing whether the recurrence is diminished.

Even if recurrence is not observed in a particular molecular dynamics run, this might be accidental. It may be that recurrence is initiated by the environment, similar to the initiation of dissipation. Therefore a several MD runs with an enlarged unit cell are needed to solve the question of spurious recurrence due to finite size.

As the molecular dynamics as presented here were already quite demanding, this would be a sizeable undertaking in itself.

Coming back to the reinterpretation of the scattering experiments of HCl on MgO, this chapter has demonstrated that an excitation of the OH$^-$ stretch can survive for a considerable time before dissipation sets in. This supports the mechanism presented in fig. 4.18.

Figure 5.17: Diagram illustrating recurrence due to the finite size of the unit cell. 4 x 4 unit cells are drawn instead of 8 x 8 for clarity. The outgoing wave carrying vibrational energy travels through 64 ions at the perimeter of the diagram, out of which eight are adsorption sites. Conversely, each adsorption site is surrounded by eight other adsorption sites. Based on this picture, the surrounding adsorption sites should donate one eighth of the dissipated energy back to the central one. site (for example by the breathing mode component of the OH$^-$ stretch mode), so that more than one eighth of the energy recurs at the adsorption site due to the finite size of the unit cell.
5.9. Extraction of a Dissipation Lifetime Parameter for Use with Quantum Dynamics

I have decided to use the Lindblad dissipation operator (section E.2.6) in order to model the energy dissipation from the excited OH\(^{-}\) stretch mode to the other phonon modes of the combined molecule-surface system in nuclear quantum dynamics simulations. For the moment it suffices to say that in order to do this, an exponential lifetime parameter is needed. It is readily obtained from the results of the molecular dynamics simulations presented in this chapter.

5.9.1. Analysis Using the Autocorrelation Function

The dissipation of vibrational energy from the OH\(^{-}\) stretch mode can be analysed by considering the velocity autocorrelation function of this mode. The autocorrelation function is formally the same as the cross-correlation function of a function with itself. Fig. 5.18 shows the autocorrelation functions of the OH\(^{-}\) velocity extracted from (a) equilibrium dynamics and (b) dissipation dynamics, both with exponential fits to their envelopes. It can be seen that both decay and that the one from dissipation dynamics (fig. 5.18b) decays faster. Lifetimes can be extracted from an exponential fit of the envelope of each autocorrelation function. \(\tau = 2.2\) ps results from equilibrium dynamics and \(\tau = 0.6\) ps results from dissipation dynamics. For this purpose, the parts of the dissipation dynamics autocorrelation function beyond a shift of 2 ps were disregarded, as they are the signatures of recurrence.

In the frequency domain, sharp peaks corresponding to the OH\(^{-}\) stretch mode frequency are seen, including a downward shift where this mode was excited. As this was already discussed in detail above, the Fourier transform is not shown. It also has to be kept in mind that the OH\(^{-}\) stretch is not quite exactly a normal mode, as the corresponding normal mode involves lattice ions and chlorine to a small extent.

The signal-to-noise ratio in the frequency domain is insufficient to identify the

\[\text{stretch mode.}\]

**Figure 5.18.** Autocorrelation functions of OH\(^{-}\) stretch mode. (a) From equilibrium dynamics and (b) from dissipation dynamics.

5.9.2. Analysis of the Velocity Evolution

A dissipation lifetime may also be extracted by immediately looking at the time-dependence of the kinetic energy in the OH\(^{-}\) stretch mode. Fitted envelopes are shown in fig. 5.19. Fig. 5.19a shows running time averages of the kinetic energy of the OH\(^{-}\) stretch mode (from the result of the molecular dynamics calculation shown in fig. 5.5 on p. 174). The rapidly oscillating line is the original result; running time averages over 10, 100 and 1000 time steps (\(\Delta t = 0.5\) fs) are drawn over it. The time averages are doubled to allow visual comparison with the envelope of the original result. As can be seen from the image, even the longest running average over 1000 time steps retains the character of a plateau shape followed by dissipation and later recurrence of the kinetic energy, as in the original result. I therefore used the 1000 step running average to fit a lifetime for the excitation.

I disregarded the shape of the kinetic energy curve after 3.05 ps, as the recurrence of the kinetic energy seen after three and a half picoseconds may be unphysical and

\[\text{i.e. during dissipation dynamics}\]
Table 5.6.: Parameters for the dissipation lifetime depending on the assumed starting time of dissipation.

<table>
<thead>
<tr>
<th>Fit</th>
<th>Lifetime (ps)</th>
<th>Decay Starts at</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp</td>
<td>2.14</td>
<td>0</td>
</tr>
<tr>
<td>const</td>
<td>0.82</td>
<td>1.38</td>
</tr>
</tbody>
</table>

There are two ways to fit an exponential lifetime to the molecular dynamics result. Both fits are shown in fig. 5.19b. The simplest way to assign a lifetime to the energy dissipation process is to assume purely exponential decay starting from \( t = 0 \) and fit to a least square difference from the data set. This is in disregard to the actual plateau shape of the energy during the initial period but retains the picture of a simple exponential decay. The fitted curve is shown circled in fig. 5.19b.

A qualitatively more accurate description of the decay can be obtained by assuming that the kinetic energy stays constant for a certain amount of time and only then decays exponentially (labelled as “const -> exp”). This procedure yields the squared line in fig. 5.19b as a fit. Table 5.6 shows the parameters gained from the different fitting procedures. The lifetime from the “const -> exp” fit is of the same order as that extracted from the autocorrelation function. Note that according to the “const -> exp” fit the decay only starts 1.38 ps after the excitation. This is longer than the whole length of the reaction I propose in chapter 6. Were I to adopt this model of dissipation, the excitation process would be entirely unaffected by dissipation and the proposed process could be simulated by a dissipation-free wave packet propagation method.

However, this model would have been obtained from just one single MD run with a single quantum excitation of the OH\(^-\) stretch mode. Different classical molecular dynamics would yield different time delays for the set-in of dissipation. I have therefore decided to use the purely exponential dissipation model as a crude representation of the average dissipation with arbitrary onset times as low as zero.

5.10. Conclusion

I have performed lattice dynamics and molecular dynamics simulations of HCl adsorbed on the MgO(001) surface based on a force field extracted from the ab initio results presented in chapter 4.

The localisation of modes can be analysed quantitatively by the adsorption site attenuation parameter \( \alpha_{\text{surf}} \). Using this criterion, I found modes localised at an HCl molecule adsorbed at the MgO (001) surface terrace.

I have consequently performed MD simulations of the system: An equilibrium run of 7.5 ps followed by a sudden excitation of the OH\(^-\) stretch mode by one vibrational quantum, i.e. 0.356 eV. I have used the technique presented in section 5.2.4 to simulate the sudden excitation. The decay of this excitation was simulated by a continuation of the molecular dynamics simulation for another 6 ps.

I have analysed the results of these MD simulations by considering the evolution of the kinetic energy of the vibrational modes of interest, calculating their FROG traces and searching for maxima in the cross-correlation functions between them. The molecular dynamics simulations demonstrated that the vibrational energy of the excited OH\(^-\) stretch mode goes mainly into the OH\(^-\) rotation and librational modes and that the chlorine ion plays only a minor role in the dissipation process.

Although the kinetic energy function of the nearest neighbour MgO atoms around the adsorption site has a shape similar to that of the OH\(^-\) stretch, the FROG method showed that this is not due to coupling but to an overlap between the chosen modes which, in the case of the nearest neighbour motion, is not a normal mode. Instead, I have presented evidence of coupling between the OH\(^-\) rotational and librational modes and the nearest neighbour atoms using the cross-correlation function. This method quantified the dissipation lifetime between the OH\(^-\) stretch and rotation/libration at about 2 ps.

As it is bound to the adsorption site merely by electrostatic attraction, chlorine plays only a spectator role in the dissipation from the OH\(^-\) stretch mode. However, it seems to be important for the initiation of the dissipation process by providing a perturbative environment for the OH\(^-\) molecule.

Finally, I have fitted a simple exponential decay model for use with dissipative quantum dynamics methods to the OH\(^-\) stretch population from molecular dynamics. The dissipation lifetime extracted from fitting this model is 2.14 ps. With increasing computing power available, it may become possible in the future to extend this study in the following ways:

1. A large number of dissipation dynamics runs should be performed to gauge the shape of the probability distribution of the onset time of dissipation.
2. On the other hand, a number of dissipation dynamics runs should be performed with a considerably enlarged unit cell in order to estimate the influence of the finite unit cell size on the recurrence of vibrational energy in the OH\(^-\) stretch and all OH\(^-\) modes as a whole.
3. In the analysis of the results of molecular dynamics runs it would be desirable to know the normal mode structure at every point along the trajectory of an MD run. Corresponding normal modes could then be identified for the purpose of recording their population over time. This would allow a more detailed analysis of the coupling between normal modes than presented in this chapter based on educated guesses for the normal modes involving OH\(^-\).
Chapter 6. Quantum Control of HCl on MgO(001)

Aims: The aim of this chapter is to propose a laser-excitation scheme to desorb hydrogen from the surface as example for a photoinduced reaction in a molecule in contact with a crystal.

The idea is to use a specially tailored femtosecond laser pulse to create highly excited vibrational states \((v=10)\) of the OH\(^-\) stretch mode and subsequently apply a static field to desorb hydrogen off the surface from this highly excited state.

Methods: The wave function is represented on a grid and the FFT technique is used to calculate differential operators. The split operator propagation scheme is used to simulate wave function dynamics. The optimal control technique is used to design laser fields that maximise the yield of OH\(^-\) molecules in a highly excited state. FROG traces (section 5.6) of the predicted fields are used to extract their main frequencies and chirp parameters.

An analytic dissipation operator for the Morse oscillator is used to model dissipation and implemented with the MCTDH quantum dynamics propagation code. Its form is given in section E.2.6. The dissipation parameters extracted from the MD simulations in chapter 5 are used for this. A complex absorbing potential (CAP) is used to predict the desorption rate from a highly excited state under the influence of a static field.

Results: The eigenstates of the Morse oscillator modelling the OH\(^-\) stretch are calculated and compared with the analytic result to gauge accuracy. While excitations to high vibrational states of OH\(^-\) have been predicted before, previously proposed excitation schemes were based on strong fields with lengths of of several picoseconds.\(^{185}\) Such a comparatively long-time process would, however, suffer from dissipation. A femtosecond pulse is proposed in order to minimise the adverse impact of dissipation.

FROG analysis reveals that the pulses for lower excitations consist of a single frequency with a negative linear chirp that sets in as soon as the first excited state is populated. The pulses for higher excitations also involve considerable contributions from double excitations. Taking dissipation into account, a lowered yield is predicted but the proposed process is not fully quenched. A simulated static field subsequent to the vibrational excitation yields a desorption of 20% of the irradiated species. An iterative radiative approach is proposed to repeatedly desorb a fraction of the reactive species off the surface.

6.1. Introduction

The previous chapters have dealt with the character of the chemical bonding between HCl and the MgO(001) surface and the exchange of vibrational energy between them. Ultimately, I aim to study the possibility to control the dynamics of OH\(^-\) formed at the surface due to HCl adsorption. This chapter describes the results of quantum dynamics simulations I have performed to study a scenario of control for the OH\(^-\) molecule at the MgO(001) surface.

Lasers impinging on a reactant in an optical control experiment have typical spot sizes on the order of 0.1 mm diameter.\(^{184,185}\) This means that many reactive species are irradiated simultaneously. For the system consisting of HCl on the MgO(001) surface at a coverage of every 16th surface oxygen ion, as in the \(4 \times 4 \times 4\) unit cell used for the PW-DFT calculations in chapter 4, this area would cover \(1.4 \times 10^{10}\) OH\(^-\) molecules. Indeed, a large number of species needs to be affected to get appreciable signal strengths when measuring the effect of an excitation spectroscopically.

The ideal situation in a control experiment would be if all reactive species were in exactly the same state at the beginning and remained phase-locked throughout the experiment. At finite temperatures, however, the reactive species will be at different initial states. Also, they will dissipate energy to the surface and de-phase with respect to each other.

In a simulation, the range of initial states must be represented by the initial wave function. The loss of phase between the reactive species and dissipation of vibrational energy from them can be included by introducing decoherence in a density matrix propagation. To construct the dissipation operator, I have used the dissipation lifetime extracted from the MD calculations described in chapter 5.

The structure of this chapter is as follows: The model Hamiltonian is introduced in section 6.1.1. Section 6.1.2 briefly reviews some methods used in this chapter: wave-packet propagation, the relaxation method, optimal control theory and density matrix theory. A more detailed review of the methods used is too extensive to be included and is therefore presented in appendix E.

In section 6.2.1, the numerical eigenstates for the model potential are calculated and compared to the corresponding analytical eigenstates in order to gauge the accuracy of the model. Consequently, the optimal control technique is applied in sections 6.2.3 and 6.2.4 to generate theoretical laser fields for the excitation of successively
higher eigenstates.

These laser fields have to be analysed thoroughly to establish their experimental viability. I have used the Frequency Resolved Optical Gating (FROG) technique (see section 2.4) to do this and demonstrate that the optimal fields are experimentally viable.

All results up to this stage are simulated for isolated (dissipationless) theoretical systems. In section 6.2.5, simulation results of the dynamics driven by the previously generated optimal fields with dissipation are presented. It turns out that dissipation slightly diminishes the population of the desired vibrational state but does not fully quench it. The action of a static field on the target and the true final states was subsequently simulated (results in section 6.2.6) to demonstrate desorption of hydrogen from the surface.

6.1.1. Model Hamiltonian

6.1.1.1. Diatomic Molecule

The Hamiltonian operator for a diatomic molecule interacting with a time-dependent electric field due to a laser pulse, is

\[
\hat{H} = \frac{\hat{p}^2}{2m} + \frac{\hat{\varphi}^2}{2\mu} + V(\hat{R}, \hat{r}) + \hat{V}_{\text{ext}}(\hat{r}, t),
\]

where \(m\) is the total mass and \(\mu\) is the reduced mass of the molecule (0.948 a.m.u. for OH\(^-\)), \(\hat{r}\) is the centre of mass of the molecule, \(\hat{r}\) is the internal coordinate (neglecting rotation), \(V\) and \(\hat{V}_{\text{ext}}\) are the potential energy and the coupling to the external electric field of the laser. The coupling term written in the multipole expansion is then

\[
\hat{V}_{\text{ext}} = q \cdot \phi(\hat{R}) - \mu_\alpha \delta_\alpha(\hat{R}) - \frac{1}{3} \Theta_{\alpha\beta} \delta_{\alpha\beta}(\hat{R}) - \cdots,
\]

where \(q\) is the electric potential, \(\hat{R}\) denotes the centre of mass of the charge density \(\rho\), \(\hat{R}\) is the total charge of the molecule (\(q = \int \rho d\hat{R}\)), \(\mu_\alpha = \int \rho(\hat{R}_\alpha - \hat{R}_b) d\hat{R}\) is the \(\alpha\) component of the dipole moment determined at an arbitrary but fixed reference point \(\hat{R}_b\), \(\delta_\alpha\) is the corresponding component of the electric field \(\delta_\alpha = -\nabla_\alpha \phi(\hat{R}_b)\), \(\Theta_{\alpha\beta}\) is the component of the quadrupole moment with

\[
\Theta_{\alpha\beta} = \frac{1}{2} \int \rho \left[ 3(\hat{R}_\alpha - \hat{R}_b)(\hat{R}_\beta - \hat{R}_b) - (\hat{R} - \hat{R}_b)^2 \delta_{\alpha\beta} \right] d\hat{R},
\]

and \(\delta_{\alpha\beta}\) is the field gradient \(\delta_{\alpha\beta} = -\nabla_\alpha \nabla_\beta \phi(\hat{R}_b)\).

As I will attempt to excite the stretch mode of \(\text{OH}^-\) (\(h\nu = 0.356\) eV), the laser fields driving the excitation will be at the corresponding frequency (or, for overtones, twice as high). This implies laser wavelengths around 3.48 \(\mu\m (1.78\) \(\mu\m\)). This is very long compared to the dimensions of the molecule controlled (1.0 \(\AA\) = \(1 \times 10^{-8}\) \(\mu\m\)). The long wavelength photon approximation can then be invoked: At each time step, the electric field is assumed to be homogeneous.

This approximation corresponds to \(\varepsilon(\hat{R}) \equiv \text{const}, \phi = (\hat{R}_c - \hat{R}_b) \cdot \varepsilon, \) and \(\varepsilon_{\alpha\beta} \equiv 0\). All higher derivatives of the field are also zero. The multipole expansion then terminates at the second order, so that \(\hat{V}_{\text{ext}}\) can be written as

\[
\hat{V}_{\text{ext}} = -q \cdot (\hat{R}_c - \hat{R}_b) \varepsilon(t) + \mu(\hat{R}_b) \varepsilon(t).
\]

Note that the dipole moment

\[
\mu(\hat{R}_b) = \int \rho(\hat{R}) \cdot (\hat{R} - \hat{R}_b) d\hat{R},
\]

where \(\rho\) is the charge density of the molecule, as well as the electrostatic potential \((\hat{R}_c - \hat{R}_b) \cdot \varepsilon(t)\) of the homogeneous field \(\varepsilon\) depend on the reference point \(\hat{R}_b\).

Assume a different reference point \(\hat{R}_1\) were used, then

\[
\hat{V}_{\text{ext}}(\hat{R}_1) = -q \cdot (\hat{R}_c - \hat{R}_1) \varepsilon(t) + \mu(\hat{R}_1) \varepsilon(t)
\]

\[
\begin{align*}
&= -q \cdot (\hat{R}_c - \hat{R}_1) \varepsilon(t) + \mu(\hat{R}_1) \varepsilon(t)
\quad + \int \rho(\hat{R}) \left( \hat{R} - \hat{R}_1 \right) \cdot (\hat{R} - \hat{R}_b) d\hat{R} \cdot \varepsilon(t)
\quad = -q \cdot (\hat{R}_c - \hat{R}_1) \varepsilon(t) + \mu(\hat{R}_1) \varepsilon(t)
\quad + q \cdot (\hat{R}_c - \hat{R}_1) \varepsilon(t) + \int \rho d\hat{R} \cdot \left( \hat{R}_c \cdot \varepsilon(t) \right)
\quad = \hat{V}_{\text{ext}}(\hat{R}_b),
\end{align*}
\]

since \(q = \int \rho d\hat{R}\). This means that the interaction term \(\hat{V}_{\text{ext}}\) is independent of the reference point which is needed to satisfy coordinate-independence of the dynamics.

On the other hand the charge density \(\rho\), and with it \(\mu\), depend on the internal coordinate \(\hat{r}\) of the molecule (here the stretch mode of \(\text{OH}^-\)). The total charge \(q\), however, does not. Now fix a reference point \(\hat{R}_0\) (for example the centre of mass of the molecule) and write the dipole as

\[
\mu(\hat{R}_0, \hat{r}) = \mu_0 + \mu(\hat{r}).
\]

Then the coupling potential has the form

\[
\hat{V}_{\text{ext}}(\hat{r}) = \left\{ -q \cdot (\hat{R}_c - \hat{R}_0) + \mu_0 + \mu(\hat{r}) \right\} \varepsilon(t).
\]

The first term in the curly braces is dependent only on \(\hat{R}_c\), the charge density centre of mass of the molecule, and the second is constant. The constant term \(\mu_0\) merely leads to a field-dependent phase factor in the propagation operator

\[
\hat{U} = e^{-i \int \hat{H}_{\text{rad}} dt}
\]

and therefore does not affect the dynamics of the system.

To gauge the impact of the \(\hat{R}\) dependent term in \(\hat{V}_{\text{ext}}\), it is necessary to remember that the frequencies of the laser fields constructed in this chapter will be such that the stretch mode of the OH\(^-\) molecule is excited. The frequencies in the laser pulse are then of the same order (or higher in the case of overtones) as the frequency of the stretch motion. The dynamics of the molecule as a whole are not resonant with this field and will therefore remain unaffected by it, although the monopole term is
the leading term in the multipole expansion.

6.1.1.2. OH\(^-\) on the MgO(001) Surface

The task of this chapter is to simulate the dynamics of the OH\(^-\) molecule formed due to adsorption of HCl on the MgO(001) surface. Although an isolated molecule was considered in the preceding section, much the same argument holds at the surface: Now the molecule as a whole is not free but takes part in the motion of some normal modes.

To quantify the statement made above concerning compound OH\(^-\) motion, I have included the two major normal modes of the crystalline system moving OH\(^-\) as a whole in table 5.4 on p. 168. Their frequencies are 3.9 THz and 14.3 THz and as such well separated from the OH\(^-\) stretch mode (86 THz). Rather than considering the monopole of OH\(^-\), one may also look at the (neutral) system as a whole and the dependence of the total dipole on the relative coordinates of OH\(^-\) on one hand and \((\text{Mg}_n\text{O}_{n-1})^{2+}\) CI\(^+\) on the other hand. The fact remains that this motion is not resonant with the laser field to be applied and hence can be disregarded. The same considerations hold for the dependence of the dipole moment function on any other normal mode of the system, as the OH\(^-\) stretch mode is spectrally well separated from the main vibrational band of the system.

This resonance argument hence allows to reduce the Hamiltonian to involve only the internal coordinate \(r\) of the OH\(^-\) molecule.

To further simplify matters, it can be remembered that the DFT calculations of chapter 4 predict that the OH\(^-\) molecules are pointing away from the surface with a narrow distribution of angles. Assuming a laser field polarised normal to the surface, the internal product of the dipole moment \(\hat{\mu}\) and the electric field \(\hat{\epsilon}\) can be replaced by the product of the scalars \(\mu\) and \(\epsilon\), so that the resulting model Hamiltonian can be written as

\[
\hat{H} = \frac{\hat{p}^2}{2M} + V(r) + \mu(r) \hat{\epsilon}(t).
\]

Note that this is not coordinate-independent but instead relies on a-priori considerations of the outcome of the simulation. After the excitation of a high vibrational state of OH\(^-\), the application of a quasi-static field \(\hat{\epsilon}(t)\) is resonant, causing desorption of hydrogen from the surface. Since at large separation of neutral hydrogen from the neutral surface a static field does not influence the dynamics, the asymptote of the dipole moment at large separation must be zero. This condition determines the reference point \(\tilde{R}_0\).

The above discussion can be understood further by considering the dynamics of the expectation values of the system. Ehrenfest’s theorem states

\[
\frac{d \langle \hat{O} \rangle}{dt} = -\left\langle \frac{d(V + \mu \epsilon(t))}{dx} \right\rangle,
\]

where \(\langle \hat{O} \rangle = \left\langle \psi(t) \hat{O} \psi(t) \right\rangle\) denotes the expectation value of the operator \(\hat{O}\).

This implies that it is the derivative of the dipole that determines the dynamics of the system (and not the magnitude of the dipole, which depends on the reference point \(\tilde{R}_0\)). In order to continuously inject vibrational energy into the system, the momentum \(\langle \hat{p} \rangle(t)\) and its derivative must have the same sign, implying resonance between the field \(\epsilon(t)\) and the molecular motion (to which the laser-driven excitation is only a small perturbation). This is a time-resolved justification for Fermi’s golden rule.

6.1.1.3.Model Potential – Quantum Mechanical Properties of the Morse Potential

It was seen in the previous chapter that the OH\(^-\) stretch mode is spectrally isolated from all other modes in the HCl/MgO(001) system. It is therefore a good approximation to consider this mode on its own and simulate its coupling to the other modes (such as the OH\(^-\) rotation and libration) by the action of a thermal bath within the density matrix formalism.

As a potential for the OH\(^-\) stretch coordinate, I used the same Morse potential

\[
V(r) = D (e^{-2\beta(r-r_0)} - 2e^{-\beta(r-r_0)})
\]

(6.3)
as the one used throughout the lattice dynamics and molecular dynamics simulation of the OH\(^-\) stretch in chapter 5. Here \(D = 5\) eV, \(\beta = 2.15\) A\(^-1\) and \(r = 1.0\) A. This corresponds to a ground state frequency of 109 THz (3638 cm\(^{-1}\)). The deviation from this frequency observed in lattice dynamics and molecular dynamics (ch. 5) was due to interaction with the MgO lattice. The latter is, however, simulated implicitly in the present quantum dynamics simulations in the form of a dissipation operator.

Some properties of this potential that are specifically relevant for quantum dynamics are explained in detail in this section. The Morse potential was formulated originally in ref. 186 as an anharmonic model for molecular bonds whose energy levels depend on \(\nu\) up to second order:

\[
E(\nu) = -D + \hbar \omega \left( \nu + \frac{1}{2} \right) - \frac{\hbar^2 \omega^2}{4D} \left( \nu + \frac{1}{2} \right)^2,
\]

(6.4)
where \(\omega = \beta \sqrt{2D}\) is the Morse frequency, i.e. the frequency of the harmonic oscillator approximating the Morse potential at the minimum \(r_0\).

The anharmonicity \(\xi\) of the Morse potential is straightforwardly defined as the ratio between the coefficient modulus of the square term and the harmonic vibrational quantum \(\hbar \omega\):

\[
\xi = \frac{\hbar \omega}{2D} = \frac{\hbar \beta}{2\sqrt{2Dm}}
\]

(6.5)
Using eq. (6.1.1.3) it is straightforward to show that definition (6.5) is commensurate with the more general definition of the anharmonicity in eq. (3.5). The anharmonicity of the OH\(^-\) Morse potential is 0.0226. This is compared to the value of 0.0029 for MgO.

The analytic eigenstates are given in refs. 186–188. I calculated them according to ref. 188:

\[ \Psi (r) = z^\lambda \cdot L_\nu^\lambda (r) \cdot e^{-\frac{r}{2}} \cdot e^{-\frac{z^2}{2}}, \]  
(6.6)

\[ z = \frac{4}{\omega} e^{-\beta (r - r_0)}, \]  
(6.7)

\[ L_\nu^\lambda (r) = \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \left( \frac{\nu + \zeta}{\nu - m} \right) x^m, \]  
(6.8)

which yields non-normalised functions. The quantum number enumerating the eigenstates, \( \nu \) is the quantum number enumerating the Laguerre polynomials, and \( L \) stands for the Laguerre polynomial which can be expressed either as in eq. (6.8) or recursively for easier implementation.\(^{189}\)

I have compared the analytical eigenstates eqs. (6.6–6.8) to the numerical ones to gauge how accurate the numerical method is. It is important to note that this solution for the Morse potential eigenstates and energies relies on the boundary conditions

\[ \lim_{r \to -\infty} \Psi (r) = 0 \]  
(6.9)

\[ \lim_{r \to +\infty} \Psi (r) = 0, \]  
(6.10)

whereas for a diatomic molecule, distances \( r \) smaller than zero are non-physical and therefore the boundary conditions eq. (6.9) and

\[ \psi (r) = 0, \ r \in [ -\infty, 0] \]  
(6.11)

should be imposed. This means that the analytic solutions given above are only approximations to the molecular situation. However, it turns out that for parameters fitting to most diatomic molecules the value of the wave function is very small at zero and therefore this is an adequate approximation.\(^{186,187}\)

### 6.1.1.4. Model Dipole Moment

The model for the dipole coordinate-dependence is of the form

\[ \mu (x) = A_\mu \cdot (x - x_\mu) \cdot e^{-\frac{x^2}{2}} \]  
(6.12)

with \( A_\mu = 18.0 \) e, \( x_\mu = -3.0 \) Å and \( r_\mu = 2.0 \) Å. This form was used previously to fit the dipole of the free OH molecule.\(^{34,190}\) The parameters used are arbitrary but I will rationalise the physical relevance of this model in the following paragraphs.

At \( r = 0 \), the (hypothetical) molecule is a monopole, with zero dipole moment. At the equilibrium OH bond distance of around 1 Å, the dipole moment is strictly monotonically decreasing, i.e. oxygen donates electron charge to the proton with increasing distance. This is the correct tendency, as the molecule is polar in the bound configuration but in the dissociation limit, a neutral hydrogen atom is separated from a neutral crystal substrate. This means that the system should not respond to infrared radiation at large distances, which is the case as the dipole moment becomes zero at infinite distance.

Concerning the physical relevance of the coefficient \( A_\mu \), it may be noted that it occurs in the interaction Hamiltonian as a factor in the product \( \mu \cdot \mathbf{E} \) with the electric field, i.e. any errors in its magnitude can be offset by the amplitude of the field (and correspondingly the laser power).

Contrasting with this model dipole, a simpler, linear model dipole of the form \( \mu = q \cdot x \) as used in refs. 31, 191, 192 does not have these properties. Particularly, it suggests controllability of the system even at large separations which is clearly not the case and may result in wrong predictions.

### 6.1.2. Methods Used in this Chapter

#### 6.1.2.1. Wave Function Propagation

To simulate vibrational dynamics on this potential surface, I have used quantum dynamics propagation methods. Such methods are in wide use today. A review can be found, for example, in ref. 193. I will constrain myself here to a brief description of the methods used in this project. A more detailed review of the methods is presented in appendix E.

Starting from the time-dependent Schrödinger equation

\[ i \hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi, \]  
with the Hamiltonian from eq. (6.1), propagation of wave packets in time means application of the operator

\[ \hat{U} = \mathbf{T} e^{-i \int H dt}, \]  
(6.13)

to a given wave function \( \psi (t = t_0 = 0) \), where \( \mathbf{T} \) is the time ordering operator.

I will use propagation methods where the wave function is represented on an equally-spaced grid. Frequency-domain operators such as the kinetic energy are evaluated on the grid by using the Fast Fourier Transform (FFT) technique. The action of the exponential of eq. (6.13) on the wave function is then approximated by the Split Operator Method (SOD). This consists of splitting the Hamiltonian into a potential and kinetic energy part and evaluating the exponential directly in the space where each is local, i.e. in real space for the potential and in frequency space for the kinetic energy.

This approach is reviewed in more detail in appendix E.1.2, where some simple example calculations are also presented. Propagation methods are also useful for the numerical calculation of eigenstates by applying the relaxation operator

\[ e^{-i \hat{H} t}, \]  
to the wave function. This operator corresponds to propagation in imaginary time via the relation \( t = -\imath \hbar s \) and damps the eigenstates present in the wave function according to their energy. This means that in the case of a non-degenerate ground state (which is considered here) the ground state is damped least and can therefore...
be extracted by a long-time relaxation during which the wave function is repeatedly normalised.

After finding the ground state a similar process can be used to find the first excited vibrational eigenstate. This is done by subtracting the ground state component from the wave function prior to each renormalisation. These states can then be used to find the next higher excited state and so on.

6.1.2.2. Optimal Control Method and a New Extension

Assuming a controllable branching reaction, the optimal control method allows to construct a laser pulse that drives a reaction approximately transforming a specified initial state into a target state in a specified reaction time \( \tau \). This method is covered in refs. 34, 190.

Briefly, differential equations are derived from a variational approach with a functional involving the target yield and a penalty term for unphysical laser fields. They are the time-dependent Schrödinger equation for the simultaneous backward and forward propagation of the initial and target wave functions and the laser field update

\[
\varepsilon (t) = -\frac{s(t)}{\hbar \alpha_0} \text{Im} \left\{ (\psi_i(t) | \psi_f(t)) (\psi_f(t) | \mu | \psi_i(t)) \right\},
\]

(6.14)

where \( \varepsilon \) is the electric field of the laser pulse, \( s \) is a \( \sin^2 \) shape function for smooth switch-on and switch-off of the pulse, \( \alpha_0 \) is the penalty coefficient for large field amplitudes, \( \mu \) is the dipole moment, and \( \psi_i \) and \( \psi_f \) are the time-propagated initial and target wave functions, respectively.

An improved electric field results from each propagation cycle, so that an optimal result is approached by the application of many cycles. Due to the effective competition between the target yield and the penalty for large field strengths in the optimal control method it can be possible that with a small penalty parameter \( \alpha_0 \) only unphysical fields result while with a larger one the penalty wins and a zero field results.

I have therefore extended the optimal control method by introducing an increase of the penalty parameter \( \alpha_0 \) after each propagation cycle. This destroys the self-consistency but allows the method to find a physically relevant solution more reliably and more quickly.\(^*\)

\(^*\)It has come to my attention that this technique has been developed independently in the group of de Vivie-Riedle.\(^{194}\)

I call this variant of the method “Swept Penalty Parameter”. It is reviewed in more detail in appendix E.1.5. In essence, it supports the method in finding an appropriate initial guess field mediating the process that is sought. It also allows to pick the cycle, and hence penalty parameter, at which the most agreeable result in terms of laser pulse and yield has been achieved from the optimal control cycles performed.

6.1.2.3. Total Reaction Time as a Parameter

If \( \tau \) is large compared to the decoherence time of the reactive species, they cannot remain resonant with the laser field over all of \( \tau \), again lowering the yield of the reaction. Therefore a compromise for the total reaction time \( \tau \) should be found such that the reaction becomes feasible. If this optimisation is difficult, several optimal control calculations have to be performed with different parameters \( \tau \). Generally it is advisable to use a \( \tau \) that is at least several tens of vibrational periods of the reactive species and shorter than its decoherence time. This is in this case (OH\(^-\) stretch) possible, so not many values of \( \tau \) needed to be tried.

I have used \( \tau = 870 \) fs which is 95 vibrational periods of OH\(^-\) and less than half the dissipation lifetime of 2.14 ps extracted from the MD simulations of chapter 5. Wave packet propagation was performed using the split operator propagation method (section E.1.2) with a time step of \( \Delta t = 72.6 \) a.u (1 a.s = \( 10^{-18} \) s). The optimal control runs consisted of 250 iterations with a penalty parameter swept from \( \alpha_T = 0.1 \) a.u to \( \alpha_T = 250 \) a.u as described in section E.1.5 on p. 270.

6.1.2.4. Density Matrix Propagation

The optimal control method is only useful in the framework of wave packet dynamics. The reaction predicted by optimal control therefore has to be examined for its robustness against the effects of dissipation. In the worst case, the yield of the desired target wave function is fully quenched by dissipation. Since I have chosen an excitation time much shorter than the dissipation lifetime, this should not happen. Instead the yield will be slightly diminished.

Dissipative quantum dynamics calculations are performed within the density matrix formalism which is briefly reviewed in section E.2.2 of the appendix. In terms of numerical effort, it is most important that density matrix dynamics scale the same as wave packet dynamics with a doubled number of degrees of freedom. The number of DoF is therefore limited. Since only one DOF is considered here (the OH\(^-\) stretch mode) this is not a problem.

A particular dissipator operator which I have used because it is best suited to the Morse potential\(^{195,196}\) is reviewed in section E.2.6 of the appendix. The decisive parameter used by this operator is the dissipation lifetime of 2.14 ps derived in chapter 5.
kT is of the order $T = 450$ K, and hence the thermal distribution factor $e^{-\frac{kT}{T}}$ is of the order $10^{-6}$.

After a highly vibrational state has been populated with the aid of an optimal pulse, a quasistatic electric field could be applied to desorb atomic hydrogen. A far infrared pulse at the right phase relative to the optimal pulse populating $\nu = 10$ would suffice. In order to avoid disturbing the Morse excited state population, this pulse should only impinge the reactive species after the excitation process has finished. Ideally, the far-IR pulse should be shorter than one period as demonstrated by Baltuska et al. and Huber et al., albeit at shorter wavelengths.

The static field will also desorb positively charged protons. However, when the static field is switched off, the energy of the binding energy between the surface and the proton becomes much larger than the binding energy between the surface and atomic hydrogen due to electrostatic attraction to the surface. Unless the static field is held constant until the detection of desorbed species, a desorbed proton will therefore return to the surface while atomic hydrogen will continue to leave the surface due to the momentum picked up on the slope of the potential, as illustrated in fig. 6.1b.

In the following, I will concentrate on the desorption of atomic hydrogen, since the experimental realisation of a quasistatic field at the field strength needed is more likely to be an infrared pulse rather than a static field.

### 6.1.3. Reaction Scenario

As was seen from the molecular dynamics results (ch. 5), the vibrational normal modes involving the chlorine ion are coupled strongly to the substrate, so that the energy of a vibrational excitation is dissipated after only a few vibrational periods. This makes it impossible to control the chlorine motion, as the coupling between the laser and atomic vibration is based on resonance effects, necessitating constructive coupling with the laser over several vibrational periods to pump an appreciable amount of energy into the system. This means that the OH$^-$ ion at the surface must be the target of my endeavours to propose a reaction scenario for coherent control of the molecule. Due to the high vibrational frequency of the OH$^-$ stretch mode, it couples only little to the substrate, so that resonance with a laser field can be achieved.

As vibrational excitation is based on resonance between the laser field and the vibrational motion of the wave packet representing the reactive species, I will use bound initial and target states in the optimal control method. This will allow a ladder-type excitation scheme to attain a high vibrational excitation.

It may be argued that a “proper” chemical reaction must involve the desorption of one of the participating reactive species, so I propose the following reaction scenario:

The stretch mode of OH$^-$ is excited to a high vibrational state from the ground state and subsequently a static (or very low frequency) electric field is applied to desorb hydrogen from the surface. The availability of highly excited molecules allows desorption with relative ease compared to direct desorption with a static field from the vibrational ground state.

An illustration of this reaction scenario is seen in fig. 6.1. As initial state, the vibrational ground state is assumed. Due to the large quantum in the OH$^-$ molecule – about 0.35 eV – this is a good approximation even at room temperature. Even at

$$T = 450 \text{ K}, \quad \frac{kT}{T} \approx 12$$

and hence the thermal distribution factor $e^{-\frac{kT}{T}}$ is of the order $10^{-6}$.

The static field will also desorb positively charged protons. However, when the static field is switched off, the energy of the binding energy between the surface and the proton becomes much larger than the binding energy between the surface and atomic hydrogen due to electrostatic attraction to the surface. Unless the static field is held constant until the detection of desorbed species, a desorbed proton will therefore return to the surface while atomic hydrogen will continue to leave the surface due to the momentum picked up on the slope of the potential, as illustrated in fig. 6.1b.

In the following, I will concentrate on the desorption of atomic hydrogen, since the experimental realisation of a quasistatic field at the field strength needed is more likely to be an infrared pulse rather than a static field.

### 6.2. Results of Simulations of HCl on MgO

#### 6.2.1. Numerical Accuracy: Comparison of Eigenstate Energies with Analytic Solutions

In order to estimate the accuracy of the calculation on a simulation grid, I calculated the eigenstates of the Morse oscillator using the relaxation method introduced in section E.1.3 with the split operator method (section E.1.2) and compared this result to the analytic solution (equations 6.4 – 6.8).

Fig. 6.2 shows a comparison of the energies of the highest bound eigenstates, based on a relaxation method calculation performed on different grids. These grids were:

(a) 256 points with grid spacing $\Delta x = 0.030$ au ($x = 0 \ldots 4.0$ Å)

(b) 512 points with grid spacing $\Delta x = 0.015$ au ($x = 0 \ldots 4.0$ Å)

(c) 1024 points with grid spacing $\Delta x = 0.015$ au ($x = 0 \ldots 8.0$ Å)

A potential cutoff of 8.1 eV has been used throughout. The self-consistency cycle was exited when the wave function overlap with the result of the previous cycle deviated from unity by less than $10^{-4}$.

Fig. 6.2b demonstrates that there is no difference in the energies calculated from grids a and b, i.e. the accuracy of the simulation is not limited by the grid spacing $\Delta x$.

A direct comparison of grids b and c, which differ by the simulation region, shows that grid c describes the highest bound state $\nu = 21$ better. Up to $\nu = 20$, however, the results of grids a and b coincide, so for the purpose of considering processes involving states up to $\nu = 20$, it is sufficient to use grid a.

The above results enable me to gauge which of the following two sources of error dominates the numerical simulation:

1. The maximum momentum presentable is limited by the grid spacing, i.e. the states with large $\nu$ and therefore large kinetic energy are represented less well than the ones with small kinetic energy. The grid spacing is the limiting factor for the representation of the kinetic energy operator through the relation

$$T_{\text{max}} = \frac{\pi^2}{2M \Delta x^2}$$

2. The simulated region is finite. This means that the potential barrier seen on the left in fig. 6.3 is repeated at the right-hand side boundary due to periodic boundary conditions. States filling the entire simulation region are therefore pushed up in energy. Additionally, the eigenstates with energy above zero (and below the numeric potential cut-off) are therefore numerically still states bound by the periodic images of the barrier.

We have seen that errors occur exclusively at the dissociative end of the Morse potential, i.e. error 2 dominates and hence a calculation on grid a is sufficiently accurate to represent any eigenstates with $\nu \leq 20$, as can be seen also in fig. 6.2.

Fig. 6.3 shows several eigenstates calculated with the relaxation method on grid a. The eigenstates are drawn with their base lines at their respective energies.

It can be seen that the $\nu = 20$ state already covers the whole simulation region. A correct representation of the state $\nu = 21$ should be even less localised and therefore incommensurate with the periodic boundary conditions, which impose a potential barrier at the right hand side. This gives direct evidence to the exclusive relevance of error 2 in the calculation of the eigenstates.

In what follows, I will concentrate on the states $\nu = 0, \ldots, 12$. The modulus of the tenth excited state ($\nu = 10$) at the boundary of grid a is below $10^{-24}$, which speaks for an accurate description. As already mentioned above I have therefore used grid a in the computation of the results presented in the following, as it allows shorter computation times.

### 6.2.2. Experimental Viability of Proposed Electric Fields

In order to recognise whether the fields proposed by optimal control computations are viable for experimental implementation, one has to look at the shape of the field and its amplitude. The amplitude of a proposed laser field should be compared to laser powers attainable in current experiments.

I will present electric fields resulting from my optimal control calculations in atomic units of electric field strength. Atomic units are the most natural system to work in when doing wave packet propagation and therefore electric fields are presented in these units.

One atomic unit of electric field strength corresponds to

$$[E] = 1 \text{ au} = 1 \text{ Ryd} \cdot a_0^{-1} \cdot e^{-1} = 5.134 \times 10^{14} \text{ V m}^{-1}.$$  

The relation between the module $H$ and $E$ of $\vec{H}$ and $\vec{E}$ is

$$H = \sqrt{\frac{\mu_0}{\epsilon_0}} E.$$  

Hence for an electromagnetic field with $\vec{E} \perp \vec{H}$ the modulus $S$ of the Poynting

\[ S = \sqrt{\frac{\mu_0}{\epsilon_0}} E \times H. \]
vector $S$, which is the power density of the field is

$$S = \sqrt{\frac{\hbar \omega}{E_0^2}}.$$

This means that a field with $E = 1$ au electric field strength corresponds to a power density of

$$S = 7 \times 10^{16} \text{Wcm}^{-2}.$$

Note that $S$ depends quadratically on $E$, so a typical field strength of $E = 10^{-4}$ au of the results presented below corresponds to $S = 700 \text{MWcm}^{-2}$, which is attainable with today’s laser technology. For comparison, laser powers up to several GW cm$^{-2}$ are attainable with solid-state lasers and much higher powers of up to $10^{14}$ W cm$^{-2}$ have been reported using Chirped-Pulse Amplifier (CPA) laser systems, which use pulse-stretcher and pulse-compressor grating pairs before and after the amplifier in order to circumvent the self-focusing effect at high laser powers.$^{69,302}$ These lasers operate at the femtosecond time scale and are therefore comparable to the kind of fields proposed in the following.

Apart from these laser power considerations, the electric field intensity can be regarded as arbitrary, as it is the spectrum of the pulse which is most important for resonant coupling, not the power. Any errors in the modelling of the magnitude of the dipole moment are offset by scaling the electric field strength as detailed in section 6.1.1.

6.2.3. First Excited State with Optimal Control

The simplest excitation is a transfer of the molecule from the vibrational ground state to the first excited state of the Morse potential. A laser pulse mediating this transfer was calculated with the technique of optimal control (section 6.1.2.2).

An initial guess field with a frequency near the energy difference between ground and first excited state was used, with a large frequency sweep ("chirp", see p. 25) to guarantee that the actual resonance frequency is tuned in at some point during the pulse. The chirp was chosen such that the frequency becomes zero at the end of the pulse.

Fig. 6.4 shows the laser fields produced by this algorithm after 10, 50 and 250 iterations. A comparison of the plates in fig. 6.4 shows the following tendency: With rising optimal control penalty, the scale of the field becomes much smaller, reaching $10^{-4}$ au at $\alpha_0 = 250$ au, as indicated in section 6.2.2. The envelope approaches the $\sin^2$ shape indicated by the shape of the penalty function. The insets reveal that the field evolves from very noisy to a nice, sinusoidal shape. This too is, of course, a vital demand to be satisfied by the theoretically proposed laser field to make it viable for experimental realisation.

The new field follows the dynamics of the wave functions due to the current laser field, as shown by eq. (6.14). This means that, as a tougher restriction is imposed upon the field by the penalty parameter $\alpha_0$, the field must become weaker with a smaller impact on the dynamics of the wave functions. The more unperturbed the dynamics of these wave functions are, the smoother the field produced in the algorithm becomes. In the light of these considerations, the results of fig. 6.4 are no surprise.

Fig. 6.5a shows the eigenstate populations $\langle \psi | \phi_0 \rangle$ – in other words, the coefficients of the wave function in the eigenstate representation – over time in the propagation according to the electric field of fig. 6.4c.

Fig. 6.5a shows the FROG trace of the pulse which, like all following FROG traces, is drawn with ten contour levels at linearly increasing intensity.

It can be seen that the excitation does not only involve the ground and first excited states, but also the second excited state at intermediate times. This opens the opportunity to use this field as initial guess for an excitation from the ground to the second excited state, $\nu = 0 \rightarrow 2$.

Higher level excitation processes are quantum-forbidden if the potential is harmonic and the dipole moment is linear. Here, however, the potential (Morse) is anharmonic and the dipole moment (exponential) is non-linear, so that higher excitations can be achieved.
6.2.4. Higher Level Excitations

While the excitation $\nu = 0 \rightarrow 1$ has been demonstrated with the unaltered optimal control method as described in section 6.1.2.2, using the swept penalty parameter method of becomes necessary to reach higher target states with justifiable computational effort.

I produced optimal control fields for the excitations $\nu = 0 \rightarrow n$, $n = 2, \ldots, 10$ by using the resulting field from the preceding lower excitation $\nu = 0 \rightarrow n - 1$ as initial guess, as each reaction involves the next higher state in the reaction at some point during irradiation. This process allows climbing the ladder to get laser fields that excite the ground state into high excited states.

Figs. 6.6 and 6.7 show the eigenstate populations during the transitions from the ground state to higher excited states along with the laser fields mediating these transitions and their FROG traces.

As before, I have used the FROG technique with a Gaussian gate function $g$ with $\sigma = \frac{1}{\sqrt{2}}T$ (see section 2.4). This means the window had a width of $\sigma = 22$ fs for the pulses discussed in this section, as seen in fig. 6.5b and all other pulses calculated in this section. This is a time resolution attained routinely in experiments. For example in refs. 199, 200 the FROG technique is used to characterise a pulse of only 4.5 fs length.

Fig. 6.5b shows a contour plot of the field mediating the excitation $\nu = 0 \rightarrow 1$. Also drawn are lines at the energy differences $E_1 - E_0$, $E_2 - E_1$ and $E_3 - E_2$. Fig. 6.5b demonstrates that the pulse contains a noticeable component at $E_2 - E_1$. This is the cause for the slight population of the second excited state excitation shown in fig. 6.5a. The large frequency width of the FROG trace is due to the finite width of the analysis “window” function $g$.

It can be seen from the diagrams that the fields become more complicated as more highly excited states are produced. This had to be expected, as the Morse potential is anharmonic and therefore the distance between two adjacent energy levels decreases with $\nu$.

It turns out that in each excitation $\nu = 0 \rightarrow n$, the state $\nu = n + 1$ is involved in the process at some intermediate time. This is, as earlier, what allows using the laser pulse generating each excitation to be used as initial guess for the next higher excitation. This represents a general method for excitations $\nu = 0 \rightarrow n$, for any $n$.

For the highest state, $\nu = 10$, I present the result for $\alpha_0 = 236$, as the yield collapses for higher penalty parameters. It is another advantage of using a swept penalty parameter $\alpha_0$ that it allows to pick out the penalty at which sensible fields and satisfactorily high yields of the desired final state result.

As a comparison, many runs with many iterations each would have to be done with the fixed penalty parameter method to attain such a solution, resulting in a lot of computational time wasted on runs that yield one of either unrealistic laser field

\[ \text{(a)} \quad \text{(b)} \quad \text{(c)} \quad \text{(d)} \quad \text{(e)} \quad \text{(f)} \quad \text{(g)} \quad \text{(h)} \quad \text{(i)} \quad \text{(j)} \quad \text{(k)} \quad \text{(l)} \quad \text{(m)} \quad \text{(n)} \quad \text{(o)} \]

Figure 6.6: Eigenstate populations of the wave function over time for the transition from the ground state to the excited states $\nu = 1, \ldots, 5$ shown next to pulses mediating these transitions and their FROG traces.
or insufficient yield. This is of course assuming that a result can be achieved with a single penalty parameter at all, which is not always the case.

All eigenstate population images suggest that the states are excited in ascending order. The excitation energy from the ground to the first excited state is held for a while, as the pulse gains amplitude. At a later time, a linear chirp sets in that smoothly lowers the pulse frequency to stay in resonance to the various excitation energies as the ladder is climbed, as opposed to a stepped FROG traces corresponding to skipped intermediate states.

From the process $\nu = 0 \rightarrow 4$ onward, another feature starts becoming noticeable in the FROG traces. It is found at energies higher than the main frequency range. These frequencies must be attributed to double excitations $\nu = n \rightarrow (n+2)$ (see also fig. 6.8). Since a competition between yield and pulse power has been built into the optimal control technique, it appears that in the Morse potential – as an example of an anharmonic molecular potential – an admixture of single and double excitation energies in the pulse is more successful in reaching the target than a pulse consisting of single excitation energies alone.

The excitation using a pulse created with optimal control theory to the state $\nu = 10$ is the process on which I will concentrate from here on. The yield with which this state can be produced in the given excitation time of 870 fs, i.e. the overlap between the normalised target wave function and the final wave function is 75%.

The choice of $\nu = 10$ as target state is an arbitrary decision based on accuracy considerations – the 10th excited state is still represented highly accurately on the grid used and it is of sufficiently high energy to be close to the dissociation energy level.

Fig. 6.8 once more shows the FROG trace from fig. 6.7(o) of the optimal control pulse mediating the excitation from $\nu = 0$ to $\nu = 10$, this time with two lines fitted to the chirp behaviour of the single and double excitation branches of the pulse. Only the main branch of the FROG trace has been fitted, the upper line is exactly twice its energy. This turns out to be a good fit to the top features of the FROG trace, once again supporting the notion that these features represent double excitations $\nu = n \rightarrow (n+2)$. Note that chirp of the pulse only sets in at around 400 fs. Before this, the pulse frequency is constant, at the excitation energy of the first vibrational state.

An alternative method to reach high excited states has been proposed by Korolkov, Manz and Paramonov. Pulses for the processes $\nu = 0 \rightarrow 5$, $\nu = 5 \rightarrow 10$ and so on were applied in sequence to excite OH$^-$, modelled by a Morse potential, skipping all intermediate states. However, it relies on very strong laser fields – a laser power of...
about \(6.5 \times 10^{14} \text{Wcm}^{-2}\) is proposed, as opposed to a power of \(10^9\) to \(10^{18} \text{Wcm}^{-2}\) for the laser fields presented in the middle column of the diagrams in figs. 6.6 and 6.7. The shortest pulse proposed by Korolkov et al. is 1.5 ps long, where the precursor state \(\nu = n\) just reaches its maximum population when the next pulse component mediating the transition \(\nu = n \rightarrow n + m\) sets in.

In contrast, the pulses I propose here are only 870 fs long. This helps to minimise dissipation of the system before the excitation process is finished. The excitation processes proposed by Korolkov et al. are therefore more vulnerable to dissipation due to their longer time scales. It may be argued that the pulse shapes proposed by Korolkov et al. were simpler and therefore easier to realise in experiments, however, they demand coordination of several different pulses, while the pulses proposed by optimal control can be created by applying linear chirp in conjunction with frequency doubling – both techniques frequently applied in laser technology – to one single pulse.

#### 6.2.5. Optimal Control Yield Lowering due to Dissipation

In order to simulate dissipation in nuclear quantum dynamics, the Liouville operator from section E.2.6 was used in the density matrix formalism. The lifetime parameters necessary for this model were fitted to the molecular dynamics results, as described in section 5.9.

The model Liouvillian operator method is most readily implemented in the Heidelberg Multi-Configuration Time-Dependent Hartree (MCTDH) code.\(^{201,204}\) I have used an exponential DVR basis with 255 grid points. This is an equivalent grid to the FFT based simulations presented in section 6.2.1 above.

In order to estimate the accuracy to which the results of both methods agree, I did a dissipation-free density matrix run using ABM in the MCTDH code, which should reproduce the results from the split operator (SPO) optimal control run. Fig. 6.9a shows the eigenstate populations during propagation with the optimal control field compared to the corresponding image for the SPO run. The previous result of a significant excitation of the tenth eigenstate is qualitatively reproduced. However, the are differences between the yields predicted by the different methods – while SPO predicts a yield of 75\%, the ABM method predicts only 65\%.

In order to find the source of this discrepancy, I have tried altering several parameters of the propagation: An SPO run with a time-step of \(\Delta t\)\(^{2}\), i.e. a quarter the previously used time-step, with linear interpolation of the electric field yields the same results as the previous SPO run with time-step \(\Delta t\). This excludes the time-step and the linear interpolation as error sources.

The overlaps \(\langle \phi_i | \psi \rangle\) of the corresponding eigenstates calculated by relaxation with the two different methods never deviate from unity by more than \(10^{-7}\), which is not sufficient to produce such a large deviation of the states populations.

The remaining explanation for the discrepancy is in the propagation methods themselves. The SPO method is third order in the time-step, while the ABM method is fifth order. Taking this large difference between the methods into account and remembering that the population of a single state as observable is very sensitive to changes in the wave function, the qualitative agreement of the two methods is satisfactory.

The ABM method has to be regarded as superior, so that the pulse predicted by

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**Figure 6.8.** Linear chirp fit to the frequency time-dependence in the FROG trace of the excitation \(\nu = 0 \rightarrow 10\) (bottom decline). The declining line at the top is this fit, doubled. It can be seen that it falls into the area covered by higher features of the FROG trace, suggesting they are responsible for excitations at the doubled energy, i.e. double excitations (which are allowed in anharmonic potentials).

**Figure 6.9.** (a) Squared eigenstate populations for MCTDH propagation. Qualitatively comparable with fig. 6.7m, which is repeated here as sub-figure (b).

I have altered the MCTDH code in order to allow it to employ the pulse shape constructed using the optimal control technique (section 6.1.2.2). The fifth-order Adams-Bashforth-Moulton (ABM) predictor-corrector integrator\(^{182}\) with variable time-step was used with MCTDH. Linear interpolation was used for the electric field at times between the time steps of the optimal control runs. This is a sufficiently good approximation, as the time-step used with optimal control was short compared to the period of the relevant vibration.

In order to estimate the accuracy to which the results of both methods agree, I did a dissipation-free density matrix run using ABM in the MCTDH code, which should reproduce the results from the split operator (SPO) optimal control run. Fig. 6.9a shows the eigenstate populations during propagation with the optimal control field compared to the corresponding image for the SPO run. The previous result of a significant excitation of the tenth eigenstate is qualitatively reproduced. However, the are differences between the yields predicted by the different methods – while SPO predicts a yield of 75\%, the ABM method predicts only 65\%.

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The overlaps \(\langle \phi_i | \psi \rangle\) of the corresponding eigenstates calculated by relaxation with the two different methods never deviate from unity by more than \(10^{-7}\), which is not sufficient to produce such a large deviation of the states populations.

The remaining explanation for the discrepancy is in the propagation methods themselves. The SPO method is third order in the time-step, while the ABM method is fifth order. Taking this large difference between the methods into account and remembering that the population of a single state as observable is very sensitive to changes in the wave function, the qualitative agreement of the two methods is satisfactory.

The ABM method has to be regarded as superior, so that the pulse predicted by...
optimal control with the SPO method is actually slightly sub-optimal. Implementing optimal control with different higher order propagation methods is possible but outside the scope of this project. For the present purpose of demonstrating excitation of OH\(^\cdot\), it will be sufficient to deal with the pulse of 65% yield.

A simulation of the excitation process with dissipations turned on, using the present laser field and 2.14 ps as lifetime (as discussed in section 5.9) results in eigenstate populations as seen in fig. 6.10a. It can be seen that the excitation of the state \(\nu = 10\) survives, i.e. the dissipation is not strong enough to quench the desired result completely. Quantitatively speaking, the population of the 10th state at the end of the irradiation with the electric field is 42%. The maximum yield is reached slightly before the end of the propagation: At \(t = \tau - 87\) fs the overlap is 45%. This is because at the end of the simulation the excitation field is very weak while dissipation acts to decrease the excited state population.

A yield of 45% compared to a prediction of 65% without dissipation, taking into account the squaring of yields to calculate the populations, means that the dissipation prevents 50% of the 10th excited state population.

**Figure 6.10.** (a) Populations during excitation with dissipation turned on (MCTDH method). (b) MCTDH propagation without dissipation for comparison.

6.2.6. H\(^0\) Dissociation from OH\(^\cdot\) Vibrational Excited States

In order to demonstrate the dissociation from a highly excited state using a static electric field, I have performed further propagation runs. A static electric field of \(E = 0.005\) au was used with the model dipole moment to bend the potential toward the dissociation direction. This field corresponds to a static electric field with \(E = 2.6 \times 10^9\) Vm\(^{-1}\) (see appendix G) or a low-frequency laser with a power of \(1.75 \times 10^{12}\) Wcm\(^{-2}\) (see section 6.2.2 about viability). These values are very high but higher bound vibrational states than \(\nu = 10\) which are closer to the dissociation energy are available for excitation, lowering the static field necessary to desorb hydrogen from the surface. I will however continue using the state \(\nu = 10\) as an example.

A dissociating wave packet will at some point run into the boundary of the simulation unit cell, leading to unwanted results, as shown in fig. 6.11a, where a dissociating part of the wave function has been reflected off the periodic image of the Morse potential barrier at the boundary causing ripples at the length of the grid spacing. These ripples are seen across the whole wave function due to the non-local kinetic energy operator, impacting not only the dissociating part but also the part that is still bound via the non-local kinetic energy operator.

In order to overcome this problem, I have added the standard Complex Absorbing Potential (CAP) method\(^{205,206}\) to the propagation code. This method consists of adding a negative imaginary part \(V_{\text{CAP}}\) to the potential which is nonzero only at the boundary. It acts in a similar fashion to the relaxation method (section E.1.3), damping the wave function at the boundary via the action of the propagation operator

\[
e^{-i\int V_{\text{CAP}}(x)dt} = e^{-\frac{|V_{\text{CAP}}(x)|}{1}}
\]

thereby preventing reflections from the boundary.

The absorbing imaginary part of the potential is presented in fig. 6.11b. The thin red line shows the original potential without a static field. The resulting potential after a static field is switched on (bold line) is shifted up to match the bound region of the original potential for easy comparison, and the complex absorbing potential \(V_{\text{CAP}}\) is shown as a crossed line. Note that the CAP is zero in the region around the potential minimum and analytic, so that it does not disturb the dynamics of the bound part of the wave function.

Fig. 6.12 shows snapshots of the dynamics using a CAP on a propagation from the eigenstate \(\nu = 10\) with a constant electric field of \(E = 0.005\) au. Fig. 6.12 demonstrates how a wave packet leaves the bound region, leaving a state with fewer nodes than the initial \(\nu = 10\) state behind (sub-figures a – d) and how the desorbed wave packet gets absorbed by the CAP (sub-figures e – f). The norm of the remaining wave function is a measure of how much of the initial system desorbs from the surface (and was absorbed by the CAP).

Quantum Control of HCl on MgO(001)

6.2.7. Estimate of the Desorption Yield Lowering due to Dissipation

As seen in section 6.2.5 above, dissipation diminishes the excitation yield expected from a dissipation-free propagation with the optimal control field of 65% to 49% with dissipation turned on. This is a lowering due to dissipation by 50%.

As the desorption process under the influence of a static field only takes about 60 fs, i.e. adds only a marginal amount of reaction time to the 870 fs needed to populate the \( \nu = 10 \) vibrational state, the total time needed for the desorption reaction should be less than 1 ps.

A conservative estimate of the lowering of desorption yield due to dissipation would therefore be between 50% and 75%. According to the result of the previous section, where a desorption yield of 20% is predicted without taking dissipation into account, the desorption yield with dissipation should be between 5% and 10%.

Fig. 6.13a shows the time dependence of this norm, alongside with the eigenstate populations in sub-figure (b). It can be seen that about 25% of the wave function dissociates, meaning that 25% of the irradiated hydrogen atoms desorb from the MgO surface. The population of the state \( \nu = 10 \) decreases rapidly and later the populations of the eigenstates of the unperturbed potential oscillate. It may be noted that lower eigenstates with \( \nu < 5 \) remain almost unpopulated.

The same process can be performed starting from the state produced by the optimal field in fig. 6.7m, which only partly yields the 10th eigenstate. Fig. 6.14 shows the corresponding wave functions. Fig. 6.15a shows the wave function norm. In this case, about 20% of the irradiated species are predicted to desorb. The populations behave similar to the earlier case except that the lower states are more populated.

6.2.8. Proposed Experiment

Experimentally, the proposed excitation laser pulse (fig. 6.8) could be realised by sending the pulse through a frequency doubling material and then through a chirping material. Mirrors and gratings may be used to split the pulse and different running lengths may be used to control the relative timing of the parts. The relative timing of different lasers can also be controlled to some extent by pumping them with the same primitive laser pulse. These techniques offer an experimentally viable way to construct the pulse needed for the selective excitation of a high vibrational state of OH\(^-\) at the MgO(001) surface. Note the dissipation lifetime used in the simulation presented here is based on the classical simulation (in chapter 5). This means that the real dissipation lifetime is likely to be longer as some dissipation channels may be closed due to quantum-mechanical selection rules. This means that the population of the desired vibrational target state will not be diminished as greatly as predicted by the calculations presented here.

A low-frequency pulse can be used to eject atomic hydrogen from the excited molecules. Far infrared pulses with frequencies of a few terahertz (e.g. 3.4 THz) have been reported.\(^{197,198}\) Their periods are of the order of hundreds of femtoseconds, so these pulses may be used as a quasi-static field to drive the desorption process.

In the long term, dissipation causes the vibrational state of all excited OH\(^-\) molecules to relax towards the ground state.\(^*\) It can be safely assumed that after one nanosecond the ground state is reached to a very high accuracy.

This means that the cycle consisting of vibrational excitation and subsequent desorption can be performed in quick succession, as dissipation swiftly leads the ground state of the system.

Most importantly, the desorption process can be done with the same laser field every time. Many subsequent applications of the desorption process can be used to clean the surface of OH\(^-\) molecules. For example, using a conservative estimate of only 5% desorption yield for the process proposed, ninety applications of the desorption reaction are needed to clean the surface of 99% of the OH\(^-\) molecules formed due to adsorption of HCl.

The desorption process could be observed directly by capturing the desorbed hydrogen atoms or, maybe more easily, by the quenching of the characteristic OH line from the surface’s vibrational spectrum.

OH\(^-\) molecules are often present at freshly cleaved MgO surfaces when these are cleaved in air due to water vapour in the atmosphere. As chlorine is only a spectator in all dynamical processes of OH\(^-\) in the system with adsorbed HCl, the hydrogen desorption reaction proposed here should also work in this case. After all, the chlorine ion associated electrostatically to the proton adsorption site would

\(^*\) “Long term” here means several tens of picoseconds.

Figure 6.14.: CAP dynamics starting from the state produced by the optimal pulse in fig. 6.7m. (a) initial state and state after (b) 14.5 fs, (c) 29 fs, (d) 43.5 fs, (e) 58 fs and (f) 72.6 fs.

Figure 6.15.: CAP propagation results, starting from state produced by interaction with optimal field from fig. 6.7m as initial state. (a) Wave function norm, (b) eigenstate populations.
merely be replaced by \( \text{OH}^- \) which should behave very similarly. The associated \( \text{OH}^- \) is even more similar to a free \( \text{OH}^- \) ion, so that dissipation would have even less of an adverse effect on it.

This would offer an effective method of preparing clean MgO surfaces for experimental application. Annealing subsequent to the cleaning from hydrogen would then produce very clean, ordered surfaces without the necessity to cleave in vacuum, which is very inconvenient.

### 6.3. Conclusion

I have demonstrated a feasible reaction scenario, the desorption of atomic hydrogen from an \( \text{OH}^- \) molecule formed at the MgO(001) surface via a high vibrational excitation (demonstrated with \( \nu = 10 \)).

Ab initio calculations were used as the basis for the parameters of the physical system in question. I have introduced the swept penalty parameter extension to optimal control theory to calculate an optimal laser field which effects the desired vibrational excitation in a dissipation-free environment.

Unlike other methods, the optimal control method allows to impose the constraint of setting the reaction time to only 870 fs, so that the effect of dissipation on the efficiency of the process can be minimised a priori. Under this constraint, it turns out that the optimal field does not only contain frequencies corresponding to single excitations but also, to a lesser extent, to double excitations. This seems to increase the yield beyond what is achievable within this constrained time interval by exclusive use of single excitations.

The optimal pulse consists of a linearly chirped sine wave plus a small admixture with roughly doubled frequency (i.e. with double the chirp rate) and corresponding to the double excitations. This can be realised experimentally with today’s laser technology.

A remarkable feature of this reaction is that the anharmonicities in the electrical dipole moment and the potential lead to increased yields of high vibrationally excited states due to double excitations.

The method presented to generate an excited state is general, i.e. any intermediate or higher state \( \nu \) might have been chosen. The swept parameter method allows to readily achieve the desired compromise between high yield and low laser power for experimental viability.

I have applied a quantum-mechanical model dissipation operator based on the vibrational lifetime extracted in chapter 42 to the process proposed by optimal control theory. I have shown that dissipation does not quench the desired product entirely. 50% of the desired excitation survives the adverse effects of dissipation.

Taking dissipation into account, I have also demonstrated the subsequent desorp-
Chapter 7. Quantum Control of the STE Separation in Alkali Halides

Aims: After having completed the process necessary to predict quantum control at a crystal surface, the next step is to look for a system inside a crystal on which quantum control can be applied. One of the best-studied such systems is the self-trapped exciton (STE) in alkali halides.

Rather than deriving the system’s chemical properties myself, as I have done for the HCl molecule on the MgO surface, I will use existing theoretical and experimental results for the STE in NaCl. From these, I parameterise a model potential. I will concentrate on the nuclear quantum dynamics in this model. A photoinduced reaction is sought that separates the STE into a pair of point defects (F-H centre pair).

Methods: Grid-based wave function propagation techniques (section 6.1.2).

Results: A purely vibrational excitation scheme is excluded due to the difficulty of finding a resonant excitation for the double minimum potential. A control scheme based on purely vibrational excitation would also have a time scale that invites dissipative quenching of the process. However, the electronically excited state of the STE can be used to take the wave packet to a dissociative flank of the potential, thereby separating the STE into the F-H centre pair.

A double-pump, double-dump pulse scheme is proposed to attain a satisfactory yield of separated defect pairs. A pump-dump time delay minimising the population of the barrier area in the two-dimensional potential is proposed to avoid quenching of the process due to non-radiative coupling.

7.1. Introduction

Having described the results of nuclear quantum dynamics simulations for a system at a surface (the HCl molecule adsorbed on the MgO(001) surface) in chapter 6, this chapter will deal with nuclear quantum dynamics of a defect inside a crystal.
Figure 7.1.: Stable configurations of the triplet excited state of NaCl. Upper panel: Ground state geometry of the crystal. The charge of the excited electron (illustrated by the dashed line encompassing the unit cell) is delocalised over all anions. If anion 1 moves towards anion 2 and the electron localises near the vacancy a self-trapped exciton (STE) can form, shown in the middle panel. The anion pair 1-2 has donated an electron charge to the vacancy, and hence is regarded as a hole, which is illustrated by the colouring of the anion pair. The visible $p$ orbitals in the spin density plot on the right demonstrate the bond formation between the halide ions 1 and 2. As a next step, the pair 1-2 may approach anion 3, so that it gets polarised. Then anion 2 carries most of the hole, (this is a barrier configuration and not shown). The halide 2 is now atomic, and when it moves further to anion 3 it binds to it, as shown in the lower panel. Again, the spin density demonstrates the newly formed bond. Anion 1 remains at the former lattice position of anion 2. This process can in principle continue with the pair 2-3 approaching anion 4 and so on. This way the $X_2^-$ di-haloid (H-centre) ion can successively separate from the electron in the vacancy (F-centre), forming an F-H centre pair of point defects. The hole separation from the vacancy can thus be regarded as reaction coordinate.

In this geometry, the lattice sites carry the same charges as in the ground state, as an electron is localised at the anion vacancy and the $X_2^-$ di-haloid is situated at an anion site, carrying a single negative charge. However, the spin density shows a clear contrast to the ground state and therefore I will keep using the label hole for the di-haloid.

According to experimental results and theoretical predictions, the potential energy dependence on the distance between the hole and the vacancy in most alkali halides should qualitatively resemble the sketch in fig. 7.1. This figure also contains the cartoons corresponding to the STE and the separated F-H centre pair state to indicate the geometry at the potential minima. There is theoretical evidence for an excited state of the exciton (top line in fig. 7.2) which has its minimum at the minimum of the ground state and is shown as the top potential line in fig. 7.2.

A model will be described in the following that is meant to describe the STE potential in a generic alkali halide. This model potential will be used to obtain a proof-of-principle and demonstrate a mechanism for coherent control of the STE separation. It is in no way meant to simulate the dynamics in a particular alkali halide crystal, although the mass and distance relations will be based on NaCl.

Figure 7.2.: Sketch of the electronic states in alkali halides. $a =$ lattice constant. The abscissa is the hole displacement from the vacancy. Shown are the electronic ground state of the crystal, its excited state with the STE and separated F-H centre pair and, above that, the electronically excited state of the STE. See text for details. The first occurrence of a sketch of this type can be found in Shluger and Tanimura. Reproduced with permission.
7.1.1. Reaction Coordinates

Fig. 7.3 shows some vibrational modes of the di-haloid that are important for the STE separation. As indicated above, the main reaction coordinate is the distance between the F-centre and H-centre. Rather than jumping from one anion to the next (as I have shown in the discussion of Fig. 7.1), the distance between the vacancy and the centre of mass of the hole can be used as the coordinate. This changes smoothly during the separation process, as the polarisation of the di-haloid changes according to its distance from a neighbouring anion.

I will call this the x coordinate in the following, which is illustrated in Fig. 7.3a. The x coordinate alone can be used for a first approximate study of the STE dissociation process.

Besides this, the stretching mode of the di-haloid ion (or y coordinate, Fig. 7.3b) and the three-dimensional rotation of the di-haloid ion (Fig. 7.3c) can play a role in the considered reaction. The reaction may then proceed along a minimum energy line in the PES spanned by these coordinates.

According to Puchin et al., the rotation plays an important role in the H-centre diffusion in NaCl. In other crystals, such as KBr, it appears to play a lesser role. However, as this part of my project is meant as a first study of the STE dissociation in a generic alkali halide, this distinction and the rotational mode is omitted from further considerations in order to avoid overcomplicating the task in hand. The x and y coordinates will appear in dynamical simulations reported below.

7.1.2. Model Dipole Moment

An important condition for the direct vibrational response of the system to infrared laser radiation is the coordinate-dependence of the dipole moment. Although experimental evidence has to be employed in constructing the model potential, ab initio results can be used to fit a model dipole moment.

The data points of this calculation of the dipole moment dependence on the di-haloid position are shown in Fig. 7.4. For dynamics, this result needs to be parameterised as a fit to a smooth function. I used the function

\[ \mu(x) = A_y \cdot (x - x_y) \cdot e^{-\frac{x-x_y}{r_y}}. \]  

(7.1)

7.1.3. Reaction Scenario

A sketch of the potential energy dependence on the distance between the hole and the vacancy was already shown in Fig. 7.2. On the basis of this sketch, two possible scenarios of coherent control of the separation of the STE into the F-H-pair can be proposed:

1. On the STE electronic state, purely vibrational excitation using IR pulses (Fig. 7.5a) and
2. via excitation to the electronically excited state of the STE (Fig. 7.5b). Instead of dissociating immediately, the excited (step 1) wave-packet is accelerated in the opposite direction (step 2) and consequently dumped on the dissociative flank of the STE potential (step 3). From there the system can then dissociate freely (step 4).

If the system has enough momentum when it reaches the right-hand potential minimum, it can travel to potential minima further away from the STE minimum in some alkali halides. At large enough distances, recombination is then no longer ruled by the attraction between F-centre and H-centre but becomes subject to a random meeting of the two due to diffusion. The lifetime of the F-H centre pair is
then greatly increased. The feasibility of this process will be demonstrated by the preparation of a transient state with non-zero momentum at the right-hand potential minimum.

### 7.1.4. Model PESs

A considerable part of the work presented in this chapter has been to find an analytic expression mimicking the known properties of the STE potential energy surface and to explore the dynamics on this surface in order to become able to propose heuristically a reaction scheme that was later demonstrated in the simulation. For the purpose of constructing a one-dimensional model potential along the x coordinate, the following assumptions were used:

1. The depths of the minima at the STE minimum and the F-H centre pair are 0.20 eV and 0.18 eV, respectively.
2. The distance between the minima is about one lattice diagonal, i.e. 2.94 Å.
3. The barrier height is 0.1 eV above the STE minimum.

To extend the model to two dimensions, the following considerations are made: The barrier configuration between the STE (fig. 7.1, middle panel) and the next-nearest neighbour F-H centre pair (fig. 7.1, lower panel), is at a configuration where anion 2 has equal distances to its neighbour halide ions, 1 and 3. Any break of the symmetry where two of the ions pair up, leaving the other one at a larger distance, lowers the energy.

This means that, although the potential has single minima along the y coordinate at the x coordinates corresponding to the STE and the F-H centre pair, it has a double well structure in y direction at the barrier between these. Hence the following assumptions are used to extend the model to two dimensions:

A. The minima in x direction are also minima in y direction.
B. The barrier in x direction is also a barrier for the double-minimum potential in y direction.
C. At the barrier in x direction, the y coordinate wells are one sixth lattice diagonal away from the barrier between them.
D. The minima in y direction at the barrier in x direction are about 0.1 eV below the barrier energy.

**Figure 7.5.** Ideas proposed to control the separation of the STE into a separated F-H centre pair. (a) By vibrational excitation. (1.) Excitation in STE well, (2.) transition between the wells, (3.) cooling in separated F-H centre pair well. Note that step (2.) requires resonance of the laser field with the motion between the two far barriers of the potential. The right-hand barrier, however, is only present in the model and is physically replaced by a succession of wells. (b) By electronic excitation. (1.) Excitation ("pump pulse") into the excited state of the STE, (2.) free motion in the excited state, (3.) de-excitation ("dump pulse") into the STE electronic state, (4.) free motion from flank of the left-hand barrier towards the separated F-H centre pair state.

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Table 7.1: Parameters used for the 1D STE model potential, equation (7.2).

<table>
<thead>
<tr>
<th>i</th>
<th>$C_1$</th>
<th>$\mu_1$</th>
<th>$\sigma_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20 eV</td>
<td>0.00 Å</td>
<td>0.75 Å</td>
</tr>
<tr>
<td>2</td>
<td>0.18 eV</td>
<td>2.94 Å</td>
<td>1.0 Å</td>
</tr>
</tbody>
</table>

Figure 7.6: 1D model potential for the STE. The left well is the STE minimum; the right-hand one is the minimum of the separated F-H centre pair.

7.1.4.1. One-Dimensional Model Potential

I have modelled the potential energy surface (PES) of the exciton along the x coordinate over the range from the STE to the F-H centre pair by the sum of two Gaussian functions with negative coefficients,

$$U_1(x) = C_1 \cdot e^{-\frac{1}{2} \left( \frac{x - \mu_1}{\sigma_1} \right)^2} + C_2 \cdot e^{-\frac{1}{2} \left( \frac{x - \mu_2}{\sigma_2} \right)^2}. \quad (7.2)$$

When this model is subjected to the assumptions 7.1.4.1-3, the parameters shown in Table 7.1 result. A graph of the resulting potential energy curve is shown in Fig. 7.6. This model contains only the two minima, $x_{m1}$ at the STE and $x_{m2}$ at the F-H centre pair. The minimum corresponding to the free exciton MX* is not taken into account, i.e. the formation of the STE is assumed to be completed at the start of the dynamics simulation.

I have chosen the widths $\sigma_j$ of the Gaussians forming the potential such that $x_{m1} \approx \mu_1$ and $x_{m2} \approx \mu_2$ and a local maximum at $x_M = 1.4$ Å, $U_1(x_M) = -0.09$ eV results. For $x \to \pm \infty$, the model potential goes to zero asymptotically.

7.1.4.2. Extension of the Model Potential to Two Dimensions

The one-dimensional model potential is extended to two dimensions by using a double Gaussian potential in y-direction such that the one-dimensional model potential is reproduced and the PES topology as given by the conditions 7.1.4 A-D is preserved. Fig. 7.7 shows an image of the resulting model potential.

A detailed derivation of the two-dimensional potential and further discussion of the assumptions it is based on can be found in appendix F.

Figure 7.7: Two-dimensional model potential for the STE built up of a set of double Gaussian potentials in y direction that reproduce the one-dimensional double Gaussian model potential along the x coordinate. Note the change of character of the y-coordinate potential depending on the x-coordinate.

7.1.4.3. Model Potential for the Electronically Excited State

Embedded cluster calculations and experimental work\cite{Markmann2004} suggest that a bound excited state with a minimum at the equilibrium geometry of KBr exists. I put the crystal equilibrium geometry at the reasonable estimate of $x = 0$, $y = 0$ relative to the minimum of the STE potential (see Fig. 7.2 for an illustration of how the potentials are related). As minimum energy for the harmonic model potential I used 1.2 eV, which results in an STE excitation energy of 1.5 eV which is in the range reported in experimental results.”\cite{Markmann2004}

Theoretical results\cite{Markmann2004} predict the excited state energy at the STE geometry to be about 0.1 eV higher than at the equilibrium geometry. I use a harmonic potential, hence this energy change corresponds to a spring constant of $k_y = 0.71$ eV Å$^{-2}$. For the y coordinate, I used a harmonic potential with a spring constant corresponding to that of the STE state at the minimum, $k_y = 0.76$ eV Å$^{-2}$. This assumption makes use of the fact that the Gaussian potential for the STE is almost harmonic near the minimum. The excited state potential surface will then preserve the shape in y direction of an STE vibrational ground state wave function that is electronically excited.

7.2. Results of Wave-Packet Propagation Simulations

Definitive statements about the coherence time for the STE separation dynamics cannot be made at this time, as a classical dynamics simulation analogous to that presented in chapter 5 for the HCl molecule at the MgO(001) surface is complicated

by the continuous charge transfer processes involved. However, the separation of the STE is observed experimentally so that, while dissipation may affect the quantitative yield of the coherent dynamical processes proposed in this chapter, it should not affect the qualitative outcome.

A mechanism for control will be proposed based on wave-packet dynamics simulations without taking vibrational energy dissipation into account. Due to the effects of dissipation, such an approach is more likely to yield realistic predictions at shorter time scales, as discussed in section 6.1.2.3.

It is instructive to characterise the one-dimensional model potential $U_1(x)$ by calculating its eigenstates. Fig. 7.8 shows the energy levels of the 20 lowest eigenstates of $U_1(x)$, eq. (7.2).

It can be seen that the lowest 20 eigenstates of the one-dimensional model potential $U_1(x)$ are each localised in one of the two potential wells. Their energy levels are, due to the anharmonic nature of the potential, not equidistant. Only near the minimum the quanta are approximately equally spaced because there the Gaussian potential is a very good approximation to a harmonic potential. Table 7.2 shows the lowest vibrational transition energies and periods in the two minima of the model STE and separated F-H centre pair wells of the potential.

The lowest (and largest) quantum in the left well is 4 meV, i.e. at room temperature (300 K $\approx$ 13 meV) only a few eigenstates are accessible. This means that the higher states, to which F-H centre pair separation by tunnelling through the barrier is available, are populated very little at room temperature which explains why spontaneous F-H centre pair separation only has relatively low yields (depending on the material).

Fig. 7.8 also shows the lowest non-localised vibrational state, $\nu = 64$, $\Delta E = 108$ meV, and the highest vibrational eigenstate calculated ($\nu = 100$, $\Delta E = 240$ meV).

### 7.2.1. F-H Centre Pair Separation by Vibrational Excitation

As a first step, I explored the purely vibrational transition scheme devised for the one-dimensional one-state model (fig. 7.5a). Time is plotted along the ordinate. The laser field used has a Gaussian envelope. Its parameters are shown in table 7.3. The coordinate dependence of the vibrational dipole moment operator from section 7.1.2 was used (see section 6.1.1.4 eq. (6.12) and section 7.1, eq. (7.1)). Fig. 7.9 shows the result of a simulated vibrational excitation of the STE with an infrared pulse.

The laser field is indicated at the left border of the diagram. The wave function snapshots are shown at a height corresponding to the time at which the snapshot was taken.

The initial wave function (the vibrational ground state) starts oscillating synchronously with the electric field in the STE potential well. As the wave function crosses the potential barrier between 22 and 24 ps, the total energy and the coordinate expectation values increase abruptly. This means that, rather than resulting in a globally bound wave function that has slightly higher energy than the barrier and is thus able to cross it, the electric field produces a free wave state (with energy above zero) that fills the whole simulation region. This can be seen by looking at the topmost snapshots of the wave function.

This demonstrates how difficult it is to purely by vibrational means generate a state that is energetically between the barrier and the vacuum level.

It may be noted by inspecting fig. 7.9 that the barrier energy is crossed just as the laser reaches its maximum. However, using a shorter field with smaller intensity at this time, the wave function never reaches the barrier energy and remains trapped.
7.2.2. F-H Centre Pair Separation by Electronic Excitation

The electronic excitation scheme for separating the F-H centre pair I would like to suggest is the pump-dump scheme illustrated in fig. 7.5b. This reaction will not, as is often done, rely on the presence of a dissociative excited state, so that the wave packet could be excited and, after some evolution in the excited state, just dumped in the lower electronic surface minimum one would like to reach.

Instead, the excited state is bound and the geometry change in the excited state is away from the one I would like to achieve (the right-hand minimum on the STE electronic surface in fig. 7.6 which corresponds to separated F-H centre pair). However, a dump pulse can drop the wave packet onto a dissociative flank of the STE potential surface, from which it can then pick up momentum to pass the potential barrier and subsequently reach the F-H centre pair well.

Reaction schemes involving electronic excitation will be presented based on both the one-dimensional model potential $U_1(x)$ and the two-dimensional one, $U(x, y)$. Calculations of the eigenstates of the two-dimensional model potential $U(x, y)$ are computationally far more demanding than for the one-dimensional model potential $U_1(x)$. I have therefore calculated only the first ten two-dimensional eigenstates; their appearance is more or less that of products of eigenstates of the $x$ and $y$ coordinates. However, of the lowest eigenstates only the vibrational ground state is relevant for the proposed dynamics, as it is used as initial state. It will be seen that motion along the $y$ coordinate only becomes relevant as the wave packet approaches the barrier. I will therefore not present the two-dimensional eigenstates in detail.

### 7.2.2.1. Electronic Excitation Simulated with the Surface Hopping Method

The simplest model for electronic excitation is the surface hopping method. According to this, the entire wave function is translated by a sudden excitation to a different electronic state.

The vibrational ground state wave function of the STE when displaced to the vibrational minimum of the electronically excited state.

Due to these problems, the vibrationally resonant process considered here has to be several ten ps long due to the about one picosecond vibrational period of the STE (see table 7.2). This is a time scale at which dissipation (which has been neglected here) becomes non-negligible (as was demonstrated by the considerable falloff of the yield due to dissipation in chapter 6, where the process proposed is shorter than 1 ps). This means that a process proposed from a wave packet propagation simulation of a purely vibrational infrared excitation is not realistic.

Due to these problems, I have decided to abandon the attempt to separate the F and H centres vibrationally and pursue a much more promising path, the separation by electronic excitation.

Remembering the discussion in section 6.1.1, it may be realised that the resonance argument used to greatly simplify the model Hamiltonian for the OH$^-$ molecule at the MgO(001) surface does not hold for the STE. As the vibrational frequencies of the STE are not untypical of the bulk crystal, it is quite likely that a frequency-swept laser pulse will be resonant with a larger number of normal modes, either directly or via multi-photon processes. The model for the vibrational response of the STE to infrared radiation used here that relies on specific excitation of the STE is therefore questionable at best.

Adding to these problems, the vibrationally resonant process considered here has to be several ten ps long due to the about one picosecond vibrational period of the STE (see table 7.2). This is a time scale at which dissipation (which has been neglected here) becomes non-negligible (as was demonstrated by the considerable falloff of the yield due to dissipation in chapter 6, where the process proposed is shorter than 1 ps). This means that a process proposed from a wave packet propagation simulation of a purely vibrational infrared excitation is not realistic.

Due to these problems, I have decided to abandon the attempt to separate the F and H centres vibrationally and pursue a much more promising path, the separation by electronic excitation.

Figure 7.9.: Vibrational excitation of the STE with an infrared pulse. Time is plotted along the y axis. Snapshots of the wave function are shown at the height corresponding to the time at which the snapshot was taken. The potential scaled to fit into the diagram is shown at the bottom to put the wave functions into perspective.

Due to the large mass of the system, the vibrational period is of the order of one picosecond so that a resonant process has to be several ten ps long, a timescale at which dissipation (which has been neglected here) becomes non-negligible. Note how the total energy and the coordinate expectation values jump abruptly as the wave function crosses the potential barrier between 22 and 24 ps. The result is a free wave state (with energy above zero) that fills the whole simulation region.

### 7.2.2.2. F-H Centre Pair Separation by Electronic Excitation

The electronic excitation scheme for separating the F-H centre pair I would like to suggest is the pump-dump scheme illustrated in fig. 7.5b. This reaction will not, as is often done, rely on the presence of a dissociative excited state, so that the wave packet could be excited and, after some evolution in the excited state, just dumped in the lower electronic surface minimum one would like to reach.

Instead, the excited state is bound and the geometry change in the excited state is away from the one I would like to achieve (the right-hand minimum on the STE electronic surface in fig. 7.6 which corresponds to separated F-H centre pair). However, a dump pulse can drop the wave packet onto a dissociative flank of the STE potential surface, from which it can then pick up momentum to pass the potential barrier and subsequently reach the F-H centre pair well.

Reaction schemes involving electronic excitation will be presented based on both the one-dimensional model potential $U_1(x)$ and the two-dimensional one, $U(x, y)$. Calculations of the eigenstates of the two-dimensional model potential $U(x, y)$ are computationally far more demanding than for the one-dimensional model potential $U_1(x)$. I have therefore calculated only the first ten two-dimensional eigenstates; their appearance is more or less that of products of eigenstates of the $x$ and $y$ coordinates. However, of the lowest eigenstates only the vibrational ground state is relevant for the proposed dynamics, as it is used as initial state. It will be seen that motion along the $y$ coordinate only becomes relevant as the wave packet approaches the barrier. I will therefore not present the two-dimensional eigenstates in detail.

Due to these problems, I have decided to abandon the attempt to separate the F and H centres vibrationally and pursue a much more promising path, the separation by electronic excitation.
Figure 7.11: Population of target area and barrier area over propagation time for shifted wave packet simulation. The target area decreases at the end due to reflection at the barrier limiting the simulation area at the right (see fig. 7.10).

The wave packet travels around the local maximum in the middle of the model potential, thereby avoiding the point where the coupling to the electronic ground state is likely to be maximal. This means that in this process the non-radiative decay into the ground state would be smaller than for processes where the barrier area is populated strongly, increasing the yield of separated F-H centre pairs.

This statement can be quantified by considering the population of the area near the barrier. I define this area as the area where the potential energy is higher than half the difference between the barrier energy and the lowest energy at \( x = x_M \). Fig. 7.11 shows the evolution of this population along with the evolution of the population of the target area (i.e. the area to the right of the barrier). The target area population decreases at the end of the simulation due to reflection at the barrier limiting the simulation area on the right (see fig. 7.10). It can be seen that the barrier population remains below 10% throughout the simulation, while the population of the target area to the right of the barrier reaches more than 70%.

7.2.2.2. Electronic Excitation Simulated with a Field-Dependent Electronic Transition Operator

In contrast to the surface hopping approach above, a more accurate description of the electronic transition process is the first-order perturbation approach involving the operator

\[
\hat{X} = \varepsilon(t) \mu_{ij} (x, y) (|\psi_i\rangle \langle \psi_i| + |\psi_j\rangle \langle \psi_j|)
\]

in the Hamiltonian which mediates a transition between the electronic states \( \psi_i \) and \( \psi_j \) (here the STE and its electronically excited state), caused by irradiation with an electric field strength \( \varepsilon \) and an electronic transition dipole moment \( \mu_{ij} \).

The operator \( \hat{X} \) couples the populations of the STE electronic state and its electronically excited state. If no vibrational motion took place, a long-time resonant excitation process would tend to equalise the populations of the STE and its excited state, i.e. in the limit the electronically excited state of the STE would gain only 50%. Surface hopping of the full wave function between states as used above,
however, assumes a transfer of 100% of the state population.

Another factor that is not taken into account by the surface hopping method is the change in shape of the vibrational wave function due to electronic excitation. Such changes are affected by the slope of the electronically excited potential surface. If the laser pulse is long enough to make vibrational dynamics on the excited state surface relevant, the shape of the ground state wave function changes as well. This is due to stimulated emission, i.e. electronic de-excitation during the pulse.

For the purpose of the present excitation calculations, the Born-Oppenheimer approximation is invoked by neglecting the coordinate dependence of the electronic states. This means that the electronic dipole moment \( \mu_{ij} \) is assumed to be coordinate-independent. The value of \( \mu_{ij} \) is rolled into the electric field variable, i.e. \( \mu_{ij} = 1 \text{ au} \) is assumed and hence \( \varepsilon(t) = \varepsilon(t) \mu_{ij} = 1 \text{ au} \) corresponds to an amplitude of 27.2116 eV.

As a first step, I have performed simulations on a two-state, one-dimensional model system with a time step of 0.048 fs, which is short enough to capture the dynamics due to the interaction with the electric field (since the shortest vibrational period in the fields used is 2.75 fs, i.e. 57 time steps).

Using a single Gaussian pulse with an amplitude of \( 10^{-3} \text{ au} \approx 5.1 \times 10^8 \text{ Vm}^{-1} \), a temporal width of \( \sigma = 18 \text{ fs} \), an excitation frequency \( \omega = 1.5 \text{ eV} \) and a chirp of \( \Delta \omega = 0 \) results in a population of the excited state of \( \Delta n_1 = 26\% \). Considering that the second, de-excitation, pulse will further diminish this ratio and only some part of the dumped wave packet will be able to cross the barrier, this is not satisfactory for the purpose of separating the F and H centres.

### 7.2.2.3. Double-Pulse Excitation Scheme

One way to increase the population of the excited state after the excitation pulse is to change the pulse’s amplitude or duration. This option, however, is not always available experimentally. A qualitatively different approach is to continue using a given pulse and exploit the fact that the excited wave packet immediately starts moving towards the equilibrium geometry of that electronic state, while the remaining STE wave packet remains trapped in the STE state minimum. This means that after a short time the region at the STE minimum geometry becomes vacant in the excited state and hence a second excitation pulse with the same parameters will yield another considerable excitation, without suffering from stimulated emission.

Such a double-pulse excitation with a time delay of 24.2 fs yields an excited state population of \( \Delta n_1 = 53\% \), higher than the asymptotic ratio of 50% for a long-time pulse.

This technique can be generalised to multiple pump pulses applied in short successesion. The increase in yield due to the application of additional pulses is only limited by the tendency of the STE vibrational wave function to acquire kinetic energy and hence move out of resonance with the laser frequency. This effect can be accounted for by decreasing the laser frequency. In order to not over-complicate matters and maintain experimental viability, however, we will continue discussing an excitation scheme based on a double pulse.

Following up on the excitation (pump) pulse we have placed de-excitation (dump) pulses following the same double-pulse scheme. Each of the dump sub-pulses has the same amplitude and width as the pump sub-pulses. We set the frequency of the dump sub-pulses according to the nominal excitation energy at the expectation value of the excited state wave packet at the moment temporally between the de-excitation sub-pulses. In order to assure resonance of the dump sub-pulses with the dynamics, we employed a chirp of \( -6.9 \times 10^{-2} \text{ eVps}^{-1} \), which means a frequency change of \( \pm 1.2 \text{ meV} \) at a time difference of \( \sigma = 18 \text{ fs} \) (the temporal width) from the centre of each sub-pulse. The parameters of the laser pulse used are summarised in Table 7.4.

Note that, as projected in section 7.2.2.1 on the surface hopping method above, the dumped wave packet moves to the left for some time after de-excitation due to the momentum it has built up while in the excited state. This means that after the first dump sub-pulse, the dumped ground state wave packet vacates the area it was dumped into so that, as in the pumping process, the second dump sub-pulse affects an appreciable increase in the dump yield ratio \( \Delta n_2 \).

<table>
<thead>
<tr>
<th>pump pulse</th>
<th>dump pulse</th>
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</thead>
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<tr>
<td>amplitude [a.u.</td>
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</tr>
<tr>
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</tr>
<tr>
<td>frequency [eV]</td>
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</tr>
<tr>
<td>chirp ( \Delta \omega [\text{eVps}^{-1}] )</td>
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</tr>
<tr>
<td>intra-pulse delay [fs]</td>
<td>24.2</td>
</tr>
</tbody>
</table>

Table 7.4.: Parameters of laser double pulses proposed for the control of STE separation via electronic excitation.

| 1D pump yield | \( \Delta n_1 \) [%] | 53.4 |
| 1D dump yield | \( \Delta n_2 \) [%] | 69.1 |
| 1D total dumped | \( \Delta n_1 \cdot \Delta n_2 \) [%] | 34.6 |
| 1D target hitrate after 1.74 ps | [%] | 35.4 |
| 2D pump yield | \( \Delta n_1 \) [%] | 48.1 |
| 2D dump yield | \( \Delta n_2 \) [%] | 83.5 |
| 2D total dumped | \( \Delta n_1 \cdot \Delta n_2 \) [%] | 40.2 |
| 2D target hitrate after 1.74 ps | [%] | 27.8 |

Table 7.5.: Parameters of the dump pulses used for the simulation of different pump-dump scenarios for the separation of the STE in KBr and dump and target yields for simulation runs in the one- and two-dimensional two-state model systems.
Table 7.5 lists the time delays and frequencies of the dump pulses used along with some results. The pump yield $\Delta n_1$ is the percentage of the STE electronic state wave function that is placed on the electronically excited state by the pump pulse. The dump yield $\Delta n_2$ is the percentage of the electronically excited state wave function that is put back on the STE electronic state by the dump pulse. The product $\Delta n_1 \cdot \Delta n_2$ is the percentage of the STE electronic state wave function that has been placed back after having been excited. The target hit rate is the percentage of the ground state wave function that has crossed the ground state barrier separating the STE from the separated F-H centre pair after a propagation time of 1.74 ps.

Fig. 7.12 shows snapshots of the wave packet evolution for the different runs. All figures demonstrate how the de-excited wave packet travels through the STE ground state wave packet that was left behind after the excitation, causing clearly visible interference patterns. It can be seen in the upper two panels, fig. 7.12a and (b) that the dumped wave packet travels quite far to the left before turning around and moving into the direction of the barrier.

This is the region where the free exciton is found on the STE electronic state, about 0.6 Å to the left of the STE well. See fig. 7.2 for an impression of its position (marked MX*) relative to the STE well. It has to be taken into account although it is not represented in the model potential. A part of the wave packet can remain in the well corresponding to the free exciton, decreasing the predicted yield of separated F-H centre pairs with respect to the values quoted in table 7.5. To avoid this, one would like to use shorter pulse delays that yield a dumped wave packet that does not travel so far to the left.

There are pathways in the two-dimensional potential that are energetically lower than the barrier in the one-dimensional potential, since a distortion of the $X_2^-$ molecule lowers the energy around the barrier. This has been seen already in fig. 7.10, where the evolution of the shifted ground state wave packet proceeded around the barrier. This allows to use short pulse delays that do not yield a barrier crossing in the one-dimensional model.

The purpose of performing the simulations with smaller pump-dump delays that did not yield large amounts of F-H separates pairs in the one-dimensional model (shown in fig. 7.12c and d and in the rightmost columns of table 7.5) has been to find delays at which the energy of the dumped wave packet is just below the barrier of the one-dimensional model potential. I have subsequently used these pulses to simulate pump-dump dynamics on the two-dimensional model potential that do not cross the barrier directly but circumvent it, yielding STE dissociation without touching the free exciton minimum.

The numerical results of the two-dimensional simulations with pulses of delay 205.6 fs, 157.2 fs and 133.0 fs are listed in the lower half of table 7.5. Fig. 7.13 shows the populations of the target area and the barrier area from the two-dimensional pump-dump simulation runs.

It can be seen that, while the barrier area populations of the pump-dump processes with the two longer delay times peak at around 0.05, that of the process with the shortest delay of 133 fs peaks at only 0.02. This means that non-radiative decay of the STE is less likely to occur.

Figs. 7.14, 7.15 and 7.16 show snapshots of the two-dimensional wave function for a pump-dump delay of 205.6 fs, 157.2 fs and 133.0 fs, respectively.

As before, it can be seen that for the longer two of the three time delays the dumped wave packet extends very far to the left of the simulation area, into the range where the presently ignored free exciton is situated. The smallest delay of 133 fs, however, yields a well-contained dumped wave packet. In all cases, it can be seen that the pathway around the barrier is the preferred one. However, the shortest
7.3. Conclusion

In this chapter, I have demonstrated the simulation of a proposed photoinduced reaction scheme for the separation of the self-trapped exciton (STE) into a pair of F- and H-centres with quantum nuclear dynamics techniques. As a first step for the simulation of the dynamics of the STE separation in an alkali halide, the most relevant vibrational modes taking part in this reaction were selected. They are the hole separation from the vacancy and the di-haloid stretching and are labelled x and y coordinate, respectively, in this chapter. Angular vibrational modes of the di-haloid may play a role in the STE separation dynamics but were not taken into account in this first study.

To achieve my goal, I have parameterised one- and two-dimensional model potential energy surfaces (PESs) based on theoretical and experimental evidence and considered a purely vibrational reaction scheme as well as one involving electronic excitation.

After ruling out the purely vibrational scheme because of its long time scale and consequent vibrational energy dissipation that is to be expected, I have devised a pump-dump laser excitation scheme involving electronic excitation that mediates the separation process.

The excitation yield can be increased considerably by using two pump and dump sub-pulses. This makes use of the immediate onset of vibrational motion of the wave packet after electronic excitation and the inertial motion after de-excitation. Both effects cause the Frank-Condon area to be vacated between the sub-pulses. Thus, the proposed scheme exploits the shapes of the PESs as well as the interplay between the timing of the sub-pulses and the vibrational motion of the system. The dynamics in the electronically excited state do not exhibit strong quantum effects such as widening or splitting of the wave packet, so that these do not adversely affect the outcome of the reaction.

It turns out that there is an optimal time delay between the pump and dump double-pulses that maximises the yield of separated F-H centre pairs. Shorter time delays effect decreased yields due to an insufficient potential energy of the dumped wave packet, while longer delays may cause trapping in the free exciton potential minimum and increased non-radiative crossing into the electronic ground state. Neither of these effects was taken into account explicitly but their importance can be gauged from the time-dependent probabilities of residence in the free exciton and barrier areas (where the crossing with the ground state is expected).

A pump-dump scheme with a delay of 133 fs, where each of the pulses consists of two sub-pulses with a width of 18 fs with an intra-pulse delay of 24.2 fs is predicted to yield 14% separated F-H centre pairs out of all present STEs by the simulation in the two-dimensional model potential.

The model used does not take into account vibrational dissipation. However, the proposed reaction is at 133 fs + 2 × 24 fs + 2 × 18 fs ≈ 0.22 ps very short compared to typical dissipation lifetimes (compare also with the reaction proposed in chapter 6, which is 0.87 ps long and whose yield is halved by dissipation). The proposed reaction can therefore be expected to survive the adverse effects of dissipation.

As was already proposed for the reaction proposed in chapter 6, the yield can be increased by repeatedly irradiating the same spot in the crystal. The proposed scheme can is readily updated according to new insights into the shape of the PESs, since it is based on the simple vertical excitation energies between the states and the motion of the wave function in the excited state.

Chapter 8. Conclusion of Thesis

I have considered theoretically the possibility of coherent control in reactive centres that are in direct contact with a crystal lattice. This has been a forward-looking project, as experimental work in this field currently does not exist. In fact, it is one of the aims of this project to inspire such experimental work.

Before coherent control reactions can be simulated, materials have to be identified that allow such processes to proceed. I have formulated criteria to be met by physical systems that are candidates for coherent control processes in the introductory chapter and selected example systems accordingly.

I have demonstrated quantum control processes theoretically on the example reactions

1. desorption of hydrogen from a hydroxyl ion formed due to HCl adsorption at the MgO(001) surface and
2. dissociation of the Self-Trapped Exciton (STE) in alkali halides into a pair of point defects (F-H centre pair).

In chapters 3 to 6 I have presented a complete self-contained theoretical study of the coherent control reaction (1), involving DFT calculations and classical and quantum dynamics simulations.

During the course of this project, I have developed a simple criterion for the spatial localisation of normal modes, a molecular dynamics initialisation scheme allowing dissipation dynamics at non-zero temperature and an extension of the optimal control method that greatly enhances its usability. All of these techniques are applicable to a large class of theoretical problems.

A comparative study of surface-localised phonon modes in three crystals was presented in chapter 3. I concluded that the order of the crystals with increasing localisation of surface modes is CaF₂, MgO, KBr. This chapter also contains the to my knowledge first study of normal modes localised at surface steps. For MgO and KBr, step modes were found that appear to be capable of funnelling vibrational energy to the step and transport it along the step. Finally, vibrational modes localised at the corners of a large finite cube of MgO were identified that may play an important role in the dissipation of adsorbate modes of the appropriate frequency.

The ab initio results presented in chapter 4 for the adsorption behaviour of HCl to the MgO(001) surface predict dissociative adsorption with chemisorption of the proton to a surface oxygen at low coverage. This is the first time that a previous study by Chacon-Taylor and McCarthy\textsuperscript{77} has been contradicted. Simulating different coverages, I have demonstrated that the qualitatively different prediction of the previous study is due to the high coverage simulated there. I have also demonstrated that at room temperature the hydroxyl molecule does not dissociate and hydroxyl as well as chlorine ion can rotate and librate around the adsorption site.

The first dynamical study of vibrational dissipation from a molecule adsorbed on an insulator surface is presented in chapter 5. Unlike many previous studies, this was done at a thermal population of all normal modes (with the exception of the one excited) rather than at zero Kelvin. I found that the stretch vibration of the hydroxyl ion interacts most strongly with the hydroxyl rotation and libration. Vibrational energy transfer then proceeds from these into the crystal lattice. Dissipation starts only a considerable time after the excitation. A non-symmetric collision of the proton with the chlorine ion appears to play a role in the ignition of the dissipation process.

A coherent control mechanism for the dissociation of a OH\textsuperscript{-} formed at the MgO surface due to HCl adsorption was suggested in chapter 6 and its experimental feasibility was demonstrated. In the excitation process drive by the field generated by optimal control theory for the hydroxyl ion, a remarkable effect of potential and dipole moment anharmonicity is the use of double excitations. This allows the very short time scale for the excitation process in spite of a high target yield, which in turn diminishes the adverse effects of dissipation. It was demonstrated that a static electric field can be used to desorb atomic hydrogen from the excited molecule.

The separation of the STE in alkali halides takes place within a crystal lattice, contrasting process (1), which involves a molecule adsorbed on a surface. I have proposed a laser field driving the STE separation coherently. Coherence can be maintained during the proposed reaction because it proceeds within a few hundred femtoseconds. To my knowledge, this is the first time a coherent control scheme has been proposed for a specific reactive centre within a crystal. The use of a bound excited state of the STE to deposit a wave packet on the dissociative flank of the STE electronic state is, to my knowledge, a qualitatively new reaction scheme. It involves a subtle interplay between electronic and vibrational dynamics of the wave function.

Conclusion of Thesis

Future Developments

Beyond the general usefulness of the new techniques developed in this work that are ready to be used in other problems, it would be desirable to extend this study in the future by

(a) taking more coordinates of the reactants into account, e.g. the rotational and librational modes of the hydroxyl ion at the MgO surface or the rotational coordinate of the di-haloid in the STE separation reaction,

(b) extending the DFT and dissipation dynamics studies to HCl adsorbed on a step in the surface and studying quantitatively the dynamics of the dissipation involving the STE\textsuperscript{*} and

(c) extending the molecule-on-surface example system to other materials. Systems of interest include for example carbon monoxide and nitrogen oxides on platinum catalysts or reactions involving products of different chirality. Any branching catalytic reaction can in principle probe for its controllability by illumination with coherent light.

This study has demonstrated that a complete theoretical treatment of coherent control processes in contact with and inside insulators can be performed. With some increased interest from the experimental community, the study of such processes may evolve into a rich field of research with many useful applications.

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\textsuperscript{*}It may be that this will become possible only if computing power continues growing exponentially.
Appendix A. Geometric Setup of CaF₂ Step Lattice Dynamics

Fig. A.1a shows a simple cubic supercell for the bulk CaF₂ crystal. The fcc lattice vectors relating the calcium ions are indicated in red. The large cube shown consists of eight subcubes with the simple cubic sublattice occupied by fluorine ions with calcium ions occupying alternating cubo-interstitial positions. The symmetry of this supercell is $D_{2d}$. It is often used as a simple cubic supercell to discuss the bulk CaF₂ crystal.

The ions used for the (111) surface unit cell are inserted into this supercell (plus an adjacent subcube) and indicated by the strong lines connecting them. Fig. A.2b shows the surface unit cell along with the coordinate system aligned such that the surface normal is in z-direction. This unit cell consists of three layers with one Ca plus two F ions each.

The different orientation of these layers defines the ABC stacking of the fcc lattice in (111) direction indicated in fig. A.2b. The slab thickness can be increased by adding stacks according to the ABC sequence. This surface unit cell was chosen because it has a layered structure, which makes the subsequent analysis of vibrational modes easier. The projection of each layer from the surface unit cell into the surface plane forms a regular triangle. This is shown in fig. A.2, along with a few images of the translation to illustrate the hexagonal symmetry of the surface.

In this picture, the ABC sequence of the stacking can be illustrated again. Say the image shows stack A, then in the next stack, B, there is a calcium ion below the fluorine ion marked ‘1’, while the C stack has a calcium ion under the fluorine ion marked ‘2’.

Adding two more stacks (AB) gives the slab unit cell with 15 atomic layers used in this project.

The translational vectors and fractional coordinates of a relaxed surface unit cell with five layers, i.e. 15 ions, are shown in tables A.1 and A.2.

![Geometric Setup of CaF₂ Step Lattice Dynamics](image)

**Figure A.1.:** CaF₂ (111) surface unit cell. (a) CaF₂ cubic supercell with (111) surface unit cell inscribed (strong lines). Primitive unit cell in blue, bulk translational vectors in red. (b) Isolated view of (111) surface unit cell. Note that ions drawn smaller are further away.

**Figure A.2.:** Top view of the CaF₂ surface with surface unit cell (in black) and surface lattice vectors. An equivalent, straight shape of the surface unit cell is indicated by a thick red line linking the corresponding ions.
Appendix B. MD Propagation Methods

The classical equations of motion are generally solvable by any integration algorithm. However, the evaluation of forces acting on the ions is computationally quite demanding, as it necessitates calculating the derivative of the potential (including the Ewald summation of charge interactions and the real space summation of pair potential interactions). The classical fourth-order Runge-Kutta integrator, for example, evaluates the forces four times per time step.

It is therefore worthwhile to look for algorithms that evaluate the forces only one or two times per time step. The methods are usually based on the Taylor expansion of the positions of the ions over time. The acceleration \( a_\mathbf{j} \) of ion \( \mathbf{j} \) at time \( t \) is derived from the gradient of the potential (due to the other ions) at the ion position \( \mathbf{r}_\mathbf{j}(t) \):

\[
a_\mathbf{j}(t) = \frac{\nabla U(\mathbf{r}_\mathbf{j}(t))}{\mu_\mathbf{j}},
\]

where \( \mu_\mathbf{j} \) is the mass of the ion.

Several methods are in wide use today.\textsuperscript{213,214} The most versatile and most frequently used one is the Verlet integration. In its description below, I will drop the index \( \mathbf{j} \) as well as the bold font for \( \mathbf{a} \), \( \mathbf{v} \) (the velocity) and \( \mathbf{r} \) for simplicity.

B.1. Leapfrog-Verlet Method

The Taylor series up to third order for the geometry change for forward and backward propagation steps are:

\[
r(t + \Delta t) = r(t) + v(t) \Delta t + a(t) \Delta t^2 + b(t) \Delta t^3 + O(\Delta t^4)
\]

and

\[
r(t - \Delta t) = r(t) - v(t) \Delta t + a(t) \Delta t^2 - b(t) \Delta t^3 + O(\Delta t^4).
\]

Addition of both equations leads to

\[
r(t + \Delta t) = 2r(t) - r(t - \Delta t) + a(t) \Delta t^2 + O(\Delta t^4).
\]  \hspace{1cm} (B.1)

Note that in this method, the velocity is not explicitly included and therefore the crude estimate

\[
v(t) = \frac{r(t + \Delta t) + r(t - \Delta t)}{2\Delta t} + O(\Delta t^2)
\]

has to be used. The Verlet algorithm exists in several other, equivalent variants which use a different number of operations for each time step and should be chosen according to which intermediate results are needed. They are:

1. The Leapfrog method:
   \[
   r(t + \Delta t) = r(t) + v(t + \frac{1}{2} \Delta t) \Delta t \tag{B.2}
   \]
   \[
   v(t + \frac{1}{2} \Delta t) = v(t - \frac{1}{2} \Delta t) + a(t) \Delta t \tag{B.3}
   \]

2. The velocity Verlet method:
   \[
   \begin{align*}
   r(t + \Delta t) &= r(t) + v(t) \Delta t + \frac{1}{2} a(t) \Delta t^2 \\
   v(t + \Delta t) &= v(t) + \frac{1}{2} (a(t) + a(t + \Delta t)) \Delta t
   \end{align*}
   \]

3. The Leapfrog-Verlet method:
   \[
   \begin{align*}
   r(t + \Delta t) &= r(t) + v(t) \Delta t + \frac{1}{2} a(t) \Delta t^2 \\
   v(t + \frac{1}{2} \Delta t) &= v(t) + a(t) \frac{1}{2} \Delta t \\
   v(t + \Delta t) &= v(t + \frac{1}{2} \Delta t) + a(t + \Delta t) \frac{1}{2} \Delta t
   \end{align*}
   \]

While the equivalence of 2. and 3. is obvious, the equivalence of 1. with (B.1) can be seen by substituting (B.3) into (B.2)
   \[
   r(t + \Delta t) = r(t) + v(t + \frac{1}{2} \Delta t) \Delta t
   \]
   \[
   v(t + \frac{1}{2} \Delta t) = v(t) + a(t) \frac{1}{2} \Delta t
   \]
   \[
   v(t + \Delta t) = v(t + \frac{1}{2} \Delta t) + a(t + \Delta t) \frac{1}{2} \Delta t
   \]

and writing
   \[
   v(t - \frac{1}{2} \Delta t) \Delta t = r(t) - r(t - \Delta t),
   \]

which follows directly from (B.2) after the substitution \( t = t - \Delta t \). The equivalence of 2. and (B.1) is shown in the same way.

B.2. Nordsieck-Gear Predictor-Corrector Method

This is a higher order method, which initially predicts the position and its derivatives up to the fourth derivative with a simple forward step
   \[
   \begin{align*}
   r(t + \frac{1}{2} \Delta t) &= r(t) + v(t) \Delta t + \frac{a(t)}{2} \Delta t^2 + \frac{b(t)}{3} \Delta t^3 + \frac{c(t)}{4} \Delta t^4 + \frac{d(t)}{5} \Delta t^5, \\
   v(t + \frac{1}{2} \Delta t) &= v(t) + a(t) \Delta t + \frac{b(t)}{2} \Delta t^2 + \frac{c(t)}{3} \Delta t^3 + \frac{d(t)}{4} \Delta t^4, \\
   a(t + \frac{1}{2} \Delta t) &= a(t) \Delta t + b(t) \Delta t + \frac{c(t)}{3} \Delta t^2 + \frac{d(t)}{4} \Delta t^3, \\
   b(t + \frac{1}{2} \Delta t) &= b(t) + c(t) \Delta t + \frac{d(t)}{2} \Delta t^2, \\
   c(t + \frac{1}{2} \Delta t) &= c(t) + d(t) \Delta t,
   \end{align*}
   \]
then calculates the acceleration from the potential gradient at the predicted position
   \[
   a(t + \Delta t) = -\frac{\nabla U(r(t + \frac{1}{2} \Delta t))}{\mu}
   \]
and subsequently, using the discrepancy between this and the predicted acceleration
   \[
   \Delta a(t + \Delta t) = a(t + \Delta t) - a(t + \frac{1}{2} \Delta t) \Delta t^2
   \]
corrects all values up to the fifth derivative
   \[
   \begin{align*}
   r(t + \Delta t) &= r(t + \frac{1}{2} \Delta t) + c_0 \cdot \Delta a(t + \Delta t), \\
   v(t + \Delta t) &= v(t + \frac{1}{2} \Delta t) + c_1 \cdot \Delta a(t + \Delta t) \frac{1}{2} \Delta t, \\
   b(t + \Delta t) &= b(t + \frac{1}{2} \Delta t) + c_2 \cdot \Delta a(t + \Delta t) \frac{3}{4} \Delta t^2, \\
   c(t + \Delta t) &= c(t + \frac{1}{2} \Delta t) + c_4 \cdot \Delta a(t + \Delta t) \frac{4}{5} \Delta t^3, \\
   d(t + \Delta t) &= d(t + \frac{1}{2} \Delta t) + c_5 \cdot \Delta a(t + \Delta t) \frac{5}{6} \Delta t^4,
   \end{align*}
   \]

It can be shown that using the coefficient vector
   \[
   (c_1 = \frac{3}{20}, c_2 = \frac{251}{360}, c_3 = 1, c_4 = \frac{11}{18}, c_5 = \frac{1}{6}, c_6 = \frac{1}{60})
   \]
iminises the error.
Appendix C. Methods Employed in the Analysis of DFT Results

C.1. Dipole-Dipole Interaction Energy

The dipole interaction energy between supercells can be calculated by applying the Ewald summation technique to a unit cell of two charges of equal magnitude but different sign. Their magnitude and distance are chosen such that they create the dipole whose interaction energy is sought. Then the distance is taken to zero while increasing the charges to keep the dipole constant. This approach was introduced by Kantorovich.\textsuperscript{161} In the following, I briefly sketch the derivation from this paper.

This formula was derived by using the Ewald summation technique on two charges representing the dipole and taking the limit of their distance to zero while keeping the dipole constant.

Say $E_{\text{iso}}$ is the energy corresponding to an isolated adsorbed molecule at the surface and $E_{\text{conf}}$ the energy of the same configuration in periodic boundary conditions, then

\[
E_{\text{conf}} = E_{\text{iso}} + E_{\text{dip}},
\]

where $E_{\text{dip}}$ is the dipole-dipole interaction energy. Higher order interactions (such as dipole-quadrupole and quadrupole-quadrupole) are neglected. Conversely, the energy of the isolated dipolar system can be extracted as

\[
E_{\text{iso}} = E_{\text{conf}} - E_{\text{dip}}.
\]

Since the clean MgO surface (energy $E_{\text{surf}}$) and the free molecule calculation (energy $E_{\text{mol}}$) have negligible dipoles and $E_{\text{bound}} = E_{\text{mol}} + E_{\text{surf}} - E_{\text{conf}}$, the corrected binding energy $E_{\text{corr}}$ is then

\[
E_{\text{corr}} = E_{\text{bound}} + E_{\text{dip}}.
\]

The dipole-dipole interaction energy can be expressed as:\textsuperscript{161}

\[
E_{\text{dip}} = -\frac{2G^2}{3\sqrt{\pi}} P^2 + \frac{1}{2} P_n n_{\alpha\beta} F_{\beta},
\]

where the sum convention is used for the Cartesian component indices $\alpha, \beta = 1, \ldots, 3$ and $G$ is Ewald’s parameter (with $G^2$ inversely proportional to the unit cell volume $v_c$). $P$ is the dipole moment vector and $\psi_{\beta\alpha}$ is the tensor

\[
\psi_{\beta\alpha} = \frac{4\pi}{v_c} \sum_{y \neq 0} R_{\beta \alpha} R_{y \beta} e^{-R_y/4G^2} - G^3 \sum_{l \neq 0} H_{\alpha\beta} (GR_l).
\]

In this formula $g$ indexes the reciprocal lattice vectors $R_g$ and $l$ indexes the direct lattice vectors $R_l$ with the exclusion of the zero vector to avoid self-action. $v_c$ is the unit cell volume. $H_{\alpha\beta}$ is defined by

\[
H_{\alpha\beta} (g) = -\delta_{\alpha\beta} H (y) + \frac{4\pi G^2}{y} \left[ 3H (y) + \frac{4}{\sqrt{\pi}} e^{-y^2} \right],
\]

\[
H (y) = \frac{2}{\sqrt{\pi}} y^2 e^{-y^2} + \frac{2e}{y}.
\]

C.2. Population Analysis

It is not immediately clear from DFT results which parts of the electron density should be assigned to which atom core.

In the case of a plane wave basis set, all basis functions are completely delocalised over the unit cell, so assignments can only be made numerically, based on the real space grid representation of the density. This can in theory be done for ionic systems by locating the surfaces between the nuclei where the density has turning points and integrating the charge density enclosed by them.

However, in more general situations, such as the appearance of covalent bonds, this ansatz leads to very complicated algorithms, the implementation of which lay outside the scope of this project. I therefore abstained from assigning charges from plane wave results and used simpler methods to analyse the electron density of plane wave calculations. (Notably the charge-in-sphere method where the charge density is integrated within touching spheres but neglected between them.)

I have used charge assignment methods only where they were readily available, which is the case in the EC-DFT calculations where the orbitals were represented as linear combinations of atomic orbitals (LCAO).

C.2.1. Mulliken Analysis

The earliest method of assigning charges to wave functions represented in LCAO bases is due to Mulliken.\textsuperscript{164,165}

Recalling that at the end of the self-consistent cycle the electronic density $n$ is represented in terms of Kohn-Sham orbitals, which in turn are linear combinations of basis functions $\chi_i (r)$, $r$ denoting a three-dimensional position vector, $n$ can be written directly in terms of basis functions as

\[
n (r) = \sum_{i,j} n_{ij} \chi_i (r) \chi_j^* (r).
\]

This means that if an appropriate electronic trial wave function looks like

\[
\psi (r) = \sum_{i,j} c_{ij} \chi_i (r)
\]

then

\[
n_{ij} = c_i c_j^*.\]
The basis functions \( \chi_i(r) \) are generally not orthogonal (e.g., atomic orbitals are generally non-orthogonal between centres / Gaussians of the same symmetry are never orthogonal), i.e. their overlaps

\[
S_{ij} = \langle \chi_i | \chi_j \rangle
\]

are generally non-zero. Hence it is not sufficient to just assign the populations \( n_i \) of the basis states to the atom that the basis functions are centred on. Instead, \( n \) should be expressed in terms of the normalised functions

\[
d_i(r) = \frac{\chi_i(r)}{S_{ii}}
\]

and

\[
d_{ij}(r) = \frac{\chi_i(r) \chi_j(r)}{S_{ij}}.
\]

\[
n(r) = \sum_i q_i d_i(r) + \sum_{i,j} q_{ij} d_{ij}(r)
\]

with \( q_i = n_i \) and \( q_{ij} = S_{ij}n_{ij} \). Since the integral of \( n \) over space must equal the number of electrons in the system, the charges \( q_i \) can then be assigned to the atoms and the charges \( q_{ij} \) to the overlaps (or bonds) between atomic orbitals.

However, Mulliken population analysis has several drawbacks: It can result in negative populations, which are unphysical. Moreover, a unitary transformation \( V \),

\[
\tau = \chi V, \, \pi = V^+ n V \tag{C.1}
\]

can be used to construct an equally valid assignment of charges to ions which is different from the original Mulliken assignment, which shows that the Mulliken charges are basis set dependent and therefore not unique.

### C.2.2. Löwdin Analysis

The Mulliken assignment method can be made unique by selecting a particular transformation matrix \( V \) in eq. (C.1). This is done by demanding that it consist of orthogonal eigenvectors of \( n \tau = \chi^{(k)} \) (Natural Orbitals – NO) with \( \sum_i \| \chi_i - \chi_i^{(k)} \|^2 \) minimal (Löwdin215).

This procedure specifies a unique way to assign charges to the resulting orbitals, as the sum of their populations is the number of electrons. However, the simple diagonalisation sets all the initial molecular orbitals at an equal footing.

Consider, for example, a basis set for the hydrogen atom consisting of the exact solution plus a weakly occupied orbital not orthogonal to it. A diagonalisation will occupy the latter by

\[
\frac{1}{2} \left[ 1 - \sqrt{1 - S^2} \right],
\]

where \( S \) is the overlap of the two orbitals. This shows that the two orbitals should be given different weight in the orthogonalisation according to their occupancy.

### C.2.3. Natural Population Analysis

Natural Population Analysis (NPA)166 does this.

As a first step, one-centre blocks of the density matrix

\[
\rho_{\alpha n l m' c' m''} = \langle \chi^{\text{atomic}}_n | n(r) | \chi^{\text{atomic}}_{n'} \rangle
\]

are diagonalised, situated at the nucleus (“centre”) \( \alpha = \alpha' \), where \( n, n' \) denote (atomic orbital) energy, \( l, l' \) the angular momentum and \( m, m' \) their symmetry components. This is done according to atomic (as opposed to molecular) symmetry.

The basis can then be separated into (1) the “minimal” set corresponding to atomic \( (n, l) \) subshells of large occupancy and (2) the “Rydberg” set of molecular orbitals which are less localised at the centres and have low occupancy. After that, the “minimal” set is orthogonalised into the set \( \chi^{\text{NO}} \) in an occupancy-weighted way, such that

\[
\sum_i w_i \| \chi^{\text{NO}}_i - \chi_i \|^2
\]

is minimal, where the weights \( w_i \) are equal to the occupancies of the orbitals \( \chi_i \).

The “Rydberg” sets are Gram-Schmidt orthogonalised with respect to the (new) “minimal” set and then diagonalised and orthogonalised among themselves in an occupancy-weighted way.

This method ensures that (a) the “minimal” set is altered least compared to the “Rydberg” set and (b) that strongly occupied orbitals are altered much less than weakly occupied orbitals. The dependence of this method on the occupancies preserves the physical meaning of the calculation166 while transforming it into a representation that can be used to assign charges, avoiding basis-set dependence.
Appendix D. Analytic Pair Potential Functions

The following functions are often used to parameterise pair potentials:

Lennard-Jones potential type functions (fig. D.1a): In a Lennard-Jones type function, a van der Waals potential type attraction due to the interaction between induced dipoles is modelled by a term \(-Cr^{-6}\), while the repulsive interaction between ions, modelling their size, is represented by a term \(Ar^{-12}\).

\[
\ell (r) = \frac{A}{r^{12}} - \frac{C}{r^6}.
\]

\[
\lim_{r \to \infty} \ell (r) = 0.
\]

It is easy to extract the minimum energy coordinate, \(r_{\text{min}} = \sqrt[3]{\frac{A}{C}}\), and the dissociation energy, \(E_{\text{diss}} = C^2 A\). The force constant at the minimum is a bit unwieldy at

\[
k = 12C^2 A \left( \frac{C}{3A} \right).
\]

The Lennard-Jones potential is frequently used to model rare gas fluids and crystals and molecular crystals. However, in ionic compounds, the Coulomb interaction can outweigh the repulsive part and therefore it is less useful for modelling charged species.

Buckingham potential type functions (fig. D.1b): In a Buckingham type function, a van der Waals potential type attraction due to the interaction between induced dipoles is modelled by a term \(-Cr^{-6}\). The repulsive interaction between ions, modelling their size, is represented by a term \(Ce^{-\gamma r}\).

\[
b (r) = Ae^{-\gamma r} - \frac{C}{r^6}.
\]

It is easy to see that

\[
\lim_{r \to \infty} b (r) = 0.
\]

However, this form does not allow to extract analytically properties like the minimum energy coordinate and the dissociation energy. If the parameters are chosen accordingly, the repulsive term becomes stronger than the polynomial term for smaller \(r\), thereby upholding the repulsive nature of the interaction at small distances. Hence, the Buckingham potential has a finite maximum and

\[
\lim_{r \to 0^+} b (r) = -\infty,
\]

so great care has to be taken to make sure that the energy of the simulated particles never exceeds the maximum value. Fig. D.1b shows an illustration of this weakness.

However, with well-chosen parameters, the exponential repulsion exceeds any Coulomb attraction and therefore the Buckingham potential is used to model ionic crystals.

Morse potential type functions (fig. D.1c): The Morse potential is very easy to fit to data sets, because its parameters lend themselves to interpretation readily, as can be seen by writing the Morse potential in two different ways:

\[
m (r) = D \left( (e^{-\beta (r - r_0)} - 1)^2 - 1 \right)
\]

\[
= D \left( e^{-2\beta (r - r_0)} - 2e^{-\beta (r - r_0)} \right).
\]

As before, \(m (r) = 0\). One can immediately deduce from equation (D.1) that \(r_{\text{min}} = r_0\) is the minimum coordinate and \(D\) is the dissociation energy, while equation (D.2) shows the attractive and repulsive branches of the potential. The curvature at \(r_0\) is \(2D\beta^2\), i.e. the force constant is

\[
k (r_0) = 2D\beta^2
\]

and hence the frequency of a Morse oscillator of mass \(\mu\) at \(r_0\) is

\[
\omega (r_0) = \sqrt{\frac{2D\beta^2}{\mu}}.
\]

The Morse potential is often used to model covalent bonds, for example in the OH\(^-\) and HCl molecules.
Appendix E. Propagation Methods

E.1. Wave Packet Propagation

E.1.1. Grid Representation and Evaluation of $\hat{H}\psi$

Most techniques of this first section of appendix E are reviewed in refs. 193, 216–219. I present here a concise review of the main aspects of this class of method important for this project.

Throughout the following, simulated wave functions will be represented on a grid, i.e. the wave function $\psi$ is interpolated on a finite number of points $\{x_1, \ldots, x_N\}$. The inner product of two wave functions $\psi_1$ and $\psi_2$ is evaluated as

$$\langle \psi_1 | \psi_2 \rangle = \sum_{i=1}^{N} \langle \psi_1(x_i) | \psi_2(x_i) \rangle .$$

Several electronic states are represented by storing several vibrational wave functions, one for each electronic state, e.g. two functions $\psi_a, \psi_b$ with

$$| \psi \rangle = | \psi_a \rangle \langle a | + | \psi_b \rangle \langle b |$$

for a two-state system. The inner product of two multi-state wave functions is the sum of the inner products of their vibrational components

$$\langle \psi_1 | \psi_2 \rangle = \sum_{\alpha, \beta} \langle \psi_1 | \psi_2 \rangle_{\alpha, \beta} \delta_{\alpha, \beta}$$

$$= \langle \psi_{1a} | \psi_{2a} \rangle + \langle \psi_{1b} | \psi_{2b} \rangle .$$

Writing the Hamiltonian operator as

$$\hat{H} = \hat{T} + \hat{V}_0,$$

with $\hat{V}_0$ the potential and $\hat{T}$ the kinetic energy operators, the potential operator is readily applied locally by multiplication,

$$\hat{V}_0 \psi = \sum_{i=1}^{N} V_0(x_i) \psi(x_i) \quad (E.1)$$

while difficulties arise in the application of the kinetic operator, as it involves spatial derivatives.

These are calculated here using the Fast Fourier Transform (FFT) technique. Denoting the Fourier transform of $\psi(x)$ by $FT[\psi(x)]$, the kinetic energy operator can be applied as follows:

$$\psi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx} dx = FT[\psi(x)] , \quad (E.2)$$

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(k) e^{ikx} dk = FT^{-1}[\psi(k)] , \quad (E.3)$$

$$\hat{T} \psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(k) \left( \frac{-h^2}{2M} \right) e^{ikx} dk = FT^{-1} \left[ \left( \frac{-h^2}{2M} \right) \psi(k) \right] . \quad (E.4)$$

The Fourier representation yields the exact energy spectrum

$$T_{FT}(k) = \frac{h^2 k^2}{2M} .$$

E.1.2. The Split Operator Propagation Method (SPO)

The operator $\hat{U} = e^{\lambda(\hat{T}+\hat{V}_0)}$, $\lambda = -\frac{\Delta t}{\hbar}$ is approximated as

$$\hat{U} = S_{2}(\hat{T}, \hat{V}_0, \lambda) + S'(\lambda^3) + O(\lambda^4),$$

$$S_{2}(\hat{T}, \hat{V}, \lambda) = e^{\Delta t \hat{V}_0} e^{\lambda \hat{T}} e^{-\Delta t \hat{V}_0},$$

i.e. one of the operators $\hat{T}, \hat{V}$ is split into halves for the purpose of forming the exponential.

The leading error term

$$S'(\lambda^3) = \frac{1}{24} \left[ \hat{T}^2 + 2\hat{V}_0, \left[ \hat{T}, \hat{V}_0 \right] \right] \lambda^3$$

can be easily obtained from Taylor expansion of the exponential. As the commutator occurs in this term, the eigenvalues of the kinetic and potential energies have to be bounded to achieve convergence.

By symmetry, the potential term can be split as well, in order to avoid doubling the effort spent on doing the FFT, which is the bottleneck of the method:

$$\hat{U} = S_{2}(\hat{T}, \hat{V}_0, \lambda) + S'(\lambda^3) + O(\lambda^4),$$

$$S_{2}(\hat{T}, \hat{V}, \lambda) = e^{\Delta t \hat{V}_0} e^{\lambda \hat{T}} e^{-\Delta t \hat{V}_0} .$$

The interaction with a time-dependent electric field $\varepsilon(t)$ of a laser beam impinging on the system can be expressed as a potential-like term, e.g. in a two-state system with the electronic states $a$ and $b$

$$\hat{V}(x,t) = \hat{V}_0(x) +$$

$$+ \varepsilon(t) \left( \hat{P}_{\text{ vib}}(x) \langle \psi_a | + \hat{P}_{\text{ vib}}(x) \langle \psi_b | \right) \psi_a +$$

$$+ \mu_a(x) \cdot (\langle \psi_a | + \langle \psi_b | ) \psi_a \right)$$

where $\hat{P}_{\text{ vib}}(x)$ is the vibrational dipole moment in the electronic state $\kappa$ and $\mu_a(x)$ is the electronic transition dipole moment mediating the coupling between the electronic states. Then $\varepsilon(t) \hat{P}_{\text{ vib}}(x)$ is a time-dependent potential term mediating vibrational excitation, acting on the electronic state $\kappa$.
Vibrational excitations can be treated as potential terms, i.e. as scalar multiplication (eq. E.1), only the time-step has to be chosen small enough to sample the changing electric field \( \varepsilon(t) \) sufficiently accurately.

A frequently used approach to express electronic excitation in the SPO method is splitting the term and analytically diagonalising the purely off-diagonal matrix \( \varepsilon(t) \mu_{ij}(x) \cdot (|\psi_j\rangle \langle \psi_i| + |\psi_i\rangle \langle \psi_j|) \) to calculate its exponential \( A \):

\[
S_a(T, \tilde{V}, \lambda) = A(t + \Delta t) e^{\frac{\Delta t}{2}} e^{-\frac{\Delta t}{2}} A(t),
\]

\[
A(t) = \exp \left( \frac{\Delta t}{2} \mu_{ij}(x) (|\psi_j\rangle \langle \psi_i| + |\psi_i\rangle \langle \psi_j|) \right),
\]

where the matrix expression has to be understood as \( \{\psi_i, \psi_j\} \) being the basis of the underlying vector space. If there are more than two states involved, the matrix has to be extended accordingly and the resulting transition matrices multiplied. For sufficiently small time-steps, this multiplication is approximately commutative.

### E.1.4. Optimal Control

This subject is covered for example in refs. 34, 190. Optimal control allows to specify an initial and a target state describing a reaction that is desired and calculate an electromagnetic field which produces an approximation to the target state from the initial state in a specified time.

Let \( \psi_x \) be the wave function to be acted upon by the electromagnetic field, \( \psi_x(t = 0) = \varphi_x \) the initial state of the wave function and \( \psi_f(t) \) the target state that is sought. Let \( \varepsilon(t) \) be the electric field at time \( t \), \( H \) the Hamiltonian of the system without the influence of the electromagnetic field and \( \psi_f(t) \) a time-dependent complex function which serves as Lagrangian multiplier.

The objective is to generate the best approximation of the target state. This is done by maximising a functional which includes the yield, i.e. the projection of the final state on the target, a penalty term for the strength of the field \( \varepsilon \) and a penalty term for deviations of the process from the Schrödinger equation (this is where the Lagrange multiplier \( \psi_f(t) \) is needed).

A functional with these properties is:

\[
K[\psi_x(t), \psi_f(t), \varepsilon(t)] = \left| \langle \psi_x(t) | \varphi_f \rangle \right|^2 - \alpha_0 \int_0^T \varepsilon(t)^2 dt - 2 Re \left\{ \langle \psi_x(t) | \varphi_f \rangle \int_0^T \left[ \psi_f(t) \left( \frac{1}{\hbar} \frac{\partial}{\partial t} H - \mu \varepsilon(t) \right) + \frac{\partial}{\partial \psi} \psi_f(t) \right] dt \right\}.
\]

The penalty for the field \( \varepsilon \) involves a coefficient \( \alpha_0 \) and a shape function

\[
s(t) = \sin^2 \left( \frac{t}{\tau} \right)
\]

which makes sure that the penalty function becomes larger towards the limits of the time interval so that the resulting field does not feature an abrupt start or end.

Differential equations for this approach are derived by setting the variation of the functional to zero with respect to variations of \( \psi_f, \psi_x, \varepsilon \). They are:

\[
\varepsilon(t) = -\frac{\alpha(t)}{\hbar \alpha_0} \text{Im} \left\{ \langle \psi(t) | \varphi_f \rangle \langle \psi_f(t) | \psi(t) \rangle \right\},
\]

\[
\frac{\partial}{\partial H} \psi_x(t) = [H - \mu \varepsilon(t)] \psi_x(t), \quad \psi_x(t = 0) = \varphi_x,
\]

\[
\frac{\partial}{\partial \psi} \psi_f(t) = [H - \mu \varepsilon(t)] \psi_f(t), \quad \psi_f(t = \tau) = \varphi_f.
\]

These are the Schrödinger equation for the wave function \( \psi_x \); the Lagrange multiplier \( \psi_f \) satisfies the same differential equation with different boundary conditions and hence can be viewed as a wave function. Additionally, equation (E.7) relates the functions \( \psi_x \) and \( \psi_f \) to the electric field.

The implementation of the optimal control method is based on a self-consistent cycle, where \( \psi_f \) is propagated from \( \psi_f(t = \tau) = \varphi_f \) back to \( t = 0 \), then \( \psi_f \) and \( \psi_x \) are propagated forward simultaneously, accumulating a new \( \varepsilon(t) \) along the way using (E.7). The method is stopped when a desired yield ratio is reached or the
E.1.5. Swept Penalty Parameter

Depending on the initial conditions, the optimal control method can converge to different local minima of the functional $K$ (equation E.6).

One of them is the zero field solution, where the penalty part \( \alpha_0 \int_0^T \frac{|\psi|^2}{2\hbar} \, dt \) of the functional $K$ is minimal. This is of course not what is intended. In order to increase the rate of success, I propose to alter the method to include a swept penalty parameter $\alpha_0$.\(^*\)

To avoid zero field strengths, the penalty parameter $\alpha_0$ is set to a (sometimes very) small initial value. This favours a non-zero field solution with a high yield of the target wave function. During each successive iteration, the penalty parameter is linearly increased:

\[
\alpha_0(\kappa) = \alpha_I + (\alpha_T - \alpha_I) \frac{\kappa - 1}{K-1},
\]

(E.10)

where $\alpha_I$ and $\alpha_T$ are the initial and target penalty parameters, $\alpha_T \gg \alpha_I$, $\kappa$ is the iteration number, counting from one and $K$ is the total number of iterations, so that in the last cycle $\alpha_T$ is used as penalty parameter.

At larger $\alpha_0$, the field follows the motion of the wave packets more closely (see eq. E.7), yielding, after several iterations, a smooth sinusoidal field strength as opposed to the near random-noise character of the fields yielded from small $\alpha_0$ values.

Strictly speaking, this approach does not correspond to a single functional $K$. However, it can be seen as a series of single-cycle applications of the method, each using the result of the previous one as its initial guess, thereby favouring a certain local minimum (one where the field is non-zero).

In the present optimal control calculations, a slow linear increase of the penalty operator permitted to find laser fields to reactions that did not yield any optimal field with any single constant $\alpha_0$. Other schemes of altering $\alpha_0$ during the iterative process can be designed easily, however, a linear increase proved sufficient to obtain the results presented in the following chapters.

E.1.6. Example Calculations

E.1.6.1. Simple, One-dimensional Propagation

Several propagation methods have been tested at a European Centre for Atomic and Molecular Computations (Centre Européen de Calcul Atomique et Moléculaire – CECAAM) workshop by Leforestier, Kosloff and co-workers, discussed in ref. 217.

\(^*\)It has come to my attention that this technique has been developed independently in the group of de Vivie-Riedle.\(^{194}\)

This code demonstrates the propagation of a one-dimensional wave packet with a time-independent Hamiltonian.

Besides the split operator (SPO) method, the code includes:

- the Second Order Differenting (SOD) method, a short time-step method based on a time-symmetrised Taylor expansion expression, plus a variant of SOD with a refined initialisation (SODS),
- the Chebyshev method, a high precision method which approximates the exponential $\hat{U}$ by a Chebyshev polynomial of the Hamiltonian and therefore is best suited for time independent Hamiltonians and
- the Lanczos method which performs a direct diagonalisation by successive approximation.

The different methods are described in detail in ref. 193.

I applied a number of fixes to the code, most notably in the initialisation of the SOD variants, which were done with a first order full time step. I changed this to a first order half step followed by a second order half step, thereby improving the accuracy of the method by an order of magnitude.

The methods were subsequently tested on harmonic potentials and compared to the corresponding analytic results to check that the implementations are correct. To illustrate the complex interference effects that occur during quantum dynamics in an anharmonic potential I show the result of a calculation on a Morse potential with arbitrarily chosen parameters in fig. E.1.

Following this testing period, I implemented a new code for wave packet propagation which is not, as the CECAM code, limited to one-dimensional systems but can handle an arbitrary number of degrees of freedom using the SPO method, based on a multi-index approach. I have tested this on harmonic systems with up to five degrees of freedom. A higher number of degrees of freedom is impractical due to computational constraints.

I have built in electronic excitation by implementing a transition operator linearly dependent on the electric field and a coordinate-dependent electronic transition dipole moment. Additionally, I have built in the simulation of, potentially simultaneous, vibrational excitation which is implemented as a phase factor depending on the coordinate-dependent vibrational dipole, i.e. a momentum change is effected by a gradient of the dipole. Observables such as the expectation values of the kinetic and potential energies, coordinate and momentum are calculated during propagation.

A comparison of the accuracy of different propagators for this system is shown in fig. E.2. An almost machine-accuracy Chebyshev result was used as benchmark. The Chebyshev propagator with accuracy cutoff $10^{-8}$, which can always be easily achieved, and the variants of the SOD propagator (whose curves lie on top of each other) are most accurate for short propagation times. However, the errors of the SOD, SODS and Lanczos propagators are not linear with time (the earlier’s error
Figure E.1: An illustrative propagation example in a one-dimensional Morse potential, without electronic excitation. An initially Gaussian-shaped wavepacket is placed off-minimum with a small initial momentum, drawn in light blue at the bottom. From bottom to top follow several snapshots of the wavepacket. All are represented by their square modulus (spatial probability density). The thin horizontal line marks the energy of the wavepacket. It is preserved, as no dissipation is taken into account. The two lines at around zero and two a.u. represent the momentum (scaled to 20% for clarity) and coordinate of the wavepacket, respectively.

One can see that, as the wavepacket meets the barrier at the left, its backscattered parts interfere heavily with its incoming parts. Due to the large width of the wavepacket, the average position stays at the right-hand side of the potential minimum. This diagramme demonstrates the periodic recurrence of the wave packet which can be observed to good accuracy over several periods. The picture only contains one period of recurrence for clarity.

Figure E.2: Comparison of the levels of accuracy of different propagation methods. Deviation of the projection on a run of the Chebyshev propagator with coefficient cutoff $10^{-14}$ in percent. Timestep of short time propagators 1.8 as (attoseconds), the Chebyshev propagator was run for intervals of 30 fs to obtain intermediate results. The curves of the fixed SOD and SODS propagators lie on top of each other.

Table E.1: Efficiency and accuracy of propagation methods. Left table: Runtimes of the same simulation from Fig. E.1 (5000 a.u.), timestep of short time propagators 1.8 as (attoseconds), the Chebyshev propagator was run for intervals of 30 fs to obtain intermediate results. The platform used for the calculations is a 500 MHz alpha EV6. Right table: Comparison of the accuracies of SPO and Chebyshev operators for different accuracy settings. As the magnitude of the error of the SPO propagation is decreased, the error accumulates in the phase. There is therefore an optimal time step for the SPO operator minimising the modulus of both errors.

E.1.6.2. Electronic Excitation

To demonstrate the simulation of a process involving electronic excitation, let us consider a two-level system. Fig. E.3b shows the propagation on such a system where the lower electronic state has a double well potential and the upper one has a single minimum at the barrier point of the electronic ground state. The aim in this
Propagation Methods

The de-excitation from the electronically excited state (stimulated emission), which takes place simultaneously to the excitation, causes the electronic ground state wave function to start performing a vibrational motion. The dumped parts of the ground state wave packet also interfere the stationary parts, causing interference patterns to show up in the square modulus.

After the pump laser is switched off, the electronically excited wave packet (shown in red) travels to the right-hand side (third snapshot). Note that the wave packet left behind in the electronic ground state (shown in light blue) does not have sufficient vibrational energy to cross the barrier and stays in the left well.

A subsequent dump pulse with inverted, i.e. positive, chirp de-excites the system, populating the right-hand side potential well of the ground state, which was what we intended. As both potentials are symmetric, the dump pulse is also resonant for a certain time to the electronic energy difference on the left-hand side and therefore causes some excitation there as well, which was not intended.

Additionally, strong interference effects can be seen throughout the image. This is due to the finite length of the excitation laser pulse, which means that during the excitation, the wave packets move away from their original position vibrationally and can be subsequently transported to the respective other potential.

The discrepancy between figs. E.3a and b is an example for the side effects that can arise when trying to control a system and the difficulties they can cause.

![Figure E.3.](image)

**Figure E.3.** A symmetric double well example. The task is to transport an initial wave packet from the left well into the right well.

(a) Diagram showing a process to attain this end. (0) Initial wave packet (in blue) sits in left well of electronic ground state. (1) Irradiation with an ultrashort laser pulse excites wave packet to first excited electronic state (excitation symbolised by red colour of wave packet). (2) The wave packet is now at the flank of the excited state potential and starts oscillating about the excited state minimum. (3) After half a period of this oscillation, the wave packet is at the other flank of the excited state potential and can be dumped into the right-hand side well of the ground state.

(b) Simulation of the process (a) with a wave packet propagation method. Initial population in the vibrational ground state of the left well shown at the bottom. From bottom to top follow several snapshots of the wavepacket. Of each pair of lines, the bottom, light blue one is the electronic ground state wave function and the upper, red line is the electronically excited state wave function. The thick lines are the square modulus of each wave function, while the thin lines are the real parts. It can be seen that already during the initial excitation through to the final state, strong interference effects are present, causing a considerable deviation of the process from the idealised model (a). A more detailed discussion can be found in the text (p. 273).

artificial example is to transfer the initial wave packet located at the left well to the right well in the ground state, using the excited state as an intermediate.

An illustration of the process aimed at is shown in fig. E.3a.

The vibrational ground state wave function was calculated using the relaxation method (E.1.3).

Between the first and second snapshot in fig. E.3b, a short pump pulse with negative chirp (i.e. its frequency changes linearly with time from higher to lower frequencies) excites the wave packet. The chirp makes the pulse stay in resonance with the energy difference between the electronic states for longer than an unchirped pulse.

To check my implementation, I repeated the calculations done in ref. 34 that were concerned with exciting vibrationally the first excited state of a Morse potential modelling the OH⁻ molecule from the ground state. The next step was to try and produce the fifth vibrational state of a model system Morse oscillator, starting from its ground state. To ensure that the method converges, I altered the optimal control scheme. This method is described in more detail in section E.1.5.

When using fixed penalty coefficients α, one of two consequences resulted from the application of the optimal control method. When α was moderately large, the yield of the desired target state was zero. When α was very small, an appreciable yield of the target state resulted, however with an unphysical laser field. The method in its altered form starts with a very small α, allowing the target state to be reached and only later slowly raises α in order to enforce physically attainable fields but maintaining appreciable target yields. I was able to achieve a yield of 87%.

Fig. E.4 shows the eigenstate populations over time for two Morse oscillators with different anharmonicity parameters. The magnitude of each population ranges from zero to one. Both runs start with a full population of the ground state and no population in any other state. At around 2000 a.u. (≈50 fs), the laser excitation

E.2. Density Matrix Propagation

E.2.1. The Density Matrix Formalism and Dissipation

All methods introduced and example calculations shown so far maintain strict energy conservation, i.e. the systems considered are thermodynamically closed systems. The system of interest in this project, the OH molecule embedded in the MgO(001) surface due to adsorption of an HCl molecule, can dissipate vibrational energy to the surface during the time-scale of interest (1 ps) as was shown in chapter 5 and therefore has to be simulated as an open system. The following section introduces the reduced density matrix formalism and the Lindblad Dissipation Operator by which this will be achieved.

The basic formalism of density matrices and the Liouville-von-Neumann equation are reviewed, for example, in ref. 79. I have also used material from this section.

Let \( \{ \psi_j \} \) be a set of orthonormal states. The density operator \( \rho \) is defined as

\[
\rho = \sum_j p_j |\psi_j\rangle \langle \psi_j|,
\]

where \( p_j \) is the probability to find the system described by the density operator in the pure state with the wave function \( \psi_j \). The \( p_j \) can thus be understood as populations of the state \( \psi_j \). The density matrix of a pure state can be written as \( |\psi\rangle \langle \psi| \) for some wave function \( \psi \).

A density operator \( \tilde{\rho} \) can be fully specified by its matrix elements according to a complete orthonormal set \( \{ \phi_i \} \):

\[
\rho_{mn} = \langle \phi_m | \tilde{\rho} | \phi_n \rangle = \sum_j p_j \langle \phi_m | \psi_j \rangle \langle \psi_j | \phi_n \rangle = \sum_j p_j a_{mj} a_{nj}^* \quad \text{(E.12)}
\]

where the last line defines the overlaps \( a_{nj} = \langle \phi_m | \psi_j \rangle \). The trace of \( \rho \) can be defined as

\[
\text{tr} (\tilde{\rho}) = \sum_{mn} \rho_{mn} = \sum_j p_j \sum_m \langle \psi_j | \phi_m \rangle \langle \phi_m | \psi_j \rangle = 1. \quad \text{(E.13)}
\]

According to eqs. (E.12) and (E.13), \( \rho_{mn} = \sum_j p_j |a_{mj}|^2 \geq 0 \) can be called the population of state \( \phi_m \) in the system described by \( \tilde{\rho} \).

The expectation value of an operator \( \hat{A} \) is defined as
\[
\langle \hat{A} \rangle = \text{tr} (\hat{\rho} \hat{A}) = \sum_{m,n} p_j \langle \phi_m | \hat{A} | \psi_j \rangle \langle \psi_j | \phi_m \rangle = \sum_{j} p_j \langle \hat{A} | \psi_j \rangle \psi_j \rangle.
\]

It can be seen from the last line that this definition makes sense, as the expectation value must be a weighted average of the expectation values due to the different wave function components of the density operator.

From \( \langle \hat{A} \rangle = \sum_{m,n} \rho_{mn} A_{mn} \) it can be seen that the expectation value of \( \hat{A} \) generally depends on the diagonal as well as the off-diagonal elements of the density matrix. The latter are called the coherence elements of the density matrix.

**E.2.2. Coherence Elements of the Density Matrix**

This section details a brief example, as given in ref. 79, illustrating the significance of the coherence elements of the density matrix.

Consider a spectroscopic experiment where a system is electronically excited from the ground state by a short laser pulse, i.e. the pulse has a wide range of frequencies. Then this pulse can excite the system into two close-lying states \( \phi_1 \) and \( \phi_2 \) with energies \( E_1 \) and \( E_2 \) yielding the wave function
\[
\psi (0) = a_1 \phi_1 (0) + a_2 \phi_2 (0)
\]
at the time \( t = 0 \) after the excitation, which is assumed to be instantaneous.

The time dependence of the states including decay factors \( \gamma_i \) in the two energy levels is
\[
\phi_i (t) = e^{-\gamma_i t} \hat{\rho} \psi (0) .
\]

The system can subsequently decay radiatively into the ground state \( |0\rangle \), emitting photons with polarisation vector \( \mathbf{e} \). If \( \mathbf{r} \) is the transition dipole operator, the intensity
\[
I (t) \sim |\langle 0 | \mathbf{e} \mathbf{r} | \psi (t) \rangle|^2
\]
(\( E.14 \))

Introducing
\[
A_i = \langle 0 | \mathbf{e} \mathbf{r} | \phi_i (0) \rangle \quad \text{and} \quad \gamma = \frac{\gamma_1 + \gamma_2}{2},
\]
this can be written as
\[
I (t) \sim i_{\text{osc}} (t) + i_{\text{dec}} (t), \quad \text{where}
\]
\[
i_{\text{osc}} (t) = a_1^* a_2 e^{i (E_1 - E_2) t} e^{-\gamma t} + a_2^* a_1 e^{i (E_1 - E_2) t} e^{-\gamma t}
\]
(\( E.15 \))

\[
i_{\text{dec}} (t) = |a_1 A_1|^2 e^{-\gamma t} + |a_2 A_2|^2 e^{-\gamma t}
\]
(\( E.16 \))

This oscillation is known as quantum beats and their observation is used widely to measure the energy difference \( E_1 - E_2 \). Fig. E.5 shows an example plot of the intensity featuring quantum beats.

This can be described in the density matrix formalism as follows: In energy representation, the initial density matrix is
\[
(0) = \rho_0 = a_1^* a_1 + a_2^* a_2
\]
(\( E.14 \))

This is why the off-diagonal elements of the excited state density matrix are the decaying and the oscillating part of the intensity, with circular frequency
\[
\omega = \frac{E_1 - E_2}{\hbar}
\]
Looking at eq. (E.16), it is now plausible to generalise that:

"The quantum beats are associated with the time evolution of the off-diagonal elements of the excited state density matrix."

This can be seen by expressing the decaying and oscillating parts from eqs. (E.17, E.18) in terms of density matrix elements:
\[
i_{\text{osc}} (t) = \langle 0 | \mathbf{e} \mathbf{r} | \phi_1 (0) \rangle \langle \phi_2 (0) | \mathbf{r} | 0 \rangle \rho_{11} + \langle 0 | \mathbf{e} \mathbf{r} | \phi_2 (0) \rangle \langle \phi_1 (0) | \mathbf{r} | 0 \rangle \rho_{22},
\]
(\( E.19 \))

\[
i_{\text{dec}} (t) = \langle 0 | \mathbf{e} \mathbf{r} | \phi_1 (0) \rangle \langle \phi_2 (0) | \mathbf{r} | 0 \rangle \rho_{12} + \langle 0 | \mathbf{e} \mathbf{r} | \phi_2 (0) \rangle \langle \phi_1 (0) | \mathbf{r} | 0 \rangle \rho_{21}
\]
(\( E.20 \))

The coefficients of the form \( \langle 0 | \mathbf{e} \mathbf{r} | \phi_i (0) \rangle \) remain constant over time, only the density matrix elements evolve and determine the behaviour of the components of the intensity.

This is why the off-diagonal elements of the density matrix are called coherences – when they are absent, no interference effects between the populations of the different states are visible. Conversely, when they are maximal, the interference effects are maximal (eq. E.20).


Figure E.5.: Illustration of intensity observed in spectroscopic experiments observing quantum beats. The beats are superimposed on the decaying emission.
E.2.3. The Liouville-von-Neumann Equation

According to the Schrödinger equation

\[ i\hbar \frac{\partial}{\partial t} \psi = \hat{H} \psi, \]

the evolution of the density operator (E.11) follows as

\[ i\hbar \frac{\partial}{\partial t} \rho = \int \sum\! \rho_b \left( |\psi_j\rangle \langle \psi_j| + |\psi_j\rangle \langle \psi_j| \right) \]

\[ = \sum\! \rho_b \left( \hat{H} |\psi_j\rangle \langle \psi_j| + |\psi_j\rangle \langle \psi_j| \hat{H} \right) \]

\[ = \left[ \hat{H}, \rho \right]. \]

This is the Liouville-von-Neumann equation. Using the definition of the Liouvillian super-operator \( \hat{L}_0 \) via \( \hat{L}_0 \rho = \left[ \hat{H}, \rho \right] \), it can be written as

\[ i\hbar \frac{\partial}{\partial t} \rho = \hat{L}_0 \rho. \]

Its solution can then be written formally as

\[ \hat{\rho}(t) = e^{\hat{L}_0 t} \hat{\rho}(0), \]

which can be evaluated using the usual propagation techniques introduced above.

E.2.4. Reduced Density Matrix

In order to simulate an open system, as the OH\(^-\) molecule embedded in the MgO(001) surface, a Hamiltonian

\[ \hat{H} = \hat{H}_s + \hat{H}_b + \hat{H}_i, \]

consisting of a system part \( \hat{H}_s \), a bath part \( \hat{H}_b \) and an interaction part \( \hat{H}_i \), is used. It is impractical and not in my interest to simulate both system and bath, so the open system reduced density matrix

\[ \hat{\rho}_s = \sum \left( \chi_i \langle \chi_i | \right) \]

\[ = \left[ \chi_i \langle \chi_i | \right], \]

is introduced, where \( \chi_i \) are the eigenstates of the bath Hamiltonian \( \hat{H}_b \). The bath state is not present explicitly in this reduced density matrix anymore.

The impact of the bath on the system can then be included in the Liouvillian operator by writing

\[ \hat{\mathcal{L}} = \hat{\mathcal{L}}_0 + \hat{\mathcal{L}}_d, \]

where \( \hat{\mathcal{L}}_d \) is the dissipation operator acting on \( \hat{\rho}_s \). This implies the Markov approximation, i.e. the evolution of the density operator only depends on its current state, not on the history of the density. The effect of this approximation can also be described as dissipation without memory.

The open system density matrix is usually created formally using some model for the bath where all eigenstates are known, for example a set of harmonic oscillators,

so that only the system degrees of freedom need to be simulated and the bath is represented by some approximate dissipation operator \( \hat{\mathcal{L}}_d \) derived analytically.

E.2.5. The Lindblad Dissipation Operator

A Lindblad dissipation operator is of the form

\[ \hat{\mathcal{L}}_d \rho_s = \sum_k \left( \hat{C}_k \rho_s \hat{C}_k^\dagger - \frac{1}{2} \left( \hat{C}_k^\dagger \hat{C}_k \rho_s + \rho_s \hat{C}_k \hat{C}_k^\dagger \right) \right) \]

where the Lindblad operators \( \hat{C}_k \) according to the different dissipative channels \( k \) have to obey certain mathematical restrictions. If the system is harmonic, they are often chosen to be the lowering operators of the system.

Superoperators \( \hat{\mathcal{L}} \) of the Lindblad form constitute a semi-group. They are also norm-conserving and retain positivity of the state populations. Other dissipation operators have been used in simulations, such as the one specified by Redfield theory.

E.2.6. A Special Lindblad Dissipation Operator for the Morse Oscillator

For a harmonic system \( \hat{H}_s = \hbar \omega (\hat{a}^\dagger \hat{a} + \frac{1}{2}) \) and harmonic bath with bi-linear system-bath coupling, it can be shown that at zero temperature and only allowing single phonon exchange events, the Lindblad dissipation operator takes the form

\[ \hat{\mathcal{L}}_d \rho_s = \gamma \left( \hat{a}^\dagger \hat{a}^\dagger \rho_s + \frac{1}{2} \left( \hat{a}^\dagger \hat{a} \rho_s + \rho_s \hat{a}^\dagger \hat{a} \right) \right), \]

i.e. \( \hat{C}_k = \sqrt{\alpha} \hat{a} \), \( \gamma \) is the dissipation rate and \( \hat{a}^\dagger \), \( \hat{a} \) the standard creation and annihilation operators

\[ \hat{a}^\dagger = \frac{\hbar}{\sqrt{2 M \hbar \omega}} \frac{1}{\sqrt{\omega}} \left( M \omega r - i \hat{p} \right), \]

\[ \hat{a} = \frac{\hbar}{\sqrt{2 M \hbar \omega}} \frac{1}{\sqrt{\omega}} \left( M \omega r + i \hat{p} \right). \]

\( M \) is the mass, \( \omega \) the frequency, \( r \) the coordinate and \( \hat{p} \) the momentum operator.

If the system is modelled not by a harmonic oscillator but a Morse oscillator with

\[ V (r) = D \left( e^{-2k(r-r_0)} - 2 e^{-3k(r-r_0)} \right) \]

and mass \( M \), the creation and annihilation operators have to be replaced by operators acting only on a certain state, as the energies are not equally spaced. These operators

are:\textsuperscript{224}

\[ \hat{a}_\nu = A_\nu \left( \frac{\varepsilon_\nu \exp(\nu \lambda - \frac{1}{2} \lambda)}{2\varepsilon_\nu \lambda} - \frac{1}{2\varepsilon_\nu \lambda} \right) \]

\[ A_\nu = \frac{1}{4} \left( \frac{1}{\varepsilon_\nu} + \frac{1}{\lambda} \right) \left( \frac{1}{\lambda} - \frac{1}{\varepsilon_\nu} \right) \]

\[ \lambda = 2\varepsilon^{-1} = \sqrt{2DM} \frac{\hbar}{\beta} \]

\[ \varepsilon^2 = \frac{2ME_\nu}{\hbar^2} \]

The energies \( E_\nu \) are the Morse eigenvalues

\[ E_\nu = -D + \hbar \omega \left( \nu + \frac{1}{2} \right) - \frac{\hbar^2 \omega^2}{4D} \left( \nu + \frac{1}{2} \right), \tag{E.22} \]

where \( \omega = \beta \sqrt{\frac{2\hbar}{M}} \) is the Morse frequency.

\( \hat{a}_\nu \) has a similar form with a positive sign in front of the momentum term.

These are the exact creation and annihilation operators, however they are difficult to use as part of a Lindblad dissipation operator – they depend explicitly on the quantum number of the state they act on and can hence only be applied to a fully diagonalised Hamiltonian \( \hat{H}_s \), necessitating a transformation into eigenstate representation at each time-step of the propagation.

With regard to numerical efficiency this is extremely undesirable. Therefore, approximate creation and annihilation operators are used instead.

According to\textsuperscript{225}, the steady state equation \( \hat{H}_s \psi_\nu = E_\nu \psi_\nu \) with \( \hat{H}_s \) the Morse oscillator Hamiltonian can be transformed using

\[ q = \beta r - \ln (\xi^{-1}) = \beta r - \ln \left( \frac{2\sqrt{2DM}}{\beta \hbar} \right) \]

to obtain

\[ \frac{d^2}{dq^2} \psi_\nu - \left( \frac{1}{4} e^{-2q} - \lambda e^{-q} \right) \psi_\nu - \varepsilon^2 \psi_\nu = 0. \]

According to Infeld and Hull\textsuperscript{225}, solutions to this equation exist if

\[ \lambda - \frac{1}{2} = \varepsilon_\nu, \varepsilon_\nu + 1, \varepsilon_\nu + 2, \ldots \]

i.e. for any given \( \varepsilon_\nu \) a semi-infinite set of potential parameters \( \lambda \) exists such that \( \varepsilon_\nu \) is the energy of some eigenstate of the potential.

Fig. E.6 shows an illustration of this dependence. Stepping vertically through this diagram corresponds to the application of the creation and annihilation operators \( \hat{a}_\nu \) and \( \hat{a}^\dagger \). Going horizontally through this diagram corresponds to generating the equi-energetic eigenstate of a Morse potential with a different anharmonicity parameter \( \lambda \). In the context of this other potential, this state will have a quantum number one more or one less than the original state, depending on which direction is chosen. This means that this state has one more or one less nodes than the original state. This is suggestive of using horizontal motion through the diagram as an approximation for the creation and annihilation operators.\textsuperscript{195,196}

According to\textsuperscript{225}, the operators acting as horizontal motion through the diagram are

\[ \hat{a}^\dagger = \frac{\hbar}{\sqrt{2DM} \sqrt{\hbar \omega}} \left( \lambda - \frac{1}{2} \right) \beta - \lambda \beta e^{-\beta r} - \frac{i}{\hbar} \frac{\partial}{\partial q} \]

and \( \hat{a} \) with a positive sign in the momentum part as usual.

These operators are not dependent on the state number anymore and hence can be used as approximations to the creation and annihilation operators in eq. (E.21) for the Morse oscillator.

The resulting dissipation operator

1. is non-linear, with receding coupling strength towards the dissociative end of the Morse oscillator,
2. does not necessitate transformation to the energy representation, which is particularly useful when dealing with free or almost-free states, which have been shown\textsuperscript{195,196} to be treated in a physically sensible way by this Lindblad type Liouvillian,
3. results in lifetimes for bound wave packets that are similar to analytic results for harmonic-linear coupling and anharmonic-exact creation and annihilation dissipative Liouvillians. This means that the parameter \( \gamma \) retains its meaning as inverse lifetime.\textsuperscript{195,196} Higher eigenstates with number \( \nu \) of the Morse oscillator have have accordingly lower lifetimes of \( \gamma^{-\nu} \).

Point 1 particularly is important, as a coupling that becomes stronger with increasing intramolecular distance, as is assumed in the popular bi-linear coupling model, would not yield physically meaningful results apart from very near the potential minimum.
At finite temperature, the operator can be extended\cite{221} to
\[ \hat{L}_d \rho_y = \gamma \left( \hat{a} \hat{a}^{\dagger} - \frac{1}{2} \left( \hat{a}^{\dagger} \hat{\rho} \hat{a} + \hat{\rho} \hat{a}^{\dagger} \right) \right) + \delta \left( \hat{a} \hat{\rho} \hat{a}^{\dagger} - \frac{1}{2} \left( \hat{a}^{\dagger} \hat{\rho} \hat{a} + \hat{\rho} \hat{a}^{\dagger} \right) \right). \] (E.23)
Here, \( \delta \) is the inverse lifetime multiplied by the thermal distribution factor
\[ \delta = \gamma \cdot e^{-\frac{k_B T}{2 \hbar}}. \] (E.24)

The new part added to the dissipative Liouvillian operator makes sure that dissipative channels exist where population goes up as well as down, so that the long time limit is not the ground state but a mixed state at the thermal equilibrium distribution.

In practice, the operator is implemented by using the same approximate creation and annihilation operators as before, so the previous statement about the long time limit is only met approximately.\textsuperscript{105, 106}

However, it will turn out that for OH\textsuperscript{+}, where \( \omega = 0.35 \mathrm{eV} \), \( \delta \) at room temperature becomes very small (\( \sim 10^{-10} \)), i.e. it can be neglected and (E.23) again simplifies to
\[ \hat{L}_d \rho_y = \gamma \left( \hat{a} \hat{a}^{\dagger} - \frac{1}{2} \left( \hat{a}^{\dagger} \hat{\rho} \hat{a} + \hat{\rho} \hat{a}^{\dagger} \right) \right). \]

Appendix F. Extension of the STE Model Potential to Two Dimensions

To extend the one-dimensional model potential for the STE (section 7.1.4) to two dimensions, I have represented the dependence of the energy on the \( y \) coordinate as the sum of two Gaussian functions (with negative coefficients). Their positions \( \mu_{y1} (x) \) and \( \mu_{y2} (x) \), also called “footprint” below, are symmetric with respect to the \( x \) axis:
\[ \mu_{y1} (x) = \mu_y (x), \quad \mu_{y2} (x) = -\mu_y (x). \]

The extended potential then has the form
\[ U (x, y) = C_y (x) \cdot \left( e^{-\frac{1}{2} \left( \frac{y - \mu_{y1} (x)}{\sigma_y} \right)^2} + e^{-\frac{1}{2} \left( \frac{y - \mu_{y2} (x)}{\sigma_y} \right)^2} \right) \] (F.1)

Note that I have chosen to keep \( \sigma_y \) constant over all \( x \). The positions of the two Gaussians \( \mu_{y1} (x) \) and \( \mu_{y2} (x) \) should be close together at \( x = x_m \) and \( x = x_{m2} \), resulting in single wells, but further apart at \( x_M \), creating a double well. This behaviour can be achieved by parameterising the footprint as another Gaussian function
\[ \mu_y (x) = C_y \cdot e^{-\frac{1}{2} \left( \frac{x - x_M}{\sigma} \right)^2}, \] (F.2)
where \( \mu_y = x_M \) and \( C_y = \frac{1}{3} \sqrt{2a_0} \). \( \sigma_y \) must be chosen such that the transition between the different parts of the potential (single well to double well to single well) is smooth enough, here \( \sigma_y = 1.0 \ A \). Fig. F.1a shows the footprint \( \pm \mu_y (x) \) of the potential \( U \), fig. F.1b shows a 3D view of the footprint with a few double Gaussians drawn to illustrate the change in character of the potential along the \( y \) coordinate.

For this model, I set the value of the minima of the double well in \( y \) direction at \( x = x_M \) to the average of the maximum and the larger minimum of the one-dimensional model, i.e.
\[ U (x_M, \mu_y (x_M)) = \frac{1}{2} \left( U_1 (x_M) + U_1 (x_{m2}) \right). \] (F.3)

Assuming that at the value of one Gaussian is negligible at the centre of the other Gaussian, i.e. using (F.1)
\[ \Delta x_y = C_y (x_M) \cdot e^{-\frac{1}{2} \left( \frac{2x_{m2} (x_M)}{\sigma_y} \right)^2} \approx 0, \] (F.4)
condition (F.3) can be re-written, again using (F.1), as
\[ C_y (x_M) = \frac{1}{2} \left( U_1 (x_M) + U_1 (x_{m2}) \right). \] (F.5)
The cross-section of the new two-dimensional potential along the $x$ axis should be consistent with the one-dimensional model potential introduced before, i.e.

$$U_1 (x) = U (x,0) = 2C_y (x) e^{-\frac{1}{2} \left( \frac{x-x_0}{\sigma_x} \right)^2}. \tag{F.6}$$

 Particularly, this condition should hold at $x_M$:

$$U_1 (x_M) = 2C_y (x_M) e^{-\frac{1}{2} \left( \frac{x-x_0}{\sigma_x} \right)^2}. \tag{F.7}$$

 Hence

$$\sigma_y = \pm \sqrt{\frac{-\mu_y^2 (x_M)}{2 \ln \left( \frac{U_1 (x_M)}{U_1 (x_M)} \right)}}. \tag{F.8}$$

 Since $U_1 (x_{m2}) < U_1 (x_{M}) < 0$, it follows from (F.5) that

$$|C_y (x_M)| > \frac{|U_1 (x_M)|}{2}$$

 and hence

$$\ln \left( \frac{U_1 (x_M)}{2C_y (x_M)} \right) < 0,$$

 so that the term under the root in (F.7) is positive. Since $\sigma_y$ is the width of a Gaussian function, the root with a positive sign is to be used. With $\sigma_y$ fixed, $C_y (x)$ can now be determined for all $x$ from (F.6). Fig. 7.7 shows an image of the resulting model potential.

 It remains to be ascertained that the assumption of eq. (F.4) is true. The value resulting from the parameters used is

$$\Delta \sigma_y = -1.7 \times 10^{-3} \text{ eV},$$

 which means that the error introduced during the parameterisation of the potential is well below the errors in the experimental and theoretical results used to parameterise it.

 It is important to note the influence of the parameter $\sigma_y$ on the final result. This parameter, the width of the footprint, controls how rapid the transition between

![Figure F.1.: (a) Footprint and (b) diagram showing double Gaussians in model potential. The 3D diagram shows the footprint projected into the plane as well as at the height of the apices of the Gaussians whose position it describes. The resulting sums of each pair of Gaussians is shown as strong line. The original one-dimensional potential that is extended by this construction is also shown, at $y=0$.](image)

![Figure F.2.: Comparison of $C_y (x)$ and minimum energy over all $y$ values, dependent on $x$, for different $\sigma_y$ values. (a) $\sigma_y = 0.5 \text{ Å}$: This value is too small and introduces spurious oscillations into $C_y (x)$ (upper panel), which create a spurious minimum in the minimum energy path (lower panel). (b) $\sigma_y = 1.0 \text{ Å}$: The character of the one-dimensional potential with a single barrier is maintained along the minimum energy path. While at $\sigma_y = 0.5 \text{ Å}$, spurious oscillations with large amplitude are visible in the resulting $C_y (x)$, creating a double barrier between the two main wells, the single-barrier character of the one-dimensional model potential is maintained at $\sigma_y = 1.0 \text{ Å}$. However, $\sigma_y$ cannot be made much larger because then the single wells at $x_{m1}$ and $x_{m2}$ change frequencies in the $x$ coordinate. Also, a double well character in $y$ direction at the local minima of the 1D potential can result for very high values of $\sigma_y$. Both are not physical, and therefore $\sigma_y = 1.0 \text{ Å}$ is used as optimal value for the parameterisation of the two-dimensional model potential.](image)
Appendix G. Unit Conversions

Atomic Units: For convenience, atomic units are used in all wave packet propagation methods. These units have the main advantage that

$$[S] = \hbar = 1 \text{ au}.$$  

Other observables are in units that have a convenient order of magnitude for calculations involving small scale objects (such as atoms and molecules) and are listed in table G.1.

From these basic units, the atomic units of other values can be deduced, e.g. the atomic unit of time,

$$[t] = 1 \text{ au} = 0.02419 \text{ fs}$$

from \( E = h \omega \) and the atomic unit for the electric field

$$[\varepsilon] = 1 \text{ au} = 5.14221 \times 10^{11} \text{ V m}^{-1}$$

from \( \varepsilon = \frac{\hbar c}{ mc^2} \). Section 6.2.2 describes how atomic units of electric field are interpreted for the power of laser fields required.

Other Useful Conversions: To characterise vibrational frequencies or energies, the wave number \( k = \frac{\lambda}{2} \) where \( \lambda \) is the wave length is used with the unit inverse centimetres cm\(^{-1}\). Via \( c = \lambda \cdot f = \frac{\lambda}{k} \), i.e. \( f = \frac{c}{k} \) and \( E = h \cdot f \) this can be transformed into the conversion factors for vibrational frequency and vibrational energy

\[
1 \text{ cm}^{-1} \cong 0.0300 \text{ THz},
\]
\[
1 \text{ eV} \cong 8065.54 \text{ cm}^{-1}.
\]

Accordingly, the factor between vibrational energy \( E \) in eV and frequency \( f \) in THz is

\[
1 \text{ THz} \cong 4.136 \text{ meV}.
\]

Note that the factor \( 2\pi \) is involved when a conversion into circular frequency units is to be performed via \( E = h \cdot \omega \).

### Table G.1.

<table>
<thead>
<tr>
<th>Atomic Unit</th>
<th>Conversion</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>action</td>
<td>( \hbar = 1.05459 \times 10^{-34} \text{ Js} )</td>
<td>Planck’s constant</td>
</tr>
<tr>
<td>mass</td>
<td>( m_e = 9.10938 \times 10^{-31} \text{ kg} )</td>
<td>electron mass</td>
</tr>
<tr>
<td>charge</td>
<td>( q_e = 1.60219 \text{ C} )</td>
<td>electron charge</td>
</tr>
<tr>
<td>length</td>
<td>( a_0 = 0.529177 \text{ Å} )</td>
<td>Bohr radius</td>
</tr>
<tr>
<td>energy</td>
<td>1 Hartree</td>
<td>27.2116 eV = 2 Rydberg</td>
</tr>
</tbody>
</table>

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