

Lecture Notes CHEM 470a/570a

Introductory Quantum Chemistry

Prerequisites: CHEM 130 or 330 and Math 120a or b

Instructor: Prof. Victor S. Batista

Room: SCL 21 Schedule: TTh 9-10.15

1 Syllabus

The goal of this course is to introduce *Quantum Theory* and its application to the description of atoms and molecules and their interactions with other molecular systems and electromagnetic radiation. Quantum Theory involves a *mathematical formulation* and a *physical interpretation*. The interpretation establishes the correspondence between the objects in the mathematical theory (e.g., functions and operators) and the elements of reality (e.g., observable properties of real systems). Although there are several possible interpretations of the same mathematical theory, this course will focus on the so-called *Orthodox Interpretation* developed in Copenhagen during the first three decades of the 20th century.

The official textbook for this class is:

R1: "Quantum Mechanics" by Ire N. Levine (Prentice Hall).

However, the lectures will be heavily complemented with material from other textbooks including:

R2: "Quantum Theory" by David Bohm (Dover),

R3: "Quantum Physics" by Stephen Gasiorowicz (Wiley),

R4: "Quantum Mechanics" by Claude Cohen-Tannoudji (Wiley Interscience),

R5: "Quantum Mechanics" by E. Merzbacher (Wiley),

R6: "Modern Quantum Mechanics" by J. J. Sakurai (Addison Wesley),

Students are encouraged to read the book *Thirty Years that Shook Physics* by George Gamow (Dover), during the first month of classes. The book greatly complements the lectures with an entertaining layman's description of the historical development of Quantum Theory, including the experiments that motivated the development of the theory and many personal anecdotes.

All these references are on reserve at the Kline library (KBT) to allow everyone equal usage.

The lecture notes are online at <http://xbeams.chem.yale.edu/~batista/vvv/index.html>

References to specific pages of the textbooks listed above are indicated in the notes as follows:

R1(190) indicates "for more information see Reference 1, Page 190".

Furthermore, a useful mathematical reference is R. Shankar, *Basic Training in Mathematics. A Fitness Program for Science Students*, Plenum Press, New York 1995.

A useful search engine for mathematical and physical concepts can be found at

<http://scienceworld.wolfram.com/physics/>

Grading

There will be no final exam for this class.

The final grading evaluation is the same for both undergraduate and graduate students:

homework (25%),

three mid-terms (60%) on 10/02/03, 11/04/03, and 12/04/03,

three quizzes during lecture hours on random dates (15%).

Homework includes exercises described in the lecture notes and computational assignments. Note that some exercises are inserted in the description of the specific topics to facilitate finding the relevant material in the lecture notes, while other exercises are outlined in problem sets due 10/02/03, 10/16/03, and 10/28/03, respectively. Exercises inserted in the lecture notes that precede a problem set are due the same date as the problem set. However, students are encouraged to hand in their solutions as soon as they have them ready to avoid homework

accumulation.

Students are encouraged to read the lecture notes ahead of the lectures and solve the inserted problems while studying the lecture notes.

Quizzes on random lectures will include either material from previous lectures or general questions about the material to be covered in that specific lecture.

Contact Information

Office hours will be held at SCL 239, Monday and Wednesday 4:00pm-5:00pm.

You can also send me email to victor.batista@yale.edu, or call me at (203)432-6672 if you have any question.

2 Postulates of Quantum Theory

Quantum Theory can be formulated according to a few *postulates* (i.e., theoretical principles based on experimental observations). The goal of this section is to introduce such principles, together with some mathematical concepts that are necessary for that purpose. **R1(190)** To keep the notation as simple as possible, expressions are written for a 1-dimensional system. The generalization to many dimensions is usually straightforward.

Postulate 1: Any system can be described by a function $\psi(t, x)$, where t is a parameter representing the time and x represents the coordinates of the system. Function $\psi(t, x)$ must be continuous, single valued and square integrable. **R1(57)**

Note 1: As a consequence of Postulate 4, we will see that $P(t, x) = \psi^*(t, x)\psi(t, x)dx$ represents the probability of finding the system between x and $x + dx$ at time t .

Postulate 2: Any observable (i.e., any measurable property of the system) can be described by an operator. The operator must be linear and hermitian.

What is an *operator* ? What is a *linear operator* ? What is a *hermitian operator*?

Definition 1: An operator \hat{O} is a mathematical entity that transforms a function $f(x)$ into another function $g(x)$ as follows, **R4(96)**

$$\hat{O}f(x) = g(x),$$

where f and g are functions of x .

Definition 2: **R1(190)** An operator \hat{O} that represents an observable O is obtained by first writing the classical expression of such observable in Cartesian coordinates (e.g., $O = O(x, p)$) and then substituting the coordinate x in such expression by the *coordinate operator* \hat{x} as well as the momentum p by the *momentum operator* $\hat{p} = -i\hbar\partial/\partial x$.

Definition 3: An operator \hat{O} is *linear* if and only if (iff),

$$\hat{O}(af(x) + bg(x)) = a\hat{O}f(x) + b\hat{O}g(x),$$

where a and b are constants.

Definition 4: An operator \hat{O} is *hermitian* iff, **R1(164)**

$$\int dx \phi_n^*(x) \hat{O} \psi_m(x) = \left[\int dx \psi_m^*(x) \hat{O} \phi_n(x) \right]^*,$$

where the asterisk represents the complex conjugate of the expression embraced by brackets.

Definition 5: A function $\phi_n(x)$ is an *eigenfunction* of \hat{O} iff,

$$\hat{O} \phi_n(x) = O_n \phi_n(x),$$

where O_n is a number called *eigenvalue*.

Property 1: The eigenvalues of a hermitian operator are real. **R1(166)(167)**

Proof: Using Definition 4, we obtain

$$\int dx \phi_n^*(x) \hat{O} \phi_n(x) - \left[\int dx \phi_n^*(x) \hat{O} \phi_n(x) \right]^* = 0,$$

therefore,

$$[O_n - O_n^*] \int dx \phi_n(x)^* \phi_n(x) = 0.$$

Since $\phi_n(x)$ are square integrable functions, then,

$$O_n = O_n^*.$$

Property 2: Different eigenfunctions of a hermitian operator (i.e., eigenfunctions with different eigenvalues) are orthogonal (i.e., the *scalar product* of two different eigenfunctions is equal to zero). Mathematically, if $\hat{O} \phi_n = O_n \phi_n$, and $\hat{O} \phi_m = O_m \phi_m$, with $O_n \neq O_m$, then $\int dx \phi_n^* \phi_m = 0$.

Proof:

$$\int dx \phi_m^* \hat{O} \phi_n - \left[\int dx \phi_n^* \hat{O} \phi_m \right]^* = 0,$$

and

$$[O_n - O_m] \int dx \phi_m^* \phi_n = 0.$$

Since $O_n \neq O_m$, then $\int dx \phi_m^* \phi_n = 0$.

Postulate 3: The only possible experimental results of a measurement of an observable are the eigenvalues of the operator that corresponds to such observable.

Postulate 4: The average value of many measurements of an observable O , when the system is described by function $\psi(x)$, is equal to the expectation value \bar{O} , which is defined as follows,

$$\bar{O} = \frac{\int dx \psi(x)^* \hat{O} \psi(x)}{\int dx \psi(x)^* \psi(x)}.$$

Expansion Postulate: **R1(191), R5(15)), R4(97)**

The eigenfunctions of a linear and hermitian operator form a complete basis set. Therefore, any function $\psi(x)$ that is continuous, single valued, and square integrable can be expanded as a linear combination of eigenfunctions $\phi_n(x)$ of a linear and hermitian operator \hat{A} as follows,

$$\psi(x) = \sum_j C_j \phi_j(x),$$

where C_j are numbers (e.g., complex numbers) called *expansion coefficients*.

Exercise 1: Show that $\bar{A} = \sum_j C_j C_j^* a_j$, when $\psi(x) = \sum_j C_j \phi_j(x)$,

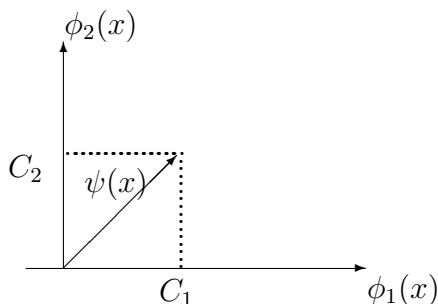
$$\hat{A} \phi_j(x) = a_j \phi_j(x), \quad \text{and} \quad \int dx \phi_j(x)^* \phi_k(x) = \delta_{jk}.$$

Note that (according to Postulate 3) eigenvalues a_j are the only possible experimental results of measurements of \hat{A} , and that (according to Postulate 4) the expectation value \bar{A} is the average value of many measurements of \hat{A} when the system is described by the expansion $\psi(x) = \sum_j C_j \phi_j(x)$. Therefore, the product $C_j C_j^*$ can be interpreted as the probability weight associated with eigenvalue a_j (i.e., the probability that the outcome of an observation of \hat{A} will be a_j).

Hilbert-Space

According to the Expansion Postulate (together with Postulate 1), the state of a system described by the *function* $\Psi(x)$ can be expanded as a linear combination of eigenfunctions $\phi_j(x)$ of a linear and hermitian operator (e.g., $\Psi(x) = C_1\phi_1(x) + C_2\phi_2(x) + \dots$). Usually, the space defined by these eigenfunctions (i.e., functions that are continuous, single valued and square integrable) has an infinite number of dimensions. Such space is called *Hilbert-Space* in honor to the mathematician Hilbert who did pioneer work in spaces of infinite dimensionality.**R4(94)**

A representation of $\Psi(x)$ in such space of functions corresponds to a vector-function,



where C_1 and C_2 are the projections of $\Psi(x)$ along $\phi_1(x)$ and $\phi_2(x)$, respectively. All other components are omitted from the representation because they are orthogonal to the “plane” defined by $\phi_1(x)$ and $\phi_2(x)$.

Continuous Representation

Certain operators have a continuous spectrum of eigenvalues. For example, the coordinate operator is one such operator since it satisfies the equation $\hat{x} \delta(x_0 - x) = x_0 \delta(x_0 - x)$, where the eigenvalues x_0 define a *continuum*. Delta functions $\delta(x_0 - x)$ define a continuum representation and, therefore, an expansion of $\psi(x)$ in such representation becomes,

$$\psi(x) = \int dx_0 C_{x_0} \delta(x_0 - x),$$

where $C_{x_0} = \psi(x_0)$, since

$$\int dx \delta(x - \beta) \psi(x) = \int dx \int d\alpha C_\alpha \delta(x - \beta) \delta(\alpha - x) = \psi(\beta).$$

According to postulates 3 and 4 (see Exercise 1), the probability of observing the system with coordinate eigenvalues between x_0 and $x_0 + dx_0$ is $P(x_0) = C_{x_0} C_{x_0}^* dx_0 = \psi(x_0) \psi(x_0)^* dx_0$ (see Note 1).

In general, when the basis functions $\phi(\alpha, x)$ are *not* necessarily delta functions but nonetheless define a continuum representation,

$$\psi(x) = \int d\alpha C_\alpha \phi(\alpha, x),$$

with $C_\alpha = \int dx \phi(\alpha, x)^* \psi(x)$.

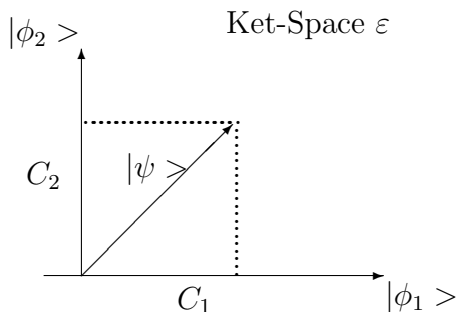
Note 2: According to the Expansion Postulate, a function $\psi(x)$ is uniquely and completely defined by the coefficients C_j , associated with its expansion in a complete set of eigenfunctions $\phi_j(x)$. However, the coefficients of such expansion would be different if the same basis functions ϕ_j depended on different coordinates (e.g., $\phi_j(x')$ with $x' \neq x$). In order to eliminate such ambiguity in the description it is necessary to introduce the concept of *vector-ket* space. **R4(108)**

Vector-Ket Space ε

The vector-ket space is introduced to represent states in a convenient space of *vectors* $|\phi_j\rangle$, instead of working in the space of *functions* $\phi_j(x)$. The main difference is that the coordinate dependence does not need to be specified when working in the vector-ket space. According to such representation, function $\psi(x)$ is the *component* of vector $|\psi\rangle$ associated with index x (*vide infra*). Therefore, for any function $\psi(x) = \sum_j C_j \phi_j(x)$, we can define a ket-vector $|\psi\rangle$ such that,

$$|\psi\rangle = \sum_j C_j |\phi_j\rangle.$$

The representation of $|\psi\rangle$ in space ε is,



Note that the expansion coefficients C_j depend only on the kets $|\psi_j\rangle$ and not on any specific vector component. Therefore, the ambiguity mentioned above is removed.

In order to learn how to operate with kets we need to introduce the *bra space* and the concept of *linear functional*. After doing so, this section will be concluded with the description of *Postulate 5*, and the *Continuity Equation*.

Linear functionals

A functional χ is a mathematical operation that transforms a function $\psi(x)$ into a number. This concept is extended to the vector-ket space ε , as an operation that transforms a vector-ket into a number as follows,

$$\chi(\psi(x)) = n, \quad \text{or} \quad \chi(|\psi\rangle) = n,$$

where n is a number. A *linear* functional satisfies the following equation,

$$\chi(a\psi(x) + bf(x)) = a\chi(\psi(x)) + b\chi(f(x)),$$

where a and b are constants.

Example: The scalar product, **R4(110)**

$$n = \int dx \psi^*(x) \phi(x),$$

is an example of a linear functional, since such an operation transforms a function $\phi(x)$ into a number n . In order to introduce the scalar product of kets, we need to introduce the *bra-space*.

Bra Space ε^*

For every ket $|\psi\rangle$ we define a linear functional $\langle\psi|$, called *bra-vector*, as follows:

$$\langle\psi|(|\phi\rangle) = \int dx \psi^*(x)\phi(x).$$

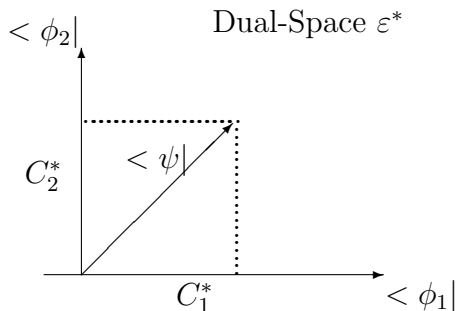
Note that functional $\langle\psi|$ is linear because the scalar product is a linear functional. Therefore,

$$\langle\psi|(a|\phi\rangle + b|f\rangle) = a\langle\psi|(|\phi\rangle) + b\langle\psi|(|f\rangle).$$

Note: For convenience, we will omit parenthesis so that the notation $\langle\psi|(|\phi\rangle)$ will be equivalent to $\langle\psi||\phi\rangle$. Furthermore, whenever we find two bars next to each other we can merge them into a single one without changing the meaning of the expression. Therefore,

$$\langle\psi||\phi\rangle = \langle\psi|\phi\rangle.$$

The space of bra-vectors is called dual space ε^* simply because given a ket $|\psi\rangle = \sum_j C_j |\phi_j\rangle$, the corresponding bra-vector is $\langle\psi| = \sum_j C_j^* \langle\phi_j|$. In analogy to the ket-space, a bra-vector $\langle\psi|$ is represented in space ε^* according to the following diagram:



where C_j^* is the projection of $\langle \psi |$ along $\langle \phi_j |$.

Projection Operator and Closure Relation

Given a ket $|\psi\rangle$ in a certain basis set $|\phi_j\rangle$,

$$|\psi\rangle = \sum_j C_j |\phi_j\rangle, \quad (1)$$

where $\langle \phi_k | \phi_j \rangle = \delta_{kj}$,

$$C_j = \langle \phi_j | \psi \rangle. \quad (2)$$

Substituting Eq. (2) into Eq.(1), we obtain

$$|\psi\rangle = \sum_j |\phi_j\rangle \langle \phi_j | \psi \rangle. \quad (3)$$

From Eq.(3), it is obvious that

$$\sum_j |\phi_j\rangle \langle \phi_j| = \hat{1}, \quad \text{Closure Relation}$$

where $\hat{1}$ is the identity operator that transforms any ket, or function, into itself.

Note that $\hat{P}_j = |\phi_j\rangle \langle \phi_j|$ is an operator that transforms any vector $|\psi\rangle$ into a vector pointing in the direction of $|\phi_j\rangle$ with magnitude $\langle \phi_j | \psi \rangle$. The operator \hat{P}_j is called the *Projection Operator*. It projects $|\phi_j\rangle$ according to,

$$\hat{P}_j |\psi\rangle = \langle \phi_j | \psi \rangle |\phi_j\rangle.$$

Note that $\hat{P}_j^2 = \hat{P}_j$, where $\hat{P}_j^2 = \hat{P}_j \hat{P}_j$. This is true simply because $\langle \phi_j | \phi_j \rangle = 1$.

Postulate 5: The evolution of $\psi(x, t)$ in time is described by the following equation:

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = \hat{H} \psi(x, t),$$

where $\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x)$, is the operator associated with the total energy of the system, $E = \frac{p^2}{2m} + V(x)$.

Continuity Equation

Exercise 2: Prove that

$$\frac{\partial(\psi^*(x, t)\psi(x, t))}{\partial t} + \frac{\partial}{\partial x}j(x, t) = 0,$$

where

$$j(x, t) = \frac{\hbar}{2mi} \left(\psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x} - \psi(x, t) \frac{\partial \psi^*(x, t)}{\partial x} \right).$$

In general, for higher dimensional problems, the change in time of probability density, $\rho(\mathbf{x}, t) = \psi^*(\mathbf{x}, t)\psi(\mathbf{x}, t)$, is equal to minus the divergence of the probability flux \mathbf{j} ,

$$\frac{\partial \rho(\mathbf{x}, t)}{\partial t} = -\nabla \cdot \mathbf{j}.$$

This is the so-called *Continuity Equation*.

Note: Remember that given a vector field \mathbf{j} , e.g., $\mathbf{j}(x, y, z) = j_1(x, y, z)\hat{i} + j_2(x, y, z)\hat{j} + j_3(x, y, z)\hat{k}$, the divergence of \mathbf{j} is defined as the dot product of the “del” operator $\nabla = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})$ and vector \mathbf{j} as follows:

$$\nabla \cdot \mathbf{j} = \frac{\partial j_1}{\partial x} + \frac{\partial j_2}{\partial y} + \frac{\partial j_3}{\partial z}.$$

3 Stationary States

Stationary states are states for which the probability density $\rho(x, t) = \psi^*(x, t)\psi(x, t)$ is constant at all times (i.e., states for which $\frac{\partial \rho(x, t)}{\partial t} = 0$, and therefore $\nabla \cdot \mathbf{j} = 0$). In this section we will show that if $\psi(x, t)$ is factorizable according to $\psi(x, t) = \phi(x)f(t)$, then $\psi(x, t)$ is a stationary state.

Substituting $\psi(x, t)$ in the time dependent Schrödinger equation we obtain:

$$\phi(x)i\hbar \frac{\partial f(t)}{\partial t} = -f(t) \frac{\hbar^2}{2m} \frac{\partial^2 \phi(x)}{\partial x^2} + f(t)V(x)\phi(x),$$

and dividing both sides by $f(t)\phi(x)$ we obtain:

$$\frac{i\hbar}{f(t)} \frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m\phi(x)} \frac{\partial^2 \phi(x)}{\partial x^2} + V(x). \quad (4)$$

Since the right hand side (r.h.s) of Eq. (4) can only be a function of x and the l.h.s. can only be a function of t for any x and t , and both functions have to be equal to each other, then such function must be equal to a constant E . Mathematically,

$$\begin{aligned} \frac{i\hbar}{f(t)} \frac{\partial f(t)}{\partial t} = E &\Rightarrow f(t) = f(0)\exp\left(-\frac{i}{\hbar}Et\right), \\ -\frac{\hbar^2}{2m\phi(x)} \frac{\partial^2 \phi(x)}{\partial x^2} + V(x) = E &\Rightarrow \boxed{\hat{H}\phi(x) = E\phi(x)}. \end{aligned}$$

The boxed equation is called the *time independent Schrödinger equation*.

Furthermore, since $f(0)$ is a constant, function $\tilde{\phi}(x) = f(0)\phi(x)$ also satisfies the time independent Schrödinger equation as follows,

$$\boxed{\hat{H}\tilde{\phi}(x) = E\tilde{\phi}(x)}, \quad (5)$$

and

$$\psi(x, t) = \tilde{\phi}(x)\exp\left(-\frac{i}{\hbar}Et\right).$$

Eq. (5) indicates that E is the *eigenvalue* of \hat{H} associated with the eigenfunction $\tilde{\phi}(x)$.

Exercise 3: Prove that \hat{H} is a Hermitian operator.

Exercise 4: Prove that $-i\hbar\partial/\partial x$ is a Hermitian operator.

Exercise 5: Prove that if two hermitian operators \hat{Q} and \hat{P} satisfy the equation $\hat{Q}\hat{P} = \hat{P}\hat{Q}$, i.e., if P and Q commute (*vide infra*), the product operator $\hat{Q}\hat{P}$ is also hermitian.

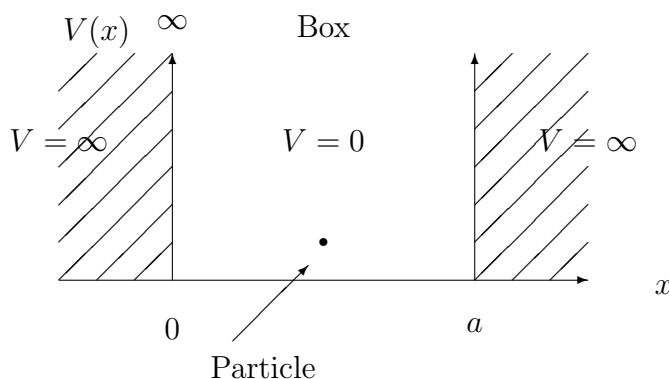
Since \hat{H} is hermitian, E is a real number $\Rightarrow E = E^*$ (see Property 1 of Hermitian operators), then,

$$\psi^*(x, t)\psi(x, t) = \tilde{\phi}^*(x)\tilde{\phi}(x).$$

Since $\tilde{\phi}(x)$ depends only on x , $\frac{\partial}{\partial t}(\tilde{\phi}^*(x)\tilde{\phi}(x)) = 0$, then, $\frac{\partial}{\partial t}\psi^*(x, t)\psi(x, t) = 0$. This demonstration proves that if $\psi(x, t) = \phi(x)f(t)$, then $\psi(x, t)$ is a stationary function.

4 Particle in the Box

The particle in the box can be represented by the following diagram:**R1(22)**



The goal of this section is to show that a particle with energy E and mass m in the box-potential $V(x)$ defined as

$$V(x) = \begin{cases} 0, & \text{when } 0 \leq x \leq a, \\ \infty, & \text{otherwise,} \end{cases}$$

has *stationary states* and a *discrete absorption spectrum* (i.e., the particle absorbs only certain discrete values of energy called *quanta*). To that end, we first solve the equation $\hat{H}\tilde{\phi}(x) = E\tilde{\phi}(x)$, and then we obtain the stationary states $\psi(x, t) = \tilde{\phi}(x)\exp(-\frac{i}{\hbar}Et)$.

Since $\tilde{\phi}(x)$ has to be continuous, single valued and square integrable (see Postulate 1), $\tilde{\phi}(0)$ and $\tilde{\phi}(a)$ must satisfy the appropriate boundary conditions both inside and outside the box. The

boundary conditions inside the box lead to:

$$-\frac{\hbar^2}{2m} \frac{\partial}{\partial x^2} \Phi(x) = E\Phi(x), \quad \Rightarrow \quad \Phi(x) = A \sin(Kx). \quad (6)$$

Functions $\Phi(x)$ determine the stationary states inside the box. The boundary conditions outside the box are,

$$-\frac{\hbar^2}{2m} \frac{\partial}{\partial x^2} \Phi(x) + \infty \Phi(x) = E\Phi(x), \quad \Rightarrow \quad \Phi(x) = 0,$$

and determine the energy associated with $\Phi(x)$ inside the box as follows. From Eq. (6), we obtain: $\frac{\hbar^2}{2m} AK^2 = EA$, and, $\Phi(a) = A \sin(Ka) = 0$,

$$\Rightarrow \quad Ka = n\pi, \quad \text{with } n = 1, 2, \dots \quad \Rightarrow$$

Note that the number of *nodes* of Φ (i.e., the number of coordinates where $\Phi(x) = 0$), is equal to $n - 1$ for a given energy, and the energy levels are,

$$E = \frac{\hbar^2}{2m} \frac{n^2 \pi^2}{a^2}, \quad \text{with } n = 1, 2, \dots$$

e.g.,

$$E(n = 1) = \frac{\hbar^2}{2m} \frac{\pi^2}{a^2},$$

$$E(n = 2) = \frac{\hbar^2}{2m} \frac{4\pi^2}{a^2}, \dots$$

Conclusion: The energy of the particle in the box is quantized! (i.e., the absorption spectrum of the particle in the box is not continuous but discrete).

Exercise 6: (i) Using the particle in the box model for an electron in a quantum dot (e.g., a nanometer size silicon material) explain why larger dots emit in the red end of the spectrum, and smaller dots emit blue or ultraviolet.

(ii) Consider the molecule hexatriene $CH_2 = CH - CH = CH - CH = CH_2$ and assume that the 6 π electrons move freely along the molecule. Approximate the energy levels using the particle

in the box model. The length of the box is the sum of bond lengths with C-C = 1.54 Å, C=C = 1.35 Å, and an extra 1.54 Å, due to the ends of the molecule. Assume that only 2 electrons can occupy each electronic state and compute:

- (A) The energy of the highest occupied energy level.
- (B) The energy of the lowest unoccupied energy level.
- (C) The energy difference between the highest and the lowest energy levels, and compare such energy difference with the energy of the peak in the absorption spectrum at $\lambda_{MAX}=268\text{nm}$.
- (D) Predict whether the peak of the absorption spectrum for $CH_2 = CH - (CH = CH)_n - CH = CH_2$ would be red- or blue-shifted relative to the absorption spectrum of hexatriene.

5 Commutator

The *commutator* $[\hat{A}, \hat{B}]$ is defined as follows:**R4(97)**

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}.$$

Two operators \hat{A} and \hat{B} are said to *commute* when $[\hat{A}, \hat{B}] = 0$.

Exercise 7: Prove that $[\hat{x}, -i\hbar\frac{\partial}{\partial x}] = i\hbar$.

Hint: Prove that $[\hat{x}, -i\hbar\frac{\partial}{\partial x}]\psi(x) = i\hbar\psi(x)$, where $\psi(x)$ is a function of x .

6 Uncertainty Relations

The goal of this section is to show that the uncertainties $\Delta A = \sqrt{\langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle}$ and $\Delta B = \sqrt{\langle (\hat{B} - \langle \hat{B} \rangle)^2 \rangle}$, of any pair of hermitian operators \hat{A} and \hat{B} , satisfy the uncer-

tainty relation: **R3(437)**

$$(\Delta A)^2(\Delta B)^2 \geq \frac{1}{4} \langle i[A, B] \rangle^2. \quad (7)$$

In particular, when $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p}$, we obtain the *Heisenberg uncertainty relation*:

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}. \quad (8)$$

Proof:

$$\begin{aligned} \hat{U} &\equiv \hat{A} - \langle A \rangle, & \phi(\lambda, x) &\equiv (\hat{U} + i\lambda\hat{V})\Phi(x), \\ \hat{V} &\equiv \hat{B} - \langle B \rangle, & I(\lambda) &\equiv \int dx \phi^*(\lambda, x)\phi(\lambda, x) \geq 0, \end{aligned}$$

$$I(\lambda) = \int dx [(\hat{A} - \langle A \rangle)\Phi(x) + i\lambda(\hat{B} - \langle B \rangle)\Phi(x)]^* [(\hat{A} - \langle A \rangle)\Phi(x) + i\lambda(\hat{B} - \langle B \rangle)\Phi(x)],$$

$$I(\lambda) = \langle \hat{U}\Phi | \hat{U}\Phi \rangle + \lambda^2 \langle V\Phi | V\Phi \rangle - i\lambda (\langle V\Phi | U\Phi \rangle - \langle U\Phi | V\Phi \rangle),$$

$$I(\lambda) = \langle \Phi | U^2 | \Phi \rangle + \lambda^2 \langle \Phi | V^2 | \Phi \rangle - i\lambda \langle \Phi | UV - VU | \Phi \rangle \geq 0, \quad (9)$$

The minimum value of $I(\lambda)$, as a function of λ , is reached when $\partial I / \partial \lambda = \partial I / \partial \lambda^* = 0$.

This condition implies that

$$2\lambda(\Delta B)^2 = i \langle [A, B] \rangle, \quad \Rightarrow \quad \lambda = \frac{i \langle [A, B] \rangle}{2(\Delta B)^2}.$$

Substituting this expression for λ into Eq. (9), we obtain:

$$(\Delta A)^2 + \frac{i^2 \langle A, B \rangle^2}{4(\Delta B)^2} - \frac{i^2 \langle A, B \rangle^2}{2(\Delta B)^2} \geq 0,$$

$$(\Delta A)^2(\Delta B)^2 \geq \frac{i^2 \langle A, B \rangle^2}{4}.$$

Exercise 8: Compute $\langle X \rangle$, $\langle P \rangle$, ΔX and ΔP for the particle in the box in its minimum energy state and verify that ΔX and ΔP satisfy the uncertainty relation given by Eq. (8)?

With the exception of a few concepts (e.g., the *Exclusion Principle* that is introduced later in these lectures), the previous sections have already introduced most of Quantum Theory. Furthermore, we have shown how to solve the equations introduced by Quantum Theory for the simplest possible problem, which is the particle in the box. There are a few other problems that can also be solved analytically (e.g., the *harmonic-oscillator* and the *rigid-rotor* described later in these lectures). However, most of the problems of interest in Chemistry have equations that are too complicated to be solved analytically. This observation has been stated by Paul Dirac as follows: *The underlying physical laws necessary for the mathematical theory of a large part of Physics and the whole of Chemistry are thus completed and the difficulty is only that exact application of these laws leads to the equations much too complicated to be soluble.* It is, therefore, essential, to introduce approximate methods (e.g., *perturbation methods* and *variational methods*).

7 Time Independent Perturbation Theory

Consider the time independent Schrödinger equation, **R2(453)**

$$\hat{H}\phi_n(x) = E_n\phi_n(x), \quad (10)$$

for a system described by the Hamiltonian $\hat{H} = \hat{p}^2/2m + \hat{V}$, and assume that all the eigenfunctions $\phi_n(x)$ are known. The goal of this section is to show that these eigenfunctions $\phi_n(x)$ can be used to solve the time independent Schrödinger equation of a slightly different problem: a problem described by the Hamiltonian $\hat{H}' = \hat{H} + \lambda\hat{\omega}$. This is accomplished by implementing the equations of Perturbation Theory derived in this section.

Consider the equation

$$(\hat{H} + \lambda\hat{\omega})\tilde{\Phi}_n(\lambda, x) = \tilde{E}_n(\lambda)\tilde{\Phi}_n(\lambda, x), \quad (11)$$

where λ is a *small* parameter, so that both $\tilde{\Phi}_n(\lambda)$ and $\tilde{E}_n(\lambda)$ are well approximated by rapidly

convergent expansions in powers of λ (i.e., expansions where only the first few terms are important).

Expanding $\tilde{\Phi}_n(\lambda)$ we obtain,

$$\tilde{\Phi}_n(\lambda, x) = \sum_j C_{jn}(\lambda) \phi_j(x).$$

Substituting this expression in the time independent Schrödinger equation we obtain,

$$\sum_j C_{jn}(\lambda) [\hat{H} \phi_j(x) + \lambda \hat{\omega} \phi_j(x)] = \tilde{E}_n(\lambda) \sum_k C_{kn}(\lambda) \phi_k(x),$$

therefore,

$$C_{ln}(\lambda) E_l + \lambda \sum_j C_{jn}(\lambda) \langle \phi_l | \hat{\omega} | \phi_j \rangle = \tilde{E}_n(\lambda) C_{ln}(\lambda). \quad (12)$$

Expanding C_{kj} and E_n in powers of λ we obtain,

$$C_{kj}(\lambda) = C_{kj}^{(0)} + C_{kj}^{(1)} \lambda + C_{kj}^{(2)} \lambda^2 + \dots,$$

and

$$\tilde{E}_n(\lambda) = E_n^{(0)} + E_n^{(1)} \lambda + E_n^{(2)} \lambda^2 + \dots$$

Substituting these expansions into Eq. (12) we obtain,

$$\begin{aligned} & (C_{ln}^{(0)} E_l - E_n^{(0)} C_{ln}^{(0)}) + \lambda (C_{ln}^{(1)} E_l + \sum_j C_{jn}^{(0)} \langle \phi_l | \hat{\omega} | \phi_j \rangle - E_n^{(0)} C_{ln}^{(1)} - E_n^{(1)} C_{ln}^{(0)}) + \\ & \times \lambda^2 (C_{ln}^{(2)} E_l + \sum_j C_{jn}^{(1)} \langle \phi_l | \hat{\omega} | \phi_j \rangle - E_n^{(2)} C_{ln}^{(0)} - E_n^{(0)} C_{ln}^{(2)} - E_n^{(1)} C_{ln}^{(1)}) + \dots = 0. \end{aligned}$$

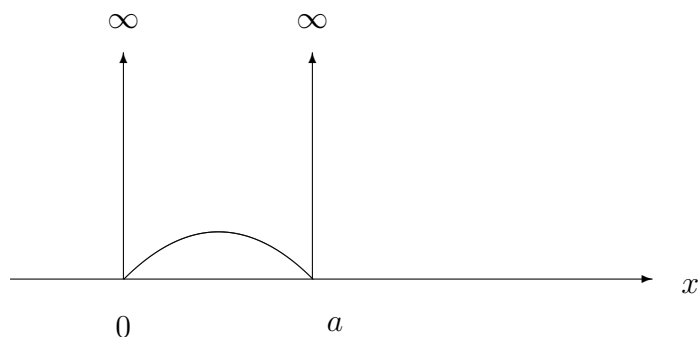
This equation must be valid for any λ . Therefore, each of the terms in between parenthesis must be equal to zero.

$$\begin{aligned} \text{Zeroth order in } \lambda & \left\{ \begin{array}{l} C_{ln}^{(0)} (E_l - E_n^{(0)}) = 0, \\ \text{if } l \neq n, \text{ then } C_{ln}^{(0)} = 0, \\ \text{if } l = n, \text{ then } C_{nn}^{(0)} = 1, \text{ and } E_l = E_n^{(0)}. \end{array} \right. \\ \text{First order in } \lambda & \left\{ \begin{array}{l} C_{ln}^{(1)} (E_l - E_n^{(0)}) = E_n^{(1)} C_{ln}^{(0)} - \sum_j C_{jn}^{(0)} \langle \phi_l | \hat{\omega} | \phi_j \rangle, \\ \text{if } l \neq n, \text{ then } C_{ln}^{(1)} (E_l - E_n^{(0)}) = -C_{nn}^{(0)} \langle \phi_l | \hat{\omega} | \phi_n \rangle, \\ \text{if } l = n, \text{ then } E_n^{(1)} C_{ln}^{(0)} = C_{nn}^{(0)} \langle \phi_n | \hat{\omega} | \phi_n \rangle. \end{array} \right. \end{aligned}$$

Note that $C_{nn}^{(1)}$ is not specified by the equations listed above. $C_{nn}^{(1)}$ is obtained by normalizing the wave function written to first order in λ .

$$\text{2nd order in } \lambda \left\{ \begin{array}{l} C_{ln}^{(2)}(E_l - E_n) + \sum_j C_{jn}^{(1)} \langle \phi_l | \hat{\omega} | \phi_j \rangle = E_n^{(2)} C_{ln}^{(0)} + E_n^{(1)} C_{ln}^{(1)}, \\ \text{if } l = n, \text{ then } E_n^{(2)} = \sum_{j \neq n} C_{jn}^{(1)} \langle \phi_n | \hat{\omega} | \phi_j \rangle = - \sum_{j \neq n} \frac{\langle \phi_n | \hat{\omega} | \phi_j \rangle \langle \phi_j | \hat{\omega} | \phi_n \rangle}{(E_j - E_n^{(0)})}, \\ \text{if } l \neq n, \text{ then } C_{ln}^{(2)}(E_l - E_n^{(0)}) = - \sum_j C_{jn}^{(1)} \langle \phi_l | \hat{\omega} | \phi_j \rangle - \frac{\langle \phi_n | \hat{\omega} | \phi_n \rangle \langle \phi_l | \hat{\omega} | \phi_n \rangle}{(E_l - E_n^{(0)})} = \\ = \sum_j \frac{\langle \phi_j | \hat{\omega} | \phi_n \rangle \langle \phi_l | \hat{\omega} | \phi_j \rangle}{(E_j - E_n^{(0)})} - \frac{\langle \phi_n | \hat{\omega} | \phi_n \rangle \langle \phi_l | \hat{\omega} | \phi_n \rangle}{(E_l - E_n^{(0)})}. \end{array} \right.$$

Exercise 9: Calculate the energy shifts to first order in λ for all excited states of the perturbed particle in the box described by the following potential:



Assume that the potential is described by perturbation $W(x) = \text{Sin}(\frac{\pi x}{a})$ to the particle in the box.

8 Time Dependent Perturbation Theory

Given an arbitrary state, **R2(410)**

$$\tilde{\psi}(x, t) = \sum_j C_j \Phi_j(x) e^{-\frac{i}{\hbar} E_j t},$$

for the initially unperturbed system described by the Hamiltonian \hat{H} , for which $\hat{H}\hat{\Phi}_j = E_j\hat{\Phi}_j$ and $i\hbar\frac{\partial\tilde{\psi}}{\partial t} = \hat{H}\tilde{\psi}$, let us obtain the solution of the time dependent Schrödinger equation:

$$i\hbar\frac{\partial\psi}{\partial t} = [\hat{H} + \lambda\hat{\omega}(t)]\psi, \quad (13)$$

assuming that such solution can be written as a rapidly convergent expansion in powers of λ ,

$$\psi_\lambda(x, t) = \sum_j \sum_{l=0}^{\infty} C_{jl}(t)\lambda^l\hat{\Phi}_j(x)e^{-\frac{i}{\hbar}E_jt}. \quad (14)$$

Substituting Eq. (14) into Eq. (13) we obtain,

$$i\hbar\sum_{l=0}^{\infty} \left(\dot{C}_{kl}(t)\lambda^l + C_{kl}(t)\lambda^l\left(-\frac{i}{\hbar}E_k\right) \right) e^{-\frac{i}{\hbar}E_kt} = \sum_j \sum_{l=0}^{\infty} C_{jl}(t)\lambda^l (\langle \Phi_k | \Phi_j \rangle E_j + \lambda \langle \Phi_k | \hat{\omega} | \Phi_j \rangle) e^{-\frac{i}{\hbar}E_jt}.$$

Terms with λ^0 : (Zero-order time dependent perturbation theory)

$$+i\hbar[\dot{C}_{k_0}(t)e^{-\frac{i}{\hbar}E_kt} + C_{k_0}(t)\left(-\frac{i}{\hbar}E_k\right)e^{-\frac{i}{\hbar}E_kt}] = \sum_j C_{j_0}(t)\delta_{kj}E_je^{-\frac{i}{\hbar}E_jt} = C_{k_0}(t)E_k e^{-\frac{i}{\hbar}E_kt}.$$

Since,

$$\dot{C}_{k_0}(t) = 0, \quad \Rightarrow \quad C_{k_0}(t) = C_{k_0}(0).$$

Therefore, the unperturbed wave function is correct to zeroth order in λ .

Terms with λ : (First-order time dependent perturbation theory)

$$i\hbar[\dot{C}_{k_1}(t)e^{-\frac{i}{\hbar}E_kt} + C_{k_1}(t)\left(-\frac{i}{\hbar}E_k\right)e^{-\frac{i}{\hbar}E_kt}] = \sum_j C_{j_1}(t)\delta_{kj}E_je^{-\frac{i}{\hbar}E_jt} + C_{j_0}(t)\langle \Phi_k | \hat{\omega} | \Phi_j \rangle e^{-\frac{i}{\hbar}E_jt},$$

$$\dot{C}_{k_1}(t) = -\frac{i}{\hbar} \sum_j \left(C_{j_0}(0) \langle \Phi_k | \hat{\omega} | \Phi_j \rangle e^{-\frac{i}{\hbar}(E_j - E_k)t} \right).$$

Therefore,

$$\dot{C}_{k_1}(t) = -\frac{i}{\hbar} \sum_j C_{j_0}(0) \langle \Phi_k | e^{\frac{i}{\hbar}E_kt} \hat{\omega} e^{-\frac{i}{\hbar}E_jt} | \Phi_j \rangle = -\frac{i}{\hbar} \sum_j C_{j_0}(0) \langle \Phi_k | e^{\frac{i}{\hbar}\hat{H}t} \hat{\omega} e^{-\frac{i}{\hbar}\hat{H}t} | \Phi_j \rangle, \quad (15)$$

Eq. (15) was obtained by making the substitution $e^{-\frac{i}{\hbar}\hat{H}t}|\Phi_j \rangle = e^{-\frac{i}{\hbar}E_j t}|\Phi_j \rangle$, which is justified in the note that follows this derivation. Integrating Eq. (15) we obtain,

$$C_{k_1}(t) = -\frac{i}{\hbar} \int_{-\infty}^t dt' \sum_j C_{j_0}(0) \langle \Phi_k | e^{\frac{i}{\hbar}\hat{H}t'} \hat{\omega} e^{-\frac{i}{\hbar}\hat{H}t'} | \Phi_j \rangle .$$

which can also be written as follows:

$$C_{k_1}(t) = -\frac{i}{\hbar} \int_{-\infty}^t dt' \langle \Phi_k | e^{\frac{i}{\hbar}\hat{H}t'} \hat{\omega} e^{-\frac{i}{\hbar}\hat{H}t'} | \tilde{\psi}_0 \rangle .$$

This expression gives the correction of the expansion coefficients to first order in λ .

Note: The substitution made in Eq. (15) can be justified as follows. The exponential function is defined in powers series as follows,

$$e^A = \sum_{n=0}^{\infty} \frac{A^n}{n!} = 1 + A + \frac{1}{2!}AA + \dots, \quad \mathbf{R4(169)}$$

In particular, when $A = -i\hat{H}t/\hbar$,

$$e^{-\frac{i}{\hbar}\hat{H}t} = 1 + \left(-\frac{i}{\hbar}\hat{H}t\right) + \frac{1}{2!}\left(-\frac{i}{\hbar}\right)^2\hat{H}\hat{H} + \dots$$

Furthermore, since

$$\hat{H}|\Phi_j \rangle = E_j|\Phi_j \rangle,$$

and,

$$\hat{H}\hat{H}|\Phi_j \rangle = E_j\hat{H}|\Phi_j \rangle = E_j^2|\Phi_j \rangle,$$

we obtain,

$$e^{-\frac{i}{\hbar}\hat{H}t}|\Phi_j \rangle = \left[1 + \left(-\frac{i}{\hbar}E_j t\right) + \frac{1}{2!}\left(-\frac{i}{\hbar}\right)^2 E_j^2 + \dots\right]|\Phi_j \rangle = e^{-\frac{i}{\hbar}E_j t}|\Phi_j \rangle,$$

which is the substitution implemented in Eq. (15).

Terms with λ^2 : (Second-order time dependent perturbation theory)

$$i\hbar[\dot{C}_{k_2}(t) + C_{k_2}(t)\left(-\frac{i}{\hbar}E_k\right)]e^{-\frac{i}{\hbar}E_k t} = \sum_j [C_{j_2}(t)\delta_{kj}E_j + C_{j_1}(t)\langle \Phi_k | \hat{\omega} | \Phi_j \rangle]e^{-\frac{i}{\hbar}E_j t},$$

$$\begin{aligned} \dot{C}_{k_2}(t) &= -\frac{i}{\hbar} \sum_j \langle \Phi_k | e^{\frac{i}{\hbar} \hat{H}t} \hat{\omega} e^{-\frac{i}{\hbar} \hat{H}t} | \Phi_j \rangle C_{j_1}(t), \\ C_{k_2}(t) &= \left(-\frac{i}{\hbar} \right) \int_{-\infty}^t dt' \sum_j \langle \Phi_k | e^{\frac{i}{\hbar} \hat{H}t'} \hat{\omega} e^{-\frac{i}{\hbar} \hat{H}t'} | \Phi_j \rangle C_{j_1}(t'), \\ C_{k_2}(t) &= \left(-\frac{i}{\hbar} \right)^2 \sum_j \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' \langle \Phi_k | e^{\frac{i}{\hbar} \hat{H}t'} \hat{\omega} e^{-\frac{i}{\hbar} \hat{H}t'} | \Phi_j \rangle \langle \Phi_j | e^{\frac{i}{\hbar} \hat{H}t''} \hat{\omega} e^{-\frac{i}{\hbar} \hat{H}t''} | \tilde{\psi}_0 \rangle. \end{aligned}$$

Since $1 = \sum_j |\Phi_j\rangle \langle \Phi_j|$,

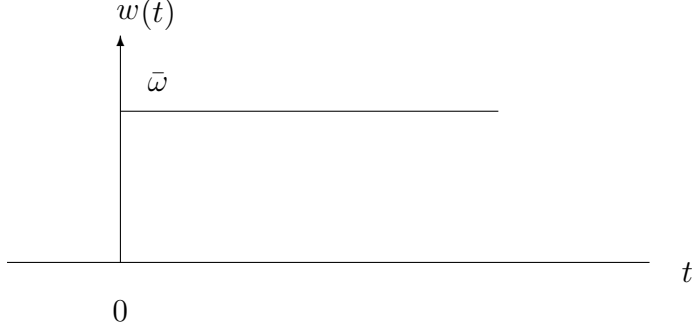
$$C_{k_2}(t) = \left(-\frac{i}{\hbar} \right)^2 \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' \langle \Phi_k | e^{\frac{i}{\hbar} \hat{H}t'} \hat{\omega} e^{-\frac{i}{\hbar} \hat{H}(t'-t'')} \hat{\omega} e^{-\frac{i}{\hbar} \hat{H}t''} | \tilde{\psi}_0 \rangle.$$

This expression gives the correction of the expansion coefficients to second order in λ .

Limiting Cases

(1) Impulsive Perturbation:

The perturbation is abruptly "switched on": **R2(412)**



According to the equations for first order time dependent perturbation theory,

$$C_{k_1}(t) = -\frac{i}{\hbar} \sum_j \langle \Phi_k | \bar{\omega} | \Phi_j \rangle C_{j_0}(0) \int_0^t dt' e^{-\frac{i}{\hbar}(E_j - E_k)t'},$$

therefore,

$$C_{k_1}(t) = \left(-\frac{i}{\hbar} \right) \sum_j \frac{C_{j_0}(0) \langle \Phi_k | \bar{\omega} | \Phi_j \rangle}{\left(-\frac{i}{\hbar}(E_j - E_k) \right)} \left[e^{-\frac{i}{\hbar}(E_j - E_k)t} - 1 \right].$$

Assuming that initially: $C_j = \delta_{lj}$, $\Rightarrow C_{j_0} = \delta_{lj}$. Therefore,

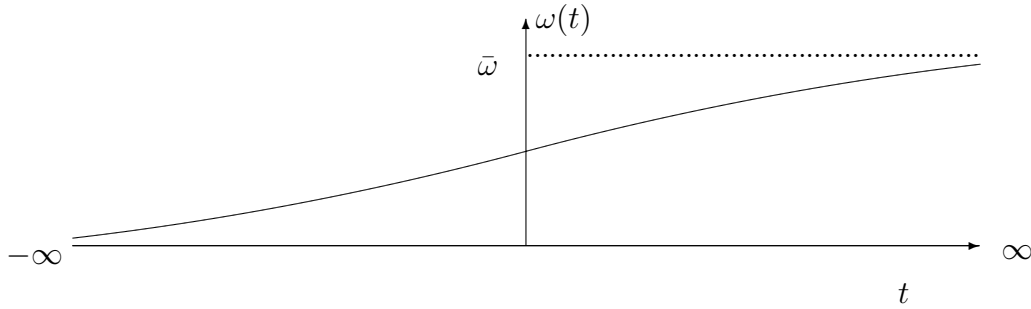
$$C_{k_1}(t) = -\frac{\langle \Phi_k | \bar{\omega} | \Phi_l \rangle}{(E_l - E_k)} [1 - e^{-\frac{i}{\hbar}(E_l - E_k)t}],$$

when $k \neq l$. Note that $C_{l_1}(t)$ must be obtained from the normalization of the wave function expanded to first order in λ .

Exercise 10: Compare this expression of the first order correction to the expansion coefficients, due to an *impulsive perturbation*, with the expression obtained according to the time-*independent* perturbation theory.

(2) Adiabatic limit:

The perturbation is "switched-on" very slowly ($\frac{d\omega_t}{dt} \ll \epsilon$, with ϵ arbitrarily small): **R2(448)**



$$C_{k_1}(t) = \left(-\frac{i}{\hbar}\right) \int_{-\infty}^t dt' \langle \Phi_k | \omega(t') | \Phi_l \rangle e^{-\frac{i}{\hbar}(E_l - E_k)t'}$$

Integrating by parts we obtain,

$$C_{k_1}(t) = \left(-\frac{i}{\hbar}\right) \left[\frac{e^{-\frac{i}{\hbar}(E_l - E_k)t'}}{\left(-\frac{i}{\hbar}\right)(E_l - E_k)} \langle \Phi_k | \omega(t') | \Phi_l \rangle \Big|_{t'=-\infty}^{t'=t} - \int_{-\infty}^t dt' \frac{e^{-\frac{i}{\hbar}(E_l - E_k)t'}}{\left(-\frac{i}{\hbar}\right)(E_l - E_k)} \langle \Phi_k | \frac{\partial \omega}{\partial t'} | \Phi_l \rangle \right],$$

and, since $\langle \Phi_k | \omega(-\infty) | \Phi_l \rangle = 0$,

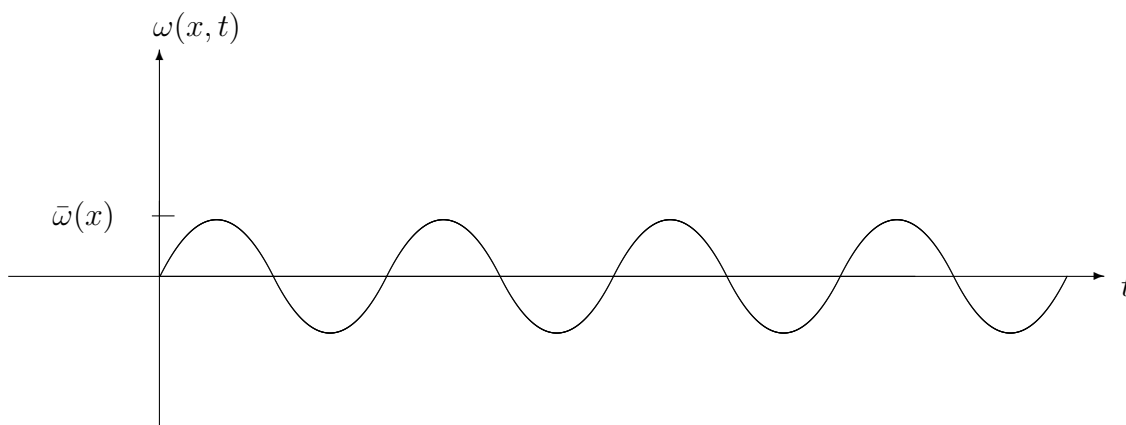
$$C_{k_1}(t) = \frac{\langle \Phi_k | \omega(t) | \Phi_l \rangle}{(E_l - E_k)} e^{-\frac{i}{\hbar}(E_l - E_k)t},$$

when $k \neq l$. Note that $C_{l_1}(t)$ must be obtained from the normalization of the wave function expanded to first order in λ .

Exercise 11: Compare this expression for the first order correction to the expansion coefficients, due to an *adiabatic perturbation*, with the expression obtained according to the time-*independent* perturbation theory.

(3) Sinusoidal Perturbation:

The sinusoidal perturbation is defined as follows, $\hat{\omega}(t, x) = \bar{\omega}(x)\text{Sin}(\Omega t)$ when $t \geq 0$ and $\hat{\omega}(t, x) = 0$, otherwise.



It is, however, more conveniently defined in terms of exponentials,

$$\hat{\omega} = \frac{\bar{\omega}(x)}{2i} [e^{i\Omega t} - e^{-i\Omega t}].$$

Therefore,

$$C_{k_1}(t) = -\frac{i}{\hbar} \int_0^t dt' \langle \Phi_k | e^{\frac{i}{\hbar} \hat{H} t'} \hat{\omega}(t') e^{-\frac{i}{\hbar} \hat{H} t'} | \tilde{\psi}_0 \rangle, \quad (16)$$

with $|\tilde{\psi}_0 \rangle = \sum_j C_j |\Phi_j \rangle$, and $\hat{H} \Phi_j = E_j \Phi_j$. Substituting these expressions into Eq. (16) we

obtain,

$$C_{k_1}(t) = -\frac{1}{2\hbar} \sum_j C_j \langle \Phi_k | \bar{\omega} | \Phi_j \rangle \int_0^t dt' \left(e^{\frac{i}{\hbar}[(E_k - E_j) + \hbar\Omega]t'} - e^{\frac{i}{\hbar}[(E_k - E_j) - \hbar\Omega]t'} \right),$$

and therefore,

$$C_{k_1}(t) = \frac{1}{i2\hbar} \sum_j C_j \bar{\omega}_{kj} \left[\frac{1 - e^{\frac{i}{\hbar}[(E_k - E_j) + \hbar\Omega]t}}{\frac{E_k - E_j}{\hbar} + \Omega} - \frac{1 - e^{\frac{i}{\hbar}[(E_k - E_j) - \hbar\Omega]t}}{\frac{E_k - E_j}{\hbar} - \Omega} \right].$$

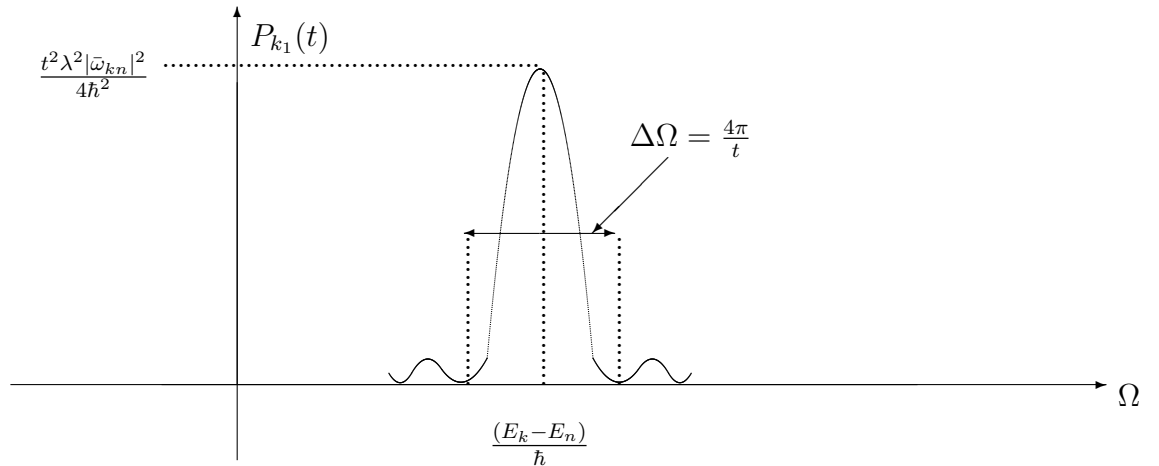
Without loss of generality, let us assume that $C_j = \delta_{nj}$ (i.e., initially only state n is occupied).

For $k \geq n$ we obtain,

$$|C_{k_1}(t)|^2 = \frac{|\bar{\omega}_{kn}|^2}{k\hbar^2} \left| \frac{1 - e^{i[\frac{(E_k - E_n)}{\hbar} + \Omega]t}}{\frac{(E_k - E_n)}{\hbar} + \Omega} - \frac{1 - e^{i[\frac{(E_k - E_n)}{\hbar} - \Omega]t}}{\frac{(E_k - E_n)}{\hbar} - \Omega} \right|^2.$$

Factor $|\bar{\omega}|_{kn}$ determines the intensity of the transition (e.g., the *selection rules*). The first term (called *anti-resonant*) is responsible for emission. The second term is called *resonant* and is responsible for absorption.

For $k \neq n$, $P_{k_1}(t) = \lambda^2 |C_{k_1}(t)|^2$ is the probability of finding the system in state k at time t (to first order in λ).



It is important to note that $P_{k_1} \ll 1$ indicates that the system has been slightly perturbed. Such

condition is satisfied only when $t \ll \frac{2\hbar}{|\omega_{kn}|\lambda}$. Therefore, the theory is useful *only* at sufficiently short times.

9 Problem Set (due 10/02/03)

Exercise 11: Consider a distribution of charges Q_i , with coordinates r_i , interacting with plane polarized radiation. Assume that the system is initially in the eigenstate Φ_j of the unperturbed charge distribution.

- (A) Write the expression of the sinusoidal perturbation in terms of Q_i, r_i , and the radiation frequency ω and amplitude ϵ_0 .
- (B) Expand the time dependent wave function ψ of the charge distribution in terms of the eigenfunctions Φ_k of the unperturbed charge distribution.
- (C) Find the expansion coefficients, according to first order time dependent perturbation theory.
- (D) What physical information is given by the square of the expansion coefficients?
- (E) What frequency would be optimum to populate state k ? Assume $E_k \geq E_j$.
- (F) Which other state could be populated with radiation of the optimum frequency found in term (E)?
- (G) When would the transition $j \rightarrow k$ be forbidden?

Exercise 12: A particle in the ground state of a square box of length $|a|$ is subject to a perturbation $\omega(t) = axe^{-t^2/\tau}$.

- (A) What is the probability that the particle ends up in the first excited state after a long time $t \gg \tau$?
- (B) How does that probability depend on τ ?

Exercise 13:

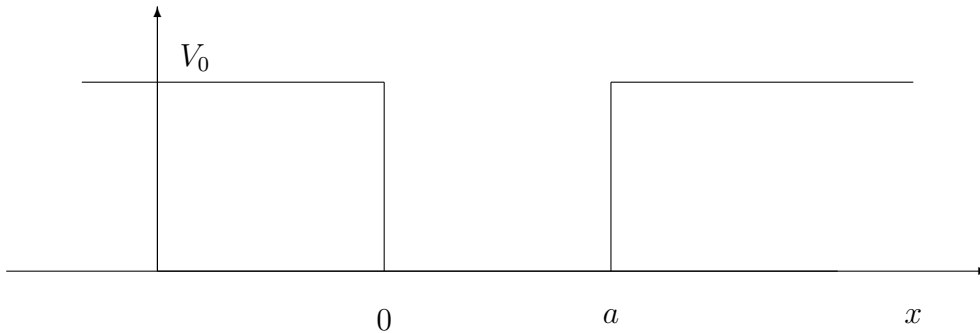


Figure 1

- (a) Compute the minimum energy stationary state for a particle in the square well (See Fig.1) by solving the time independent Schrödinger equation.
- (b) What would be the minimum energy absorbed by a particle in the potential well of Fig.1?
- (c) What would be the minimum energy of the particle in the potential well of Fig.1?
- (d) What would be the minimum energy absorbed by a particle in the potential well shown in Fig.2? Assume that λ is a small parameter give the answer to first order in λ .

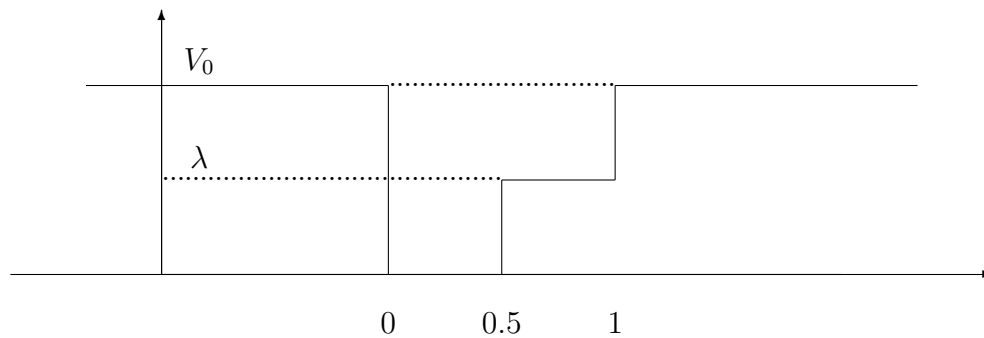


Figure 2

- Exercise 14:** (a) Prove that $\hat{P} = e^{-\hat{H}}$ is a hermitian operator.
 (b) Prove that $\hat{P} = \text{Cos}(\hat{H})$ is a hermitian operator.

10 Adiabatic Approximation

The goal of this section is to solve the time dependent Schrödinger equation,

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi, \quad (17)$$

for a time dependent Hamiltonian, $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x, t)$, where the potential $V(x, t)$ undergoes significant changes but in a very "large" time scale (e.g., a time scale much larger than the time associated with state transitions). **R2(496)**

Since $V(x, t)$ changes very slowly, we can solve the time independent Schrödinger equation at a specific time t' ,

$$\hat{H}(t')\Phi_n(x, t') = E_n(t')\Phi_n(x, t').$$

Assuming that $\frac{\partial \Phi_n}{\partial t} \approx 0$, since $V(x, t)$ changes very slowly, we find that the function,

$$\psi_n(x, t) = \Phi_n(x, t)e^{-\frac{i}{\hbar} \int_0^t E_n(t') dt'},$$

is a good approximate solution to Eq. (17). In fact, it satisfies Eq. (17) *exactly* when $\frac{\partial \Phi_n}{\partial t} = 0$.

Expanding the general solution $\psi(x, t)$ in the basis set $\Phi_n(x, t)$ we obtain:

$$\psi(x, t) = \sum_n C_n(t)\Phi_n(x, t)e^{-\frac{i}{\hbar} \int_0^t E_n(t') dt'},$$

and substituting this expression into Eq. (17) we obtain,

$$i\hbar \sum_n (\dot{C}_n \Phi_n + C_n \dot{\Phi}_n - \frac{i}{\hbar} E_n C_n \Phi_n) e^{-\frac{i}{\hbar} \int_0^t E_n(t') dt'} = \sum_n C_n E_n \Phi_n e^{-\frac{i}{\hbar} \int_0^t E_n(t') dt'},$$

where,

$$\dot{C}_k = - \sum_n C_n \langle \Phi_k | \dot{\Phi}_n \rangle e^{-\frac{i}{\hbar} \int_0^t dt' (E_n(t') - E_k(t'))}. \quad (18)$$

Note that,

$$\frac{\partial H}{\partial t} \Phi_n + H \dot{\Phi}_n = \frac{\partial E_n}{\partial t} \Phi_n + E_n \dot{\Phi}_n,$$

then,

$$\begin{aligned} \langle \Phi_k | \frac{\partial H}{\partial t} | \Phi_n \rangle + \langle \Phi_k | H | \dot{\Phi}_n \rangle &= \frac{\partial E_k}{\partial t} \delta_{kn} + E_n \langle \Phi_k | \dot{\Phi}_n \rangle, \\ \text{since } \langle \Phi_k | H | \dot{\Phi}_n \rangle &= \langle \dot{\Phi}_n | H | \Phi_k \rangle^* . \end{aligned}$$

Furthermore, if $k \neq n$ then,

$$\langle \Phi_k | \dot{\Phi}_n \rangle = \frac{\langle \Phi_k | \frac{\partial H}{\partial t} | \Phi_n \rangle}{E_n - E_k}.$$

Substituting this expression into Eq. (18) we obtain,

$$\dot{C}_k = -C_k \langle \Phi_k | \dot{\Phi}_k \rangle - \sum_{n \neq k} C_n \frac{\langle \Phi_k | \frac{\partial H}{\partial t} | \Phi_n \rangle}{(E_n - E_k)} e^{-\frac{i}{\hbar} \int_0^t dt' (E_n(t') - E_k(t'))}.$$

Let us suppose that the system starts with $C_n(0) = \delta_{nj}$, then solving by successive approximations we obtain that for $k \neq j$:

$$\dot{C}_k = \frac{\langle \Phi_k | \frac{\partial H}{\partial t} | \Phi_j \rangle}{(E_k - E_j)} e^{-\frac{i}{\hbar} \int_0^t dt' (E_j(t') - E_k(t'))}.$$

Assuming that $E_j(t)$ and $E_k(t)$ are slowly varying functions in time:

$$\begin{aligned} C_k &\approx \frac{\langle \Phi_k | \frac{\partial H}{\partial t} | \Phi_j \rangle}{\frac{i}{\hbar} (E_j - E_k)^2} [e^{-\frac{i}{\hbar} (E_j - E_k)t} - e^{-\frac{i}{\hbar} (E_j - E_k)t_0}], \\ \text{since } |e^{-\frac{i}{\hbar} (E_j - E_k)t} - e^{-\frac{i}{\hbar} (E_j - E_k)t_0}| &\leq 2. \end{aligned}$$

Therefore,

$$|C_k|^2 \approx \frac{4\hbar^2 |\langle \Phi_k | \frac{\partial H}{\partial t} | \Phi_j \rangle|^2}{(E_j - E_k)^4}.$$

The system remains in the initially populated state at all times whenever $\frac{\partial H}{\partial t}$ is sufficiently small,

$$\left| \langle \Phi_k | \frac{\partial H}{\partial t} | \Phi_j \rangle \right| \ll \frac{(E_j - E_k)^2}{\hbar}, \quad (19)$$

even when such state undergoes significant changes. This is the so-called *adiabatic approximation*.

It breaks down when $E_j \approx E_k$ because the inequality introduced by Eq. (19) can not be satisfied.

Mathematically, the condition that validates the adiabatic approximation can also be expressed

in terms of the frequency ν defined by the equation $E_j - E_k = h\nu = \frac{h}{\tau}$, (or the time period τ of the light emitted with frequency ν) as follows,

$$\frac{\tau}{2\pi} \left| \langle \Phi_k | \frac{\partial H}{\partial t} | \Phi_j \rangle \right| \ll (E_j - E_k).$$

11 Variational Theorem

The expectation value of the Hamiltonian, computed with any trial wave function, is always higher or equal than the energy of the ground state. Mathematically,

$$\langle \psi | \hat{H} | \psi \rangle \geq E_0,$$

where $\hat{H}\phi_j = E_j\phi_j$.

Proof:

$\psi = \sum_j C_j \phi_j$, where $\{\phi_j\}$ is a basis set of orthonormal eigenfunctions of the Hamiltonian \hat{H} .

$$\begin{aligned} \langle \psi | \hat{H} | \psi \rangle &= \sum_j \sum_k C_k^* C_j \langle \phi_k | \hat{H} | \phi_j \rangle, \\ &= \sum_j \sum_k C_k^* C_j E_j \delta_{kj}, \\ &= \sum_j C_j^* C_j E_j \geq E_0 \sum_j C_j^* C_j, \end{aligned}$$

where, $\sum_j C_j^* C_j = 1$.

Variational Approach

Starting with an initial trial wave function ψ defined by the expansion coefficients $\{C_j^{(0)}\}$, the optimum solution of an arbitrary problem described by the Hamiltonian \hat{H} can be obtained by minimizing the expectation value $\langle \psi | \hat{H} | \psi \rangle$ with respect to the expansion coefficients.

12 Heisenberg Representation

Consider the eigenvalue problem, **R4(124)** **R3(240)**

$$\hat{H}|\psi\rangle = E|\psi\rangle, \quad (20)$$

for an arbitrary system (e.g., an atom or molecule) described by a state $|\psi\rangle$, expanded in a basis set $\{\phi_j\}$ as follows,

$$|\psi\rangle = \sum_j C_j |\phi_j\rangle, \quad (21)$$

where $C_j = \langle \phi_j | \psi \rangle$, and $\langle \phi_j | \phi_k \rangle = \delta_{jk}$.

Substituting Eq. (21) into Eq. (20) we obtain:

$$\sum_j \hat{H} |\phi_j\rangle C_j = \sum_j E C_j |\phi_j\rangle.$$

Applying functional $\langle \phi_k |$ to both sides of this equation we obtain,

$$\sum_j \langle \phi_k | \hat{H} | \phi_j \rangle C_j = \sum_j E \langle \phi_k | \phi_j \rangle C_j, \quad (22)$$

where $\langle \phi_k | \phi_j \rangle = \delta_{kj}$ and $k = 1, 2, \dots, n$.

Introducing the notation $H_{kj} = \langle \phi_k | \hat{H} | \phi_j \rangle$ we obtain,

$$\begin{aligned} (k=1) & \rightarrow \left\{ \begin{aligned} H_{11}C_1 + H_{12}C_2 + H_{13}C_3 + \dots + H_{1n}C_n &= EC_1 + 0C_2 + \dots + 0C_n, \\ H_{21}C_1 + H_{22}C_2 + H_{23}C_3 + \dots + H_{2n}C_n &= 0C_1 + EC_2 + \dots + 0C_n, \\ \dots & \dots \\ H_{n1}C_1 + H_{n2}C_2 + H_{n3}C_3 + \dots + H_{nn}C_n &= 0C_1 + 0C_2 + \dots + EC_n, \end{aligned} \right. \end{aligned} \quad (23)$$

that can be conveniently written in terms of *matrices* and *vectors* as follows,

$$\begin{bmatrix} H_{11} & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22} & \dots & H_{2n} \\ \dots & & & \\ H_{n1} & H_{n2} & \dots & H_{nn} \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ \dots \\ C_n \end{bmatrix} = \begin{bmatrix} E & 0 & \dots & 0 \\ 0 & E & \dots & 0 \\ \dots & & & \\ 0 & 0 & \dots & E \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ \dots \\ C_n \end{bmatrix}. \quad (24)$$

This is the *Heisenberg representation* of the eigenvalue problem introduced by Eq. (20). According to the *Heisenberg representation*, also called *matrix representation*, the *ket* $|\psi\rangle$ is represented by the *vector* \mathbf{C} , with components $C_j = \langle \phi_j | \psi \rangle$, with $j=1, \dots, n$, and the *operator* \hat{H} is represented by the *matrix* \mathbf{H} with elements $H_{jk} = \langle \phi_j | \hat{H} | \phi_k \rangle$.

The expectation value of the Hamiltonian,

$$\langle \psi | H | \psi \rangle = \sum_j \sum_k C_k^* \langle \phi_k | \hat{H} | \phi_j \rangle C_j,$$

can be written in the matrix representation as follows,

$$\langle \psi | H | \psi \rangle = \mathbf{C}^\dagger \mathbf{H} \mathbf{C} = \begin{bmatrix} C_1^* & C_2^* & \dots & C_n^* \end{bmatrix} \begin{bmatrix} H_{11} & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22} & \dots & H_{2n} \\ \dots & & & \\ H_{n1} & H_{n2} & \dots & H_{nn} \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ \dots \\ C_n \end{bmatrix}.$$

Note:

(1) It is important to note that according to the matrix representation the *ket-vector* $|\psi\rangle$ is represented by a column vector with components $C_j = \langle \phi_j | \psi \rangle$, and the *bra-vector* $\langle \psi |$ is represented by a *row vector* with components C_j^* .

(2) If an *operator* is hermitian (e.g., \hat{H}) it is represented by a *hermitian matrix* (i.e., a matrix where any two elements which are symmetric with respect to the principal diagonal are complex conjugates of each other). The diagonal elements of a hermitian matrix are real numbers, therefore, its eigenvalues are real.

(3) The eigenvalue problem has a non-trivial solution *only* when the determinant $\det[\mathbf{H} - \hat{\mathbf{1}}E]$ vanishes:

$$\det[\mathbf{H} - \hat{\mathbf{1}}E] = 0, \quad \text{where } \hat{\mathbf{1}} \text{ is the unity matrix.}$$

This equation has n roots, which are the eigenvalues of \mathbf{H} .

13 Two-Level Systems

There are many problems in Quantum Chemistry that can be modeled in terms of the two-level Hamiltonian (i.e., a state-space with only two dimensions). Examples include electron transfer, proton transfer, and isomerization reactions.

Consider two states $|\phi_1\rangle$ and $|\phi_2\rangle$, of a system. Assume that these states have similar energies, E_1 and E_2 , both of them well separated from all of the other energy levels of the system,

$$\hat{H}_0|\phi_1\rangle = E_1|\phi_1\rangle,$$

$$\hat{H}_0|\phi_2\rangle = E_2|\phi_2\rangle.$$

In the presence of a perturbation,

$$W = \begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix},$$

the total Hamiltonian becomes $H = H_0 + W$. Therefore, states $|\phi_1\rangle$ and $|\phi_2\rangle$ are no longer eigenstates of the system.

The goal of this section is to compute the eigenstates of the system in the presence of the perturbation W . The eigenvalue problem,

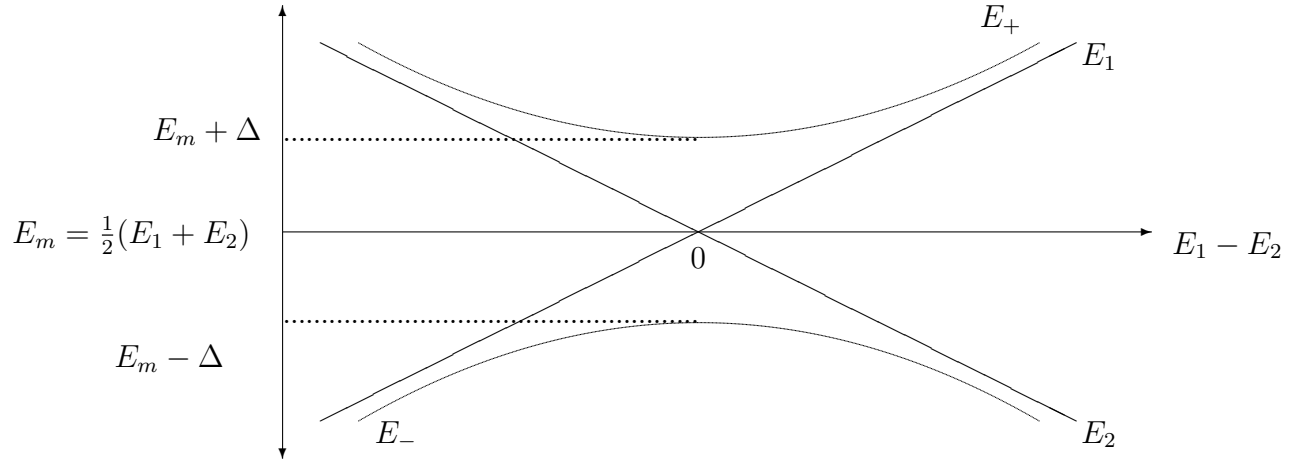
$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} E & 0 \\ 0 & E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix},$$

is solved by finding the roots of the characteristic equation, $(H_{11} - E)(H_{22} - E) - H_{12}H_{21} = 0$.

The values of E that satisfy such equation are,

$$E_{\pm} = \frac{(E_1 + E_2)}{2} \pm \sqrt{\left(\frac{E_1 - E_2}{2}\right)^2 + \Delta^2}.$$

These eigenvalues E_{\pm} can be represented as a function of the energy difference $(E_1 - E_2)$, according to the following diagram:



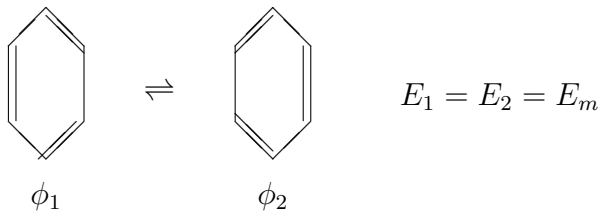
Note that E_1 and E_2 cross each other, but E_- and E_+ repel each other. Having found the eigenvalues E_{\pm} , we can obtain the eigenstates $|\psi_{\pm}\rangle = C_{1\pm}|\phi_1\rangle + C_{2\pm}|\phi_2\rangle$ by solving for $C_{1\pm}$ and $C_{2\pm}$ from the following equations:

$$C_{1\pm}(H_{11} - E_{\pm}) + C_{2\pm}H_{12} = 0,$$

$$\sum_{j=1}^2 C_{j\pm}^* C_{j\pm} = 1.$$

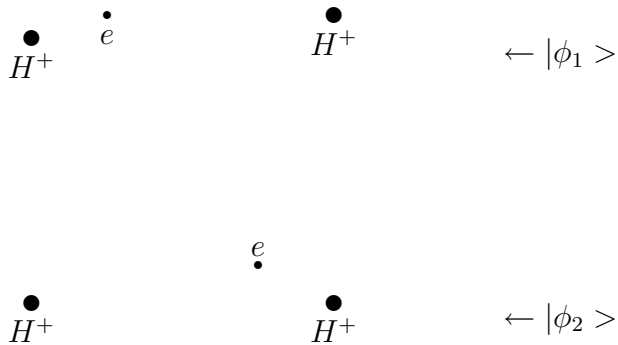
We see that in the presence of the perturbation the minimum energy state $|\psi_- \rangle$ is always more stable than the minimum energy state of the unperturbed system.

Example 1. Resonance Structure



The coupling between the two states makes the linear combination of the two more stable than the minimum energy state of the unperturbed system.

Example 2. Chemical Bond



The state of the system that involves a linear combination of these two states is more stable than E_m because $\langle \phi_1 | H | \phi_2 \rangle \neq 0$.

Time Evolution

Consider a two level system described by the Hamiltonian $H = H_0 + W$, with $H_0 | \phi_1 \rangle = E_1 |$

$\phi_1 \rangle$. Assume that the system is initially prepared in state $|\psi(0)\rangle = |\phi_1\rangle$. Due to the presence of the perturbation W , state $|\phi_1\rangle$ is not a stationary state. Therefore, the initial state evolves in time according to the time-dependent Schrödinger Equation,

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = (H_0 + W) |\psi\rangle,$$

and becomes a linear superposition of states $|\phi_1\rangle$ and $|\phi_2\rangle$,

$$|\psi(t)\rangle = C_1(t)|\phi_1\rangle + C_2(t)|\phi_2\rangle.$$

State $|\psi(t)\rangle$ can be expanded in terms of the eigenstates $|\psi_{\pm}\rangle$ as follows,

$$|\psi(t)\rangle = C_+(t)|\psi_+\rangle + C_-(t)|\psi_-\rangle,$$

where the expansion coefficients $C_{\pm}(t)$ evolve in time according to the following equations,

$$i\hbar \frac{\partial C_+(t)}{\partial t} = E_+ C_+(t),$$

$$i\hbar \frac{\partial C_-(t)}{\partial t} = E_- C_-(t).$$

Therefore, state $|\psi(t)\rangle$ can be written in terms of $|\psi_{\pm}\rangle$ as follows,

$$|\psi(t)\rangle = C_+(0)e^{-\frac{i}{\hbar}E_+t}|\psi_+\rangle + C_-(0)e^{-\frac{i}{\hbar}E_-t}|\psi_-\rangle.$$

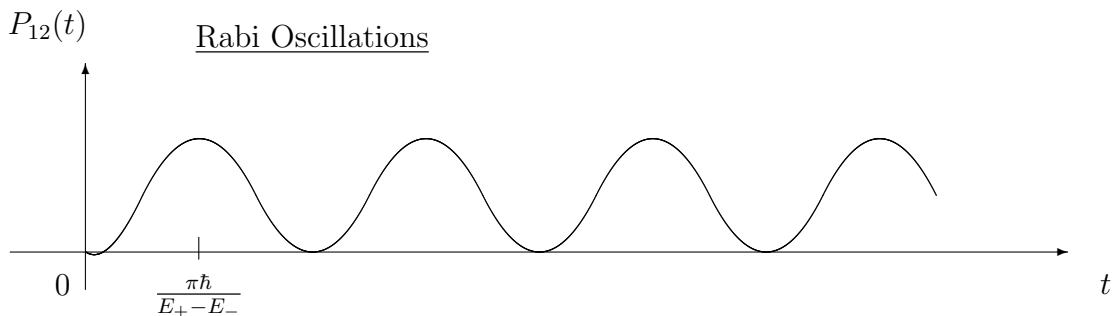
The probability amplitude of finding the system in state $|\phi_2\rangle$ at time t is,

$$P_{12}(t) = |\langle \phi_2 | \psi(t) \rangle|^2 = C_2(t)^* C_2(t),$$

which can also be written as follows,

$$P_{12}(t) = |C_{2+}C_+(0)|^2 + |C_{2-}C_-(0)|^2 + 2\text{Re}[C_{2+}^*C_+^*(0)C_{2-}C_-(0)e^{-\frac{i}{\hbar}(E_- - E_+)t}],$$

where $C_{2\pm} = \langle \phi_2 | \Psi_{\pm} \rangle$. The following diagram represents $P_{12}(t)$ as a function of time:



The frequency $\nu = (E_+ - E_-)/(\pi\hbar)$ is called *Rabi Frequency*. It is observed, e.g., in the absorption spectrum of H_2^+ (see Example 2). It corresponds to the frequency of the oscillating dipole moment which fluctuates according to the electronic configurations of $|\phi_1\rangle$ and $|\phi_2\rangle$, respectively. The oscillating dipole moment exchanges energy with an external electromagnetic field of its own characteristic frequency and, therefore, it is observed in the absorption spectrum of the system.

14 Harmonic Oscillator

Many physical systems, including molecules with configurations near their equilibrium positions, can be described (at least approximately) by the Hamiltonian of the harmonic oscillator:**R4(483)**

R1(62)

$$\hat{H} = \frac{\hat{P}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2.$$

In order to find the eigenfunctions of \hat{H} we introduce two operators called *creation* \hat{a}^+ and *annihilation* \hat{a} , which are defined as follows:

$$\hat{a}^+ \equiv \frac{1}{\sqrt{2}}(\tilde{x} - i\tilde{p}), \text{ and } \hat{a} \equiv \frac{1}{\sqrt{2}}(\tilde{x} + i\tilde{p}), \text{ where } \tilde{x} = \hat{x}\sqrt{\frac{m\omega}{\hbar}}, \text{ and } \tilde{p} = \frac{\hat{p}}{\sqrt{m\omega\hbar}}.$$

Using these definitions of \hat{a}^+ and \hat{a} , we can write \hat{H} as follows,

$$\hat{H} = (\hat{a}^+ \hat{a} + \frac{1}{2}) \hbar \omega.$$

Introducing the *number* operator \hat{N} , defined in terms of \hat{a}^+ and \hat{a} as follows,

$$\hat{N} \equiv \hat{a}^+ \hat{a},$$

we obtain that the Hamiltonian of the Harmonic Oscillator can be written as follows,

$$\hat{H} = (\hat{N} + 1/2) \hbar \omega.$$

Exercise 15: Show that if Φ_ν is an eigenfunction of \hat{H} with eigenvalue E_ν , then Φ_ν is an eigenfunction of \hat{N} with eigenvalue $\nu = \frac{E_\nu}{\hbar \omega} - \frac{1}{2}$. Mathematically, if $\hat{H}|\Phi_\nu\rangle = E_\nu|\Phi_\nu\rangle$, then $\hat{N}|\Phi_\nu\rangle = \nu|\Phi_\nu\rangle$, with $\nu = \frac{E_\nu}{\hbar \omega} - \frac{1}{2}$.

Theorem I:

The eigenvalues of \hat{N} are greater or equal to zero, i.e., $\nu \geq 0$.

Proof:

$$\int dx | \langle x | \hat{a} | \Phi_\nu \rangle |^2 \geq 0,$$

$$\langle \Phi_\nu | \hat{a}^+ \hat{a} | \Phi_\nu \rangle \geq 0,$$

$$\nu \langle \Phi_\nu | \Phi_\nu \rangle \geq 0.$$

As a consequence: $\hat{a}|\Phi_0\rangle = 0$,

$$\frac{1}{\sqrt{2}} \left[\hat{x} \sqrt{\frac{m\omega}{\hbar}} + i \frac{\hat{p}}{\sqrt{m\omega\hbar}} \right] |\Phi_0\rangle = 0,$$

$$\hat{p} = -i\hbar \frac{\partial}{\partial x},$$

$$x\Phi_0(x) + \frac{\hbar}{m\omega} \frac{\partial \Phi_0(x)}{\partial x} = 0,$$

$$\partial \ln \Phi_0(x) = -\frac{m\omega}{\hbar} x \partial x,$$

$$\Phi_0(x) = A \exp\left(-\frac{m\omega}{\hbar^2} x^2\right),$$

where $A = \sqrt{\frac{m\omega}{\pi\hbar}}$. The wave function $\Phi_0(x)$ is the eigenfunction of \hat{N} with $\nu = 0$ (i.e., the *ground state* wave function because $\nu \geq 0$).

Theorem II:

If $\nu > 0$, state $\hat{a}|\Phi_\nu\rangle$ is an eigenstate of \hat{N} with eigenvalue equal to $(\nu - 1)$.

Proof:

In order to prove this theorem we need to show that,

$$\hat{N}\hat{a}|\Phi_\nu\rangle = (\nu - 1)\hat{a}|\Phi_\nu\rangle. \quad (25)$$

We first observe that,

$$[\hat{N}, \hat{a}] = -\hat{a}.$$

Therefore,

$$[\hat{N}, \hat{a}] = \hat{a}^+\hat{a}\hat{a} - \hat{a}\hat{a}^+\hat{a},$$

$$[\hat{N}, \hat{a}] = [\hat{a}^+, \hat{a}]\hat{a},$$

$$[\hat{N}, \hat{a}] = -1\hat{a}, \quad \text{because } [\hat{a}^+, \hat{a}] = -1,$$

$$[\hat{a}^+, \hat{a}] = \frac{1}{2\hbar}(\hat{x}\hat{x} + i\hat{x}\hat{p} - i\hat{p}\hat{x} + \hat{p}\hat{p} - (\hat{x}\hat{x} - i\hat{x}\hat{p} + i\hat{p}\hat{x} + \hat{p}\hat{p})),$$

$$[\hat{a}^+, \hat{a}] = \frac{i}{2\hbar}2[\hat{x}, \hat{p}] = -1, \quad \text{since } [\hat{x}, \hat{p}] = i\hbar.$$

Applying the operator $-\hat{a}$ to state $|\Phi_\nu\rangle$ we obtain,

$$(\hat{N}\hat{a} - \hat{a}\hat{N})|\Phi_\nu\rangle = -\hat{a}|\Phi_\nu\rangle,$$

and, therefore,

$$\hat{N}\hat{a}|\Phi_\nu\rangle = -\hat{a}\nu|\Phi_\nu\rangle = -\hat{a}|\Phi_\nu\rangle, \text{ which proves the theorem.}$$

A natural consequence of theorems I and II is that ν is an *integer* number greater or equal to zero. The spectrum of \hat{N} is therefore discrete and consists of integer numbers that are ≥ 0 . In order to demonstrate such consequence we first prove that,

$$\hat{N}\hat{a}^p|\Phi_\nu\rangle = (\nu - p)\hat{a}^p|\Phi_\nu\rangle. \quad (26)$$

In order to prove Eq. (26) we apply \hat{a} to both sides of Eq. (25):

$$\hat{a}\hat{N}\hat{a}|\Phi_\nu\rangle = (\nu - 1)\hat{a}^2|\Phi_\nu\rangle,$$

and since $[\hat{N}, \hat{a}] = -\hat{a}$ we obtain,

$$(\hat{a} + \hat{N}\hat{a})\hat{a}|\Phi_\nu\rangle = (\nu - 1)\hat{a}^2|\Phi_\nu\rangle,$$

and

$$\hat{N}\hat{a}^2|\Phi_\nu\rangle = (\nu - 2)\hat{a}^2|\Phi_\nu\rangle. \quad (27)$$

Applying \hat{a} to Eq. (27) we obtain,

$$\hat{a}\hat{N}\hat{a}^2|\Phi_\nu\rangle = (\nu - 2)\hat{a}^3|\Phi_\nu\rangle,$$

and substituting $\hat{a}\hat{N}$ by $\hat{a} + \hat{N}\hat{a}$ we obtain,

$$\hat{N}\hat{a}^3|\Phi_\nu\rangle = (\nu - 3)\hat{a}^3|\Phi_\nu\rangle.$$

Repeating this procedure p times we obtain Eq. (26).

Having proved Eq. (26) we now realize that if $\nu = n$, with n an integer number,

$$\hat{a}^p|\Phi_n\rangle = 0,$$

when $p > n$. This is because state $\hat{a}^n|\Phi_n\rangle$ is the eigenstate of \hat{N} with eigenvalue equal to zero, i.e., $\hat{a}^n|\Phi_n\rangle = |\Phi_0\rangle$. Therefore $\hat{a}|\Phi_0\rangle = \hat{a}^p|\Phi_n\rangle = 0$, when $p > n$. Note that (Eq. 26) would contradict Theorem I if ν was not an integer, because starting with a nonzero function $|\Phi_\nu\rangle$ it would be possible to obtain a function $\hat{a}^p|\Phi_\nu\rangle$ different from zero with a negative eigenvalue.

Eigenfunctions of \hat{N}

In order to obtain eigenfunctions of \hat{N} consider that,

$$\hat{N}|\Phi_\nu \rangle = \nu|\Phi_\nu \rangle,$$

and

$$\hat{N}\hat{a}|\Phi_{\nu+1} \rangle = \nu\hat{a}|\Phi_{\nu+1} \rangle.$$

Therefore, $\hat{a}|\Phi_{\nu+1} \rangle$ is proportional to $|\Phi_\nu \rangle$,

$$\hat{a}|\Phi_{\nu+1} \rangle = C_{\nu+1}|\Phi_\nu \rangle \quad (28)$$

Applying \hat{a}^+ to Eq. (28) we obtain,

$$\begin{aligned} \hat{N}|\Phi_{\nu+1} \rangle &= C_{\nu+1}\hat{a}^+|\Phi_\nu \rangle, \\ |\Phi_{\nu+1} \rangle &= \frac{C_{\nu+1}}{(\nu+1)}\hat{a}^+|\Phi_\nu \rangle, \\ \langle \Phi_{\nu+1}|\Phi_{\nu+1} \rangle &= 1 = \frac{C_{\nu+1}^2}{(\nu+1)^2} \langle \Phi_\nu|\hat{N}+1|\Phi_\nu \rangle, \\ C_{\nu+1} &= \sqrt{\nu+1}. \end{aligned}$$

Therefore,

$$\boxed{|\Phi_{\nu+1} \rangle = \frac{1}{\sqrt{\nu+1}}\hat{a}^+|\Phi_\nu \rangle = \frac{(\hat{a}^+)^{\nu+1}}{\sqrt{(\nu+1)!}}|\Phi_0 \rangle}$$

The eigenfunctions of \hat{N} can be generated from $|\Phi_0 \rangle$ as follows,

$$\begin{aligned} |\Phi_\nu \rangle &= \frac{1}{\sqrt{\nu!}} \left(\hat{x} \sqrt{\frac{m\omega}{\hbar}} - i \frac{\hat{p}}{\sqrt{\hbar\omega m}} \right)^\nu |\Phi_0 \rangle, \\ \Phi_\nu(x) &= \frac{1}{\sqrt{\nu!}} \left(x \sqrt{\frac{m\omega}{\hbar}} - \frac{\hbar}{\sqrt{\hbar\omega m}} \frac{\partial}{\partial x} \right)^\nu \Phi_0(x). \end{aligned}$$

For example,

$$\Phi_1(x) = \left(x \sqrt{\frac{m\omega}{\hbar}} + \sqrt{\frac{\hbar}{m\omega}} \frac{m\omega}{\hbar} x \right) A e^{-\frac{m\omega}{2\hbar} x^2},$$

$$\Phi_1(x) = 2x \underbrace{\sqrt{\frac{m\omega}{\hbar}} \sqrt{\frac{m\omega}{\pi\hbar}}}_{\text{normalization}} e^{-\frac{m\omega}{2\hbar} x^2}.$$

The pre-exponential factor is the Hermite polynomial for $\nu = 1$.

Time Evolution of Expectation Values

In order to compute a time-dependent expectation value,

$$\bar{A}_t = \langle \psi_t | \hat{A} | \psi_t \rangle,$$

it is necessary to compute $|\psi_t\rangle$ by solving the time dependent Schrödinger equation, $i\hbar\partial|\psi_t\rangle/\partial t = \hat{H}|\psi_t\rangle$. This can be accomplished by first finding all eigenstates of \hat{H} , Φ_n , with eigenvalues E_n , and then computing $|\psi_t\rangle$ as follows,

$$\langle x | \psi_t \rangle = \sum_n C_n e^{-\frac{i}{\hbar} E_n t} \langle x | \Phi_n \rangle,$$

where the expansion coefficients C_n are determined by the initial state $\langle x | \psi_0 \rangle$. The time dependent expectation value $\langle \psi_t | \hat{A} | \psi_t \rangle$ is, therefore,

$$\bar{A}_t = \sum_{nm} C_m^* C_n e^{-\frac{i}{\hbar} \hbar\omega(n-m)t} \langle \Phi_m | \hat{A} | \Phi_n \rangle.$$

Note that this approach might give you the *wrong* impression that the computational task necessary to solve the time *dependent* Schrödinger equation can always be reduced to finding the eigenstates and eigenvalues of \hat{H} by solving the time *independent* Schrödinger equation. While this is possible in principle, it can only be implemented in practice for very simple problems (e.g., systems with very few degrees of freedom). Most of the problems of interest in Chemical Dynamics, however, require solving the time *dependent* Schrödinger equation explicitly by implementing other numerical techniques.

15 Problem Set (due 10/16/03)

Exercise 16: (A) Show that, $\langle \Phi_{n'} | x | \Phi_n \rangle = \sqrt{\frac{\hbar}{2m\omega}} [\sqrt{n+1} \delta_{n',n+1} + \sqrt{n} \delta_{n',n-1}]$.

(B) Show that, $\langle \Phi_{n'} | p | \Phi_n \rangle = i \sqrt{\frac{m\hbar\omega}{2}} [\sqrt{n+1} \delta_{n',n+1} - \sqrt{n} \delta_{n',n-1}]$.

(C) Show that, $\hat{a}^+ | \Phi_\nu \rangle = \sqrt{\nu+1} | \Phi_{\nu+1} \rangle$; $\hat{a} | \Phi_\nu \rangle = \sqrt{\nu} | \Phi_{\nu-1} \rangle$.

(D) Compute the ratio between the minimum vibrational energies for bonds C-H and C-D, assuming that the force constant $k = m\omega^2$ is the same for both bonds.

(E) Estimate the energy of the first excited vibrational state for a Morse oscillator defined as follows: $V(R) = D_e(1 - \exp(-a(R - R_{eq})))^2$.

Exercise 17: Prove that $\langle \Phi_k | \frac{\partial \hat{H}}{\partial t} | \Phi_n \rangle = (E_n - E_k) \langle \Phi_k | \frac{\partial}{\partial t} | \Phi_n \rangle$, when $n \neq k$ and $\langle \Phi_k | \Phi_n \rangle = \delta_n$, with

$$\hat{H}(t) \Phi_j(x, t) = E_j(t) \Phi_j(x, t).$$

Exercise 18: Prove that $\nabla \cdot j = 0$, where $j \equiv \frac{\hbar}{2mi} (\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x})$ and $\psi = R(x) e^{-\frac{i}{\hbar} E t}$.

Exercise 19: Consider a harmonic oscillator described by the following Hamiltonian,

$$\hat{H}_0 = \frac{1}{2m} p^2 + \frac{1}{2} m \omega^2 x^2.$$

Consider that the system is initially in the ground state Φ_0 , with

$$\hat{H}_0 \Phi_k = E_k \Phi_k, \quad \text{with} \quad E_k = \hbar \omega \left(\frac{1}{2} + k \right).$$

Compute the probability of finding the system in state Φ_2 at time t after suddenly changing the frequency of the oscillator to ω' .

16 Angular Momentum

The *angular momentum* operator L is obtained by substituting r and p by their corresponding quantum mechanical operators \hat{r} and $-i\hbar\nabla_r$ in the classical expression of the angular momentum $L = r \times p$. The Cartesian components of L are:

$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) = yp_z - zp_y,$$

$$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) = zp_x - xp_z,$$

$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = xp_y - yp_x.$$

These components satisfy the following *commutation relations*:

$$\begin{aligned} [L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z], \\ &= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z], \\ &= y[p_z, z]p_x - x[p_z, z]p_y, \\ &= -i\hbar(y p_x - x p_y), \\ &= i\hbar L_z. \end{aligned}$$

Exercise 20:

Show that,

$$\boxed{L \times L = i\hbar L}.$$

Hint: Show that, $i\hbar L_x = [L_y, L_z]$. Note, that this expression corresponds to the *cyclic permutation* where y is substituted by z , x by y , and z by x , in the commutation relation $i\hbar L_x = [L_y, L_z]$.

Cyclic permutations can be represented by the following diagram:

$$\begin{aligned} [L_y, L_z] &= i\hbar L_x, \\ [L_z, L_x] &= i\hbar L_y. \end{aligned}$$

Having obtained the commutation relations we can show that L^2 commutes with the Cartesian components of L , e.g.,

$$[L^2, L_x] = 0.$$

We consider that,

$$[L^2, L_x] = [L_x^2 + L_y^2 + L_z^2, L_x],$$

$$[L^2, L_x] = [L_y^2, L_x] + [L_z^2, L_x],$$

$$[L^2, L_x] = L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z, \quad \text{and}$$

since $[L_y, L_x] = -i\hbar L_z$, $[L_y, L_x] = -i\hbar L_z$, $[L_z, L_x] = i\hbar L_y$, then,

$$[L^2, L_x] = 0.$$

Due to the *cyclic permutations* we can also conclude that,

$$[L^2, L_y] = 0, \quad \text{and} \quad [L^2, L_z] = 0.$$

According to these equations both the magnitude of the angular momentum and one (any) of its components can be simultaneously determined, since there is always a set of eigenfunctions that is common to L^2 and any of the three Cartesian components. Remember, however, that none of the individual components commute with each other. Therefore, if one component is determined the other two are completely undetermined.

Eigenvalues of L^2 and L_z : Ladder Operators

In order to find eigenfunctions Y that are common to L^2 and L_z ,

$$L^2Y = aY, \quad (29)$$

and

$$L_zY = bY, \quad (30)$$

we define the *ladder operators*,

$$L_+ = L_x + iL_y,$$

$$L_- = L_x - iL_y,$$

where L_+ is the *raising operator*, and L_- is the *lowering operator*.

In order to show the origin of these names, we operate Eq. (30) with L_+ and we obtain,

$$L_+L_zY = bL_+Y.$$

Then, we substitute L_+L_z by $[L_+, L_z] + L_zL_+$, where

$$[L_+, L_z] = [L_x + iL_y, L_z] = [L_x, L_z] + i[L_y, L_z].$$

Since, $[L_x, L_z] = -i\hbar L_y$, and $[L_y, L_z] = i\hbar L_x$, then

$$L_+L_z - L_zL_+ = -i\hbar(L_y - iL_x) = -\hbar L_+.$$

Consequently,

$$(-\hbar L_+ + L_zL_+)Y = bL_+Y,$$

and,

$$L_z(L_+Y) = (b + \hbar)(L_+Y).$$

Thus the *ladder operator* L_+ generates a new eigenfunction of L_z (e.g., L_+Y) with eigenvalue $(b + \hbar)$ when such operator is applied to the eigenfunction of L_z with eigenvalue b (e.g., Y). The operator L_+ is therefore called the *raising operator*.

Applying p times the raising operation to Y , we obtain:

$$L_z L_+^p Y = (b + \hbar p) L_+^p Y.$$

Exercise 21: Show that:

$$L_z L_-^p Y = (b - \hbar p) L_-^p Y.$$

Therefore L_+ and L_- generate the following ladder of eigenvalues:

$$\dots \quad b - 3\hbar \quad b - 2\hbar \quad b - \hbar \quad b \quad b + \hbar \quad b + 2\hbar \quad b + 3\hbar \quad \dots$$

Note that all functions $L_\pm^p Y$ generated by the ladder operators are eigenfunctions of L^2 with eigenvalue equal to a (see Eq. (29)).

Proof:

$$L^2 L_\pm^p Y = L_\pm^p L^2 Y = L_\pm^p a Y,$$

since $[L^2, L_x] = [L^2, L_y] = [L^2, L_\pm] = 0$, and therefore, $[L^2, L_\pm^p] = 0$.

Note that the ladder of eigenvalues must be bounded:

$$L_z Y_k = b_k Y_k,$$

with $Y_k = L_\pm^k Y$, and $b_k = b \pm k\hbar$.

Therefore,

$$L_z^2 Y_k = b_k^2 Y_k,$$

$$L^2 Y_k = a Y_k,$$

$$\underbrace{(L_x^2 + L_y^2)}_{\text{non-negative physical quantity}} Y_k = (a - b_k^2) Y_k.$$

non-negative physical quantity $\implies (a - b_k^2)$ has to be positive:

$$a \geq b_k^2, \implies a^{\frac{1}{2}} \geq |b_k|,$$

$$\boxed{a^{\frac{1}{2}} \geq b_k \geq -a^{\frac{1}{2}}}$$

In order to avoid contradictions,

$$L_+ Y_{max} = 0, \quad \text{and} \quad L_- Y_{min} = 0.$$

$$L_+ L_- Y_{min} = 0,$$

$$L_+ L_- = (L_x + iL_y)(L_x - iL_y),$$

$$L_+ L_- = L_x^2 - i \underbrace{(L_x L_y - L_y L_x)}_{i\hbar L_z} + L_y^2,$$

$$L_+ L_- = L_x^2 + L_y^2 + \hbar L_z = L^2 - L_z^2 + \hbar L_z.$$

Therefore,

$$a - b_{min}^2 + \hbar b_{min} = 0, \tag{31}$$

because,

$$L_z^2 Y_{min} = b_{min}^2 Y_{min}, \quad L^2 Y_{min} = a Y_{min}, \quad L_z Y_{min} = b_{min} Y_{min}.$$

Analogously,

$$L_- L_+ Y_{max} = 0.$$

↓

$$(L^2 - L_z^2 - \hbar L_z) Y_{max} = 0, \text{ and}$$

$$a - b_{max}^2 - \hbar b_{max} = 0. \tag{32}$$

Eqs. (31) and (32) provide the following result:

$$(b_{min}^2 - b_{max}^2) - \hbar(b_{min} + b_{max}) = 0 \Rightarrow \boxed{b_{min} = -b_{max}}.$$

Furthermore, we know that $b_{max} = b_{min} + n\hbar$, because all eigenvalues of L_z are separated by units of \hbar . Therefore,

$$2b_{max} = n\hbar \implies b_{max} = \frac{n}{2}\hbar = j\hbar, \text{ where } j = \frac{n}{2},$$

$$a = b_{min}^2 - \hbar b_{min} = j^2\hbar^2 + \hbar^2 j = \hbar^2 j(j+1), \quad \text{and} \quad b = -j\hbar, (-j+1)\hbar, (-j+2)\hbar, \dots, j\hbar.$$

Note that these quantization rules do not rule out the possibility that j might have half-integer values. In the next section we will see that such possibility is, however, ruled out by the requirement that the eigenfunctions of L^2 must be 2π -periodic.

Spherical Coordinates

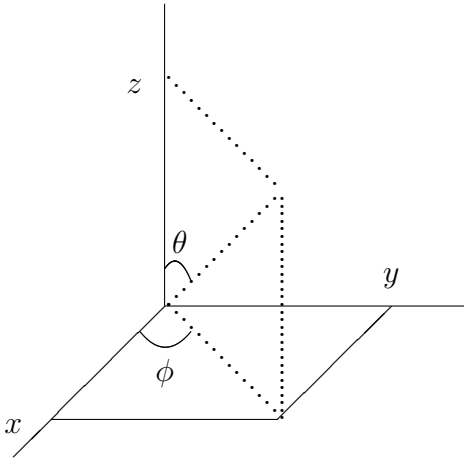
Spherical coordinates are defined as follows,

$$z = r\text{Cos}\theta,$$

$$y = r\text{Sin}\theta\text{Sin}\phi,$$

$$x = r\text{Sin}\theta\text{Cos}\phi,$$

where θ , and ϕ are defined by the following diagram,



Exercise 22: Write the Cartesian components of the linear momentum operator \hat{p} : \hat{p}_x , \hat{p}_y and \hat{p}_z in spherical coordinates.

Hint:

$$\left(\frac{\partial g}{\partial x}\right)_{y,z} = \left(\frac{\partial \theta}{\partial x}\right)_{y,z} \left(\frac{\partial f}{\partial \theta}\right)_{\phi,r} + \left(\frac{\partial \phi}{\partial x}\right)_{y,z} \left(\frac{\partial f}{\partial \phi}\right)_{\theta,r} + \left(\frac{\partial r}{\partial x}\right)_{y,z} \left(\frac{\partial f}{\partial r}\right)_{\theta,\phi},$$

where $g = g(x, y, z)$, and $f = f(r(x, y, z), \theta(x, y, z), \phi(x, y, z))$.

$$r = \sqrt{(x^2 + y^2 + z^2)},$$

$$\frac{y}{x} = \tan\phi,$$

$$\text{Cos}\theta = \frac{z}{r} = \frac{z}{(x^2 + y^2 + z^2)^{\frac{1}{2}}}.$$

$$\begin{aligned} \left(\frac{\partial \text{Cos}\theta}{\partial x}\right)_{y,z} &= -\left(\frac{\partial \theta}{\partial x}\right)_{y,z} \text{Sin}\theta = -\frac{1}{2} \frac{z \cdot 2x}{(x^2 + y^2 + z^2)^{\frac{3}{2}}} \Rightarrow \left(\frac{\partial \theta}{\partial x}\right)_{y,z} = +\frac{r^2 \text{Cos}\theta \text{Sin}\theta \text{Cos}\phi}{r^3 \text{Sin}\theta}, \\ \left(\frac{\partial \tan\theta}{\partial x}\right)_{y,z} &= \frac{1}{\text{Cos}^2\phi} \left(\frac{\partial \phi}{\partial x}\right)_{y,z} = -\frac{y}{x^2} \Rightarrow \left(\frac{\partial \phi}{\partial x}\right)_{y,z} = -\frac{r \text{Sin}\theta \text{Sin}\phi \text{Cos}^2\phi}{r^2 \text{Sin}^2\theta \text{Cos}^2\phi}, \\ \left(\frac{\partial r}{\partial x}\right)_{y,z} &= \frac{1}{2} \frac{2x}{r} \Rightarrow \left(\frac{\partial r}{\partial x}\right)_{y,z} = \frac{r \text{Sin}\theta \text{Cos}\phi}{r}. \end{aligned}$$

Exercise 23: Show that,

$$L_x = i\hbar \left(\text{Sin}\phi \frac{\partial}{\partial \theta} + \frac{\text{Cos}\theta}{\text{Sin}\theta} \text{Cos}\phi \frac{\partial}{\partial \phi} \right),$$

$$L_y = -i\hbar \left(\text{Cos}\phi \frac{\partial}{\partial \theta} - \frac{\text{Cos}\theta}{\text{Sin}\theta} \text{Sin}\phi \frac{\partial}{\partial \theta} \right),$$

and

$$L_z = -i\hbar \frac{\partial}{\partial \phi}.$$

Squaring L_x , L_y and L_z we obtain,

$$L^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \frac{\text{Cos}\theta}{\text{Sin}\theta} \frac{\partial}{\partial \theta} + \frac{1}{\text{Sin}^2\theta} \frac{\partial^2}{\partial \phi^2} \right).$$

Eigenfunctions of L^2

Since L^2 does not depend on r , $\Rightarrow Y = Y(\theta, \phi)$. Furthermore, if Y is an eigenfunction of L_z then,

$$L_z Y = bY.$$

$$-i\hbar \frac{\partial Y}{\partial \phi} = bY \quad \Rightarrow \quad \frac{\partial \ln Y}{\partial \phi} = \frac{1}{Y} \frac{\partial Y}{\partial \phi} = -\frac{b}{i\hbar}.$$

$$Y = A \exp\left(\frac{ib\phi}{\hbar}\right).$$

Since $Y(\phi + 2\pi) = Y(\phi)$, we must have

$$e^{i\frac{2\pi b}{\hbar}} = 1, \quad \Rightarrow \quad 2\pi \frac{b}{\hbar} = 2\pi m, \quad \text{with} \quad m = 0, \pm 1, \pm 2, \dots$$

Therefore, $b = m\hbar$, where m is an *integer*.

In order to find eigenfunctions that are common to L_z and L^2 we assume A to be a function of theta, $A = A(\theta)$:

$$\begin{aligned} L^2 Y &= -\hbar^2 \left(\frac{\partial^2 A}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial A}{\partial \theta} + \frac{1}{\sin^2 \theta} \left(-\frac{b^2}{\hbar^2} \right) A \right) \exp\left(\frac{ib\phi}{\hbar}\right) = aA(\theta) \exp\left(\frac{ib\phi}{\hbar}\right), \\ &-\hbar^2 \left(\sin^2 \theta \frac{\partial^2 A}{\partial \theta^2} + \sin \theta \cos \theta \frac{\partial A}{\partial \theta} - \frac{b^2}{\hbar^2} A \right) = aA(\theta) \sin^2 \theta. \end{aligned} \quad (33)$$

Making the substitution $x = \cos \theta$ we obtain,

$$(1 - x^2) \frac{d^2 A}{dx^2} - 2x \frac{dA}{dx} + \left(\frac{a}{\hbar^2} - \frac{m^2}{1 - x^2} \right) A = 0. \quad (34)$$

Exercise 24: Obtain Eq. (34) from Eq. (33).

Eq. (34) is the *associated Legendre equation*, whose solutions exist only for $a = \hbar^2 l(l + 1)$, and $b = -l\hbar, (-l + 1)\hbar, \dots, l\hbar$ (i.e., the quantum number l is an *integer* greater or equal to zero, with $|m| \leq l$). The solutions of the associated Legendre equations are the *associated Legendre polynomials*, $A(l, m) = P_l^{|m|}(\cos \theta)$,

For example, the normalized polynomials for various values of l and m are:

$$A(0, 0) = 1/\sqrt{2},$$

$$A(1, 0) = \sqrt{3/2}\text{Cos}\theta,$$

$$A(1, \pm 1) = \sqrt{3/4}\text{Sin}\theta,$$

...

The eigenstates that are common to L^2 and L_z are called *spherical harmonics* and are defined as follows,

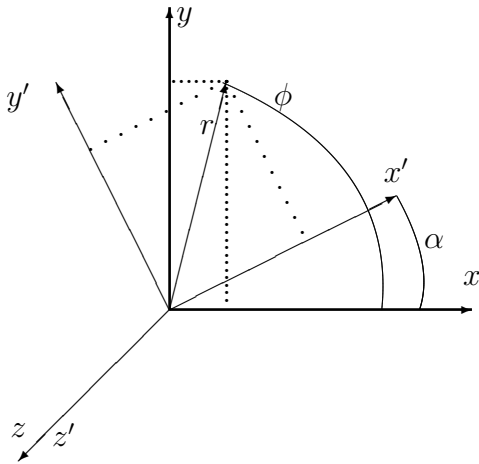
$$Y_l^m(\theta, \phi) = P_l^{|m|}(\text{Cos}\theta)e^{im\phi}.$$

The spherical harmonics are normalized as follows,

$$\int_0^{2\pi} d\phi \int_{-1}^1 d\text{Cos}\theta Y_l^{m'*}(\theta, \phi) Y_l^m(\theta, \phi) = \delta_{ll'} \delta_{mm'}.$$

Rotations and Angular Momentum

A coordinate transformation that corresponds to a rotation can be represented by the following diagram:



This diagram shows that vector \vec{r} can be specified either relative to the axes (x, y, z) , or relative

to the axes (x', y', z') , where these two sets of coordinates are defined relative to each other as follows,

$$\boxed{\vec{r}' = R(\alpha, z)\vec{r}}, \quad (35)$$

where, \vec{r}' is the same vector \vec{r} but with components expressed in the primed coordinate system.

α : Angle, z : Rotation axis

$$x = r\text{Cos}\phi,$$

$$y = r\text{Sin}\phi,$$

$$x' = r\text{Cos}(\phi - \alpha) = r(\text{Cos}\phi\text{Cos}\alpha + \text{Sin}\phi\text{Sin}\alpha),$$

$$y' = r\text{Sin}(\phi - \alpha) = r(\text{Sin}\phi\text{Cos}\alpha - \text{Cos}\phi\text{Sin}\alpha),$$

$$z' = z,$$

$$x' = x\text{Cos}\alpha + y\text{Sin}\alpha,$$

$$y' = y\text{Cos}\alpha - x\text{Sin}\alpha.$$

Therefore, the coordinate transformation can be written in matrix representation as follows,

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \text{Cos}\alpha & \text{Sin}\alpha & 0 \\ -\text{Sin}\alpha & \text{Cos}\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}.$$

The operator associated with the coordinate transformation is $P_R(\alpha)$, defined as follows:

$$\hat{P}_R(\alpha, z)f(\vec{r}) = f[R^{-1}(\alpha, z)\vec{r}],$$

where R^{-1} is the transpose of R , i.e., $R^{-1} = \begin{pmatrix} \text{Cos}\alpha & -\text{Sin}\alpha & 0 \\ \text{Sin}\alpha & \text{Cos}\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$.

Therefore, $\hat{P}_R(\alpha, z)f(\vec{r}) = f(x\text{Cos}\alpha - y\text{Sin}\alpha, x\text{Sin}\alpha + y\text{Cos}\alpha, z)$.

An infinitesimal rotation is defined as follows,

$$\hat{P}_R(\delta, z)f(\bar{r}) = f(x - y\delta, x\delta + y, z),$$

$$\hat{P}_R(\delta, z)f(\bar{r}) = f(x, y, z) - y\delta\frac{\partial f}{\partial x} + x\delta\frac{\partial f}{\partial y},$$

$$\hat{P}_R(\delta, z)f(\bar{r}) = f(x, y, z) + \delta(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})f(x, y, z)$$

recall that, $-i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}) = L_z$, therefore,

$$\hat{P}_R(\delta, z)f(\bar{r}) = (1 + \frac{i}{\hbar}\delta L_z)f(\bar{r}).$$

A finite rotation through an angle α can be defined according to n infinitesimal rotations, after subdividing α into n angle increments, $\alpha = n\delta$, and taking the limit $n \rightarrow \infty$, and $\delta \rightarrow 0$.

$$\hat{P}_R(\alpha, z) = \lim_{n \rightarrow \infty, \delta \rightarrow 0} \left(1 + i\frac{\delta}{\hbar}L_z\right)^n = e^{\frac{i}{\hbar}\alpha L_z}.$$

In general, a finite rotation through an angle α around an arbitrary axis specified by a unit vector \hat{n} is defined as follows,

$$\boxed{\hat{P}_R(\alpha, \hat{n}) = e^{\frac{i}{\hbar}\alpha \hat{n} \cdot L}}.$$

This equation establishes the connection between the operator associated with a coordinate transformation and the angular momentum operator.

Note:

It is important to note that if coordinates are transformed according to $\bar{r}' = \mathbf{R}\bar{r}$, the Hamiltonian is transformed according to a *similarity transformation*, which is defined as follows:

$$\hat{H}' = \hat{P}_R \hat{H} \hat{P}_R^{-1}.$$

Proof:

$$\text{Consider, } f(r) \equiv \hat{H}(r)\phi(r) = E\phi(r),$$

$$\hat{P}_R f(r) = \hat{P}_R H(r) \hat{P}_R^{-1} \hat{P}_R \phi(r) = E\phi(R^{-1}r),$$

$$\hat{P}_R H(r) \hat{P}_R^{-1} \phi(R^{-1}r) = E\phi(R^{-1}r) = H(R^{-1}r)\phi(R^{-1}r).$$

$$\text{Therefore, } H(R^{-1}r) = \hat{P}_R H(r) \hat{P}_R^{-1}.$$

It is, therefore, evident that the Hamiltonian is an invariant operator (i.e., $H(r) = H(R^{-1}r)$) under a coordinate transformation, $\vec{r}' = R\vec{r}$, whenever the operator associated with the coordinate transformation commutes with the Hamiltonian, $[\hat{P}_R, H] = 0$.

17 Spin Angular Momentum

The goal of this section is to introduce the *spin angular momentum* S , as a generalized angular momentum operator that satisfies the general commutation relations $[S \times S = i\hbar S]$. The main difference between the angular momenta S , and L , is that S can have half-integer quantum numbers.

Note: Remember that the quantization rules established by the commutation relations did not rule out the possibility of half-integer values for j (see page 46). However, such possibility was ruled out by the *periodicity requirement*, $Y(\theta + 2\pi) = Y(\theta)$, associated with the eigenfunctions of L_z and L^2 . Since the spin eigenfunctions (i.e., the *spinors*) do not depend on spatial coordinates, they do not have to satisfy any periodicity condition and therefore their eigenvalues can be half-integer.

Electron Spin:

A particular case of half-integer spin is the spin angular momentum of an electron with $l = 1/2$ (see <http://www.lorentz.leidenuniv.nl/history/spin/goudsmit.html>, for Goudsmit's historical recount of the discovery of the electron spin). In discussing the spin properties of a particle we adopt the notation $l = S$, and $m = m_s$.

The spin functions α and β are eigenfunctions of S_z with eigenvalues $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$, respectively. These eigenfunctions are normalized according to,

$$\sum_{m_s=-1/2}^{1/2} |\alpha(m_s)|^2 = 1, \quad \sum_{m_s=-1/2}^{1/2} |\beta(m_s)|^2 = 1, \quad (36)$$

since m_s can be either $\frac{1}{2}$, or $-\frac{1}{2}$. Also, since the eigenfunctions α and β correspond to different eigenvalues of S_z , they must be orthogonal:

$$\sum_{m_s=-1/2}^{1/2} \alpha^*(m_s)\beta(m_s) = 0. \quad (37)$$

In order to satisfy the conditions imposed by Eqs. (36) and (37),

$$\alpha(m_s) = \delta_{m_s,1/2}, \quad \text{and,} \quad \beta(m_s) = \delta_{m_s,-1/2}.$$

It is useful to define the spin angular momentum *ladder operators*, $\boxed{S_+ = S_x + iS_y}$ and $\boxed{S_- = S_x - iS_y}$.

Here, we prove that the *raising operator* S_+ satisfies the following equation:

$$\boxed{S_+\beta = \hbar\alpha}.$$

Proof:

Using the normalization condition introduced by Eq. (36) we obtain,

$$\sum_{m_s=-1/2}^{1/2} \alpha^*(m_s)\alpha(m_s) = \sum_{m_s=-1/2}^{1/2} \left(\hat{S}_+\frac{\beta}{c}\right)^* \left(\hat{S}_+\frac{\beta}{c}\right) = 1,$$

and

$$|c|^2 = \sum_{m_s} (\hat{S}_+\beta)^* (\hat{S}_x\beta + i\hat{S}_y\beta).$$

Now, using the hermitian property of S_x and S_y we obtain,

$$\sum_{m_s} f^* S_x g = \sum_{m_s} g S_x^* f^*,$$

$$|c|^2 = \sum_{m_s} \beta S_x^* (S_+\beta)^* + i\beta S_y^* (S_+\beta)^*,$$

where,

$$|c|^2 = \sum_{m_s} \beta^* S_x S_+\beta - i\beta^* S_y S_+\beta,$$

$$|c|^2 = \sum_{m_s} \beta^* S_- S_+\beta,$$

$$|c|^2 = \sum_{m_s} \beta^* (S^2 - S_z^2 - \hbar S_z)\beta,$$

$$|c|^2 = \sum_{m_s} \beta^* \left(\frac{3}{4} \hbar^2 - \frac{\hbar^2}{4} + \frac{\hbar^2}{2} \right) \beta,$$

$$|c|^2 = \hbar^2.$$

Since the phase of c is arbitrary, we can choose $c = \hbar$.

Similarly, we obtain $S_- \alpha = \hbar \beta$.

Since α is the eigenfunction with highest eigenvalue, the operator S_+ acting on it must annihilate it as follows,

$$S_+ \alpha = 0, \quad \text{and} \quad S_- \beta = 0.$$

$$S_x \alpha = (S_+ + S_-) \frac{\alpha}{2} = \frac{\hbar}{2} \beta, \quad \Rightarrow \quad S_x \alpha = \frac{1}{2} \hbar \beta.$$

$$S_y \beta = (S_+ - S_-) \frac{\beta}{2i} = \frac{\hbar}{2} \alpha, \quad \Rightarrow \quad S_y \beta = -\frac{1}{2} i \hbar \alpha.$$

Similarly, we find $S_x \beta = \frac{1}{2} \hbar \alpha$, and $S_y \alpha = \frac{1}{2} i \hbar \beta$.

$\langle S_x \rangle$	<table style="border-collapse: collapse; width: 100%;"> <tr> <td style="padding: 5px;">α</td> <td style="padding: 5px;">β</td> </tr> <tr> <td style="padding: 5px;">α</td> <td style="padding: 5px;">$0 \quad \hbar/2$</td> </tr> <tr> <td style="padding: 5px;">β</td> <td style="padding: 5px;">$\hbar/2 \quad 0$</td> </tr> </table>	α	β	α	$0 \quad \hbar/2$	β	$\hbar/2 \quad 0$
α	β						
α	$0 \quad \hbar/2$						
β	$\hbar/2 \quad 0$						

$\langle S_y \rangle$	<table style="border-collapse: collapse; width: 100%;"> <tr> <td style="padding: 5px;">α</td> <td style="padding: 5px;">β</td> </tr> <tr> <td style="padding: 5px;">α</td> <td style="padding: 5px;">$0 \quad -i\hbar/2$</td> </tr> <tr> <td style="padding: 5px;">β</td> <td style="padding: 5px;">$+i\hbar/2 \quad 0$</td> </tr> </table>	α	β	α	$0 \quad -i\hbar/2$	β	$+i\hbar/2 \quad 0$
α	β						
α	$0 \quad -i\hbar/2$						
β	$+i\hbar/2 \quad 0$						

$\langle S_z \rangle$	<table style="border-collapse: collapse; width: 100%;"> <tr> <td style="padding: 5px;">α</td> <td style="padding: 5px;">β</td> </tr> <tr> <td style="padding: 5px;">α</td> <td style="padding: 5px;">$\hbar/2 \quad 0$</td> </tr> <tr> <td style="padding: 5px;">β</td> <td style="padding: 5px;">$0 \quad -\hbar/2$</td> </tr> </table>	α	β	α	$\hbar/2 \quad 0$	β	$0 \quad -\hbar/2$
α	β						
α	$\hbar/2 \quad 0$						
β	$0 \quad -\hbar/2$						

Therefore, $S = \frac{1}{2} \hbar \sigma$, where σ are the Pauli matrices defined as follows,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

where, $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1$.

Exercise 25: Prove that the Pauli matrices anti-commute with each other, i.e.,

$$\sigma_i \sigma_j + \sigma_j \sigma_i = 0,$$

where $i \neq j$, and $i, j = (x, y, z)$.

In order to find the eigenfunctions of S_z , called *eigenspinors*, consider the following eigenvalue problem:

$$S_z \begin{pmatrix} u_{\pm} \\ v_{\pm} \end{pmatrix} = \pm \frac{\hbar}{2} \begin{pmatrix} u_{\pm} \\ v_{\pm} \end{pmatrix},$$

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} u_{\pm} \\ v_{\pm} \end{pmatrix} = \pm \begin{pmatrix} u_{\pm} \\ v_{\pm} \end{pmatrix},$$

$$\begin{pmatrix} u_{\pm} \\ -v_{\pm} \end{pmatrix} = \pm \begin{pmatrix} u_{\pm} \\ v_{\pm} \end{pmatrix}, \quad \Rightarrow \quad \begin{pmatrix} u_{+} \\ -v_{+} \end{pmatrix} = \begin{pmatrix} u_{+} \\ v_{+} \end{pmatrix}, \quad \Rightarrow \quad \boxed{v_{+} = 0}, \quad \boxed{u_{+} = 1}.$$

Similarly we obtain, $\boxed{u_{-} = 0}$, and $\boxed{v_{-} = 1}$. Therefore, electron eigenspinors satisfy the eigenvalue problem,

$$S_z \chi_{\pm} = \pm \frac{\hbar}{2} \chi_{\pm},$$

with,

$$\chi_{-} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \text{and} \quad \chi_{+} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}.$$

Any spinor can be expanded in the complete set of eigenspinors as follows,

$$\begin{pmatrix} \alpha_{+} \\ \alpha_{-} \end{pmatrix} = \alpha_{+} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \alpha_{-} \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

where $|\alpha_{+}|^2$, and $|\alpha_{-}|^2$, are the probabilities that a measurement of S_z yields the value $+\frac{1}{2}\hbar$, and $-\frac{1}{2}\hbar$, respectively, when the system is described by state $\begin{pmatrix} \alpha_{+} \\ \alpha_{-} \end{pmatrix}$.

Exercise 26: Prove that, $S^2\chi_+ = \frac{\hbar^2}{2}(\frac{1}{2} + 1)\chi_+$.

Exercise 27: Consider an electron localized at a crystal site. Assume that the spin is the only degree of freedom of the system and that due to the spin the electron has a magnetic moment,

$$M = -\frac{eg}{2mc}S,$$

where $g \approx 2$, m is the electron mass, e is the electric charge and c is the speed of light. Therefore, in the presence of an external magnetic field B the Hamiltonian of the system is,

$$H = -M \cdot B.$$

Assume that B points in the z direction and that the state of the system is,

$$\psi(t) = e^{i\omega t} \begin{pmatrix} \alpha_+ \\ \alpha_- \end{pmatrix}.$$

Consider that initially (i.e., at time $t = 0$) the spin points in the x direction (i.e., the spinor is an eigenstate of σ_x with eigenvalue $\frac{1}{2}\hbar$).

Compute the expectation values of S_x and S_y at time t .

Addition of Angular Momenta

Since L depends on spatial coordinates and S does not, then the two operators commute (i.e., $[L, S] = 0$). It is, therefore, evident that the components of the *total angular momentum*,

$$J = L + S,$$

satisfy the commutation relations,

$$J \times J = i\hbar J.$$

Eigenfunctions of J^2 and J_z are obtained from the individual eigenfunctions of two angular momentum operators L_1 and L_2 with quantum numbers (l_1, m_1) and (l_2, m_2) , respectively, as follows:

$$\psi_j^m = \sum_{l_1, m_1, l_2, m_2} \underbrace{C(jm, l_1 m_1, l_2 m_2)}_{\text{Clebsch-Gordan Coefficients}} \phi_{l_1}^{m_1} \phi_{l_2}^{m_2},$$

where,

$$J^2 \psi_{jm} = \hbar^2 j(j+1) \psi_{jm},$$

$$J_z \psi_{jm} = \hbar m \psi_{jm}.$$

Exercise 28: Show that, $\psi_j^{m+1/2} = C_1 Y_l^m \chi_+ + C_2 Y_l^{m+1} \chi_-$, is a common eigenfunction of J^2 and J_z when, $C_1 = \sqrt{\frac{l+m+1}{2l+1}}$, and $C_2 = \sqrt{\frac{l-m}{2l+1}}$, or when, $C_1 = \sqrt{\frac{l-m}{2l+1}}$, and $C_2 = -\sqrt{\frac{l+m+1}{2l+1}}$.

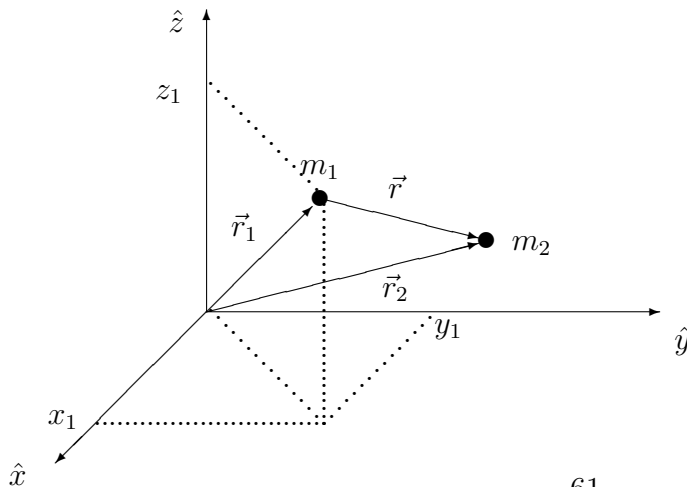
Hint: Analyze the particular case $j = l - 1/2$, and $j = l + 1/2$. Note that,

$$J^2 = L^2 + S^2 + 2LS = L^2 + S^2 + 2L_z S_z + L_+ S_- + L_- S_+,$$

$$J_z = L_z + S_z,$$

18 Central Potential

Consider a two-particle system represented by the following diagram, **R1(123) R3(168)**



where x , y and z represent distances between the two particles along the three Cartesian axes, where $\vec{r} = (x, y, z) = \vec{r}_2 - \vec{r}_1$, with \vec{r}_1 and \vec{r}_2 the position vectors of particles 1 and 2, respectively. The *central potential* $V(x, y, z)$ is a function of $|\vec{r}| = \sqrt{x^2 + y^2 + z^2}$, rather than a function of the individual Cartesian components. Assuming that such function defines the interaction between the two particles, the Hamiltonian of the system has the form,

$$H = \frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} + V(|\vec{r}_2 - \vec{r}_1|) = T + V(|\vec{r}_2 - \vec{r}_1|),$$

where, $T = \frac{m_1}{2}|\dot{\vec{r}}_1|^2 + \frac{m_2}{2}|\dot{\vec{r}}_2|^2$, with $|\dot{\vec{r}}_1|^2 = \dot{\vec{r}}_1 \cdot \dot{\vec{r}}_1$.

Changing variables \vec{r}_1 , and \vec{r}_2 , by the center-of-mass coordinates \vec{R} , and the relative coordinates, $\vec{r} = \vec{r}_2 - \vec{r}_1$, where,

$$\vec{R} \equiv \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}; \quad \vec{r} = \vec{r}_2 - \vec{r}_1,$$

we obtain,

$$\vec{r}_1 = \vec{R} - \frac{m_2}{m_1 + m_2}\vec{r}, \quad \vec{r}_2 = \vec{R} + \frac{m_1}{m_1 + m_2}\vec{r}.$$

Therefore,

$$T = \frac{m_1}{2} \left(\dot{\vec{R}} - \frac{m_2}{m_1 + m_2} \dot{\vec{r}} \right) \left(\dot{\vec{R}} - \frac{m_2}{m_1 + m_2} \dot{\vec{r}} \right) + \frac{m_2}{2} \left(\dot{\vec{R}} + \frac{m_1}{m_1 + m_2} \dot{\vec{r}} \right) \left(\dot{\vec{R}} + \frac{m_1}{m_1 + m_2} \dot{\vec{r}} \right),$$

or,

$$T = \frac{m_1 + m_2}{2} |\dot{\vec{R}}|^2 + \frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} |\dot{\vec{r}}|^2 = \frac{1}{2} M |\dot{\vec{R}}|^2 + \frac{1}{2} \mu |\dot{\vec{r}}|^2,$$

where $M = m_1 + m_2$ is the total mass of the system, and $\mu \equiv \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the two-particle system. Therefore, the total Hamiltonian of the system can be written as follows,

$$H = \frac{1}{2} M |\dot{\vec{R}}|^2 + \frac{1}{2} \mu |\dot{\vec{r}}|^2 + V(|\vec{r}|) = \frac{\vec{P}_M^2}{2M} + \frac{\vec{P}_\mu^2}{2\mu} + V(|\vec{r}|),$$

where the first term corresponds to the kinetic energy of a particle of mass M , and the second and third terms constitute the Hamiltonian of a single particle with coordinates r . Therefore,

the time-independent Schrödinger equation for the system is,

$$\left[\frac{\vec{P}_M^2}{2M} + \frac{\vec{P}_\mu^2}{2\mu} + V(|\vec{r}|) \right] \psi(\vec{R}, \vec{r}) = E\psi(\vec{R}, \vec{r}).$$

Trying a factorizable solution, by separation of variables,

$$\psi(\vec{r}, \vec{R}) = \psi_\mu(\vec{r})\psi_M(\vec{R}),$$

we obtain,

$$\underbrace{-\frac{\hbar^2\psi_\mu\nabla_R^2\psi_M}{\psi_\mu\psi_M 2M}}_{\text{depends on R}} - \underbrace{\frac{\hbar^2\psi_M\nabla_r^2\psi_\mu}{\psi_\mu\psi_M 2\mu} + \frac{\psi_\mu\psi_M}{\psi_\mu\psi_M}V(|\vec{r}|)}_{\text{depends on r}} = E\frac{\psi_\mu\psi_M}{\psi_\mu\psi_M}.$$

Therefore, each one of the parts of the Hamiltonian have to be equal to a constant,

$$-\frac{\hbar^2}{2M}\frac{1}{\psi_M}\nabla_R^2\psi_M = E_M, \quad (38)$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{\psi_\mu}\nabla_r^2\psi_\mu + V(|\vec{r}|) = E_\mu, \quad \text{with } E_M + E_\mu = E. \quad (39)$$

Eq. (38) is the Schrödinger equation for a free particle with mass M . The solution of such equation is,

$$\psi_M(R) = (2\pi\hbar)^{-3/2}e^{i\vec{k}\vec{R}}, \quad \text{where } \frac{|\vec{k}|^2\hbar^2}{2M} = E_M.$$

According to Eq. (39), the energy E_μ is found by solving the equation,

$$\boxed{-\frac{\hbar^2}{2\mu}\nabla_r^2\psi_\mu + V(|\vec{r}|)\psi_\mu = E_\mu\psi_\mu}. \quad (40)$$

Eqs. (38) and (39) have separated the problem of two particles interacting according to a central potential $V(|\vec{r}_2 - \vec{r}_1|)$ into two separate one-particle problems that include:

- (1) The translational motion of the entire system of mass M .
- (2) The relative (e.g., internal) motion.

These results apply to any problem described by a central potential (e.g., the hydrogen atom, the two-particle rigid rotor, and the isotropic multidimensional harmonic-oscillator).

Consider Eq. (40), with $\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, and $V(|\bar{r}|)$ a spherically-symmetric potential, i.e., a function of the distance $r = |\bar{r}|$. It is natural to work in spherical coordinates.

Exercise 29: Prove that the Laplacian ∇^2 can be written in spherical coordinates as follows,

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{1}{r^2 \hbar^2} \hat{L}^2, \quad \text{where } \hat{L}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right).$$

It is important to note that the commutator

$$[\nabla^2, L^2] = \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}, \hat{L}^2 \right] - \left[\frac{1}{r^2 \hbar^2} \hat{L}^2, \hat{L}^2 \right] = 0,$$

because \hat{L}^2 does not involve r , but only θ and ϕ . Also, since \hat{L}^2 does not involve r , and V is a function of r ,

$$[V, L^2] = 0.$$

Consequently,

$$[H, L^2] = 0,$$

whenever the potential energy of the system is defined by a central potential. Furthermore, $[H, L_z] = 0$, because $\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$.

Conclusion: A system described by a central-potential has eigenfunctions that are common to the operators H , L^2 and L_z :

$$\hat{H}\psi_\mu = E_\mu\psi_\mu,$$

$$\hat{L}^2\psi_\mu = \hbar^2 l(l+1)\psi_\mu, \quad l = 0, 1, 2, \dots$$

$$\hat{L}_z\psi_\mu = \hbar m\psi_\mu, \quad m = -l, -l+1, \dots, l.$$

Substituting these results into Eq. (40) we obtain,

$$-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \psi_\mu + \frac{\hbar^2}{2\mu} \frac{\hbar^2}{r^2 \hbar^2} l(l+1)\psi_\mu + V(|\bar{r}|)\psi_\mu = E_\mu\psi_\mu.$$

Since the eigenfunctions of \hat{L}^2 are spherical harmonics $Y_l^m(\theta, \phi)$, we consider the solution,

$$\psi_\mu = R(r)Y_l^m(\theta, \phi),$$

and we find that $R(r)$ must satisfy the equation,

$$-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2 R}{\partial r^2} + \frac{2}{r} \frac{\partial R}{\partial r} \right) + \frac{\hbar^2}{2\mu r^2} l(l+1)R + V(|\vec{r}|)R = E_\mu R. \quad (41)$$

19 Two-Particle Rigid-Rotor

The *rigid-rotor* is a system of two particles for which the distance between them $|\vec{r}| = d$ is constant. The Hamiltonian of the system is described by Eq. (41), where the first two terms are equal to zero, and $E_\mu = \frac{\hbar^2}{2\mu d^2} l(l+1) + V(d)$, with $\psi_\mu = Y_l^m(\theta, \phi)$.

The moment of inertia of a system of particles is $I_\zeta \equiv \sum_{i=1}^2 m_i r_i^2$, where m_i is the mass of particle i and r_i is the particle distance to the ζ axis.

Exercise 30: Prove that $I = \mu d^2$ for the two-particle rigid rotor, where $\mu = \frac{m_1 m_2}{m_1 + m_2}$, $d = r_2 - r_1$, and ζ is an axis with the center of mass of the system and is perpendicular to the axis that has the center of mass of both particles. Assume that the center of mass lies at the origin of coordinates, and that the x axis has the center of mass of both particles in the system.

The rotational energy levels of the rigid rotor are:

$$E_\mu = \frac{\hbar^2}{2I} l(l+1), \text{ with } l = 0, 1, 2, \dots \quad (42)$$

These energy levels usually give a good approximation of the rotational energy levels of diatomic molecules (e.g., the HCl molecule).

20 Problem Set (due 10/28/03)

Exercise 31: Solve problems 6.5 and 6.6 of reference 1.

Exercise 32: Prove that the angular momentum operator $L = r \times p$ is hermitian.

Exercise 33: Prove that,

$$\Psi(x + a) = e^{(i/\hbar)ap}\Psi(x),$$

where $p = -i\hbar\partial/\partial x$, and a is a finite displacement.

Exercise 34: Let \hat{H} be the Hamiltonian operator of a system. Denote ψ_k the eigenfunctions of \hat{H} with eigenvalues E_k . Prove that $\langle \psi_n | [\hat{Q}, \hat{H}] | \psi_k \rangle = 0$, for any arbitrary operator \hat{Q} , when $n = k$.

Exercise 35: Prove that,

$$[x, H] = i\hbar p/m,$$

where, $H = p^2/(2m) + V(x)$.

Exercise 36: Prove that,

$$L_- Y_l^m = \hbar \sqrt{(l+m)(l-m+1)} Y_l^{m-1},$$

where $L_z Y_l^m = m\hbar Y_l^m$, and $L^2 Y_l^m = \hbar^2 l(l+1) Y_l^m$.

Exercise 37: Consider a system described by the Hamiltonian matrix,

$$H = \begin{pmatrix} -E_0 & \Delta \\ \Delta & E_0 \end{pmatrix},$$

where the matrix elements $H_{jk} = \langle \psi_j | \hat{H} | \psi_k \rangle$. Consider that the system is initially prepared in the ground state, and is then influenced by the perturbation $W(t)$ defined as follows,

$$W(t) = \begin{pmatrix} 0 & e^{-t^2/\tau^2 - i\omega t} \\ e^{-t^2/\tau^2 + i\omega t} & 0 \end{pmatrix}.$$

Calculate the probability of finding the system in the excited state at time $t \gg \tau$.

21 Hydrogen Atom

Consider the hydrogen atom, or hydrogen-like ions (e.g., He^+ , Li^{2+} , ... etc.), with nuclear charge $+ze$, and mass M , and the electron with charge $-e$, and mass m . The potential energy of the system is a central potential (e.g., the Coulombic potential),

$$V = -\frac{ze^2k}{r},$$

where r is the electron-nucleus distance and $k = \begin{cases} 1 & \text{in a.u.} \\ 1/4\pi\epsilon_0 & \text{in SI units} \end{cases}$

The total Hamiltonian is,

$$\hat{H} = -\frac{\hbar^2}{2(m_e + m_n)} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 + V(r),$$

where $\mu = \frac{m_e m_n}{m_n + m_e}$. Note that $\boxed{\mu \approx m_e}$, since $m_e \ll m_n$. The Hamiltonian that includes only the second and third terms of \hat{H} is represented by the symbol \hat{H}^{el} and is called the *electronic Hamiltonian* because it depends only on the electronic coordinate r . In order to find the electronic eigenvalues, we must solve the equation,

$$\hat{H}^{el} \psi_{el} = E_{el} \psi_{el}. \quad (43)$$

Eq. (43) is the eigenvalue problem of a one particle central-potential. We consider the factorizable solution,

$$\psi_{el} = R(r) Y_l^m(\theta, \phi), \quad \text{with,} \quad l = 0, 1, 2, \dots \quad |m| < l,$$

where $R(r)$ satisfies the equation,

$$-\frac{\hbar^2}{2\mu} \left[\frac{\partial^2 R}{\partial r^2} + \frac{2}{r} \frac{\partial R}{\partial r} - \frac{\hbar^2}{\hbar^2 r^2} l(l+1)R \right] - \frac{Ze^2 R}{r} = ER. \quad (44)$$

This equation could be solved by first transforming it into the *associated Laguerre equation*, for which solutions are well-known. Here, however, we limit the presentation to note that Eq. (44) has solutions that are finite, single valued and square integrable only when

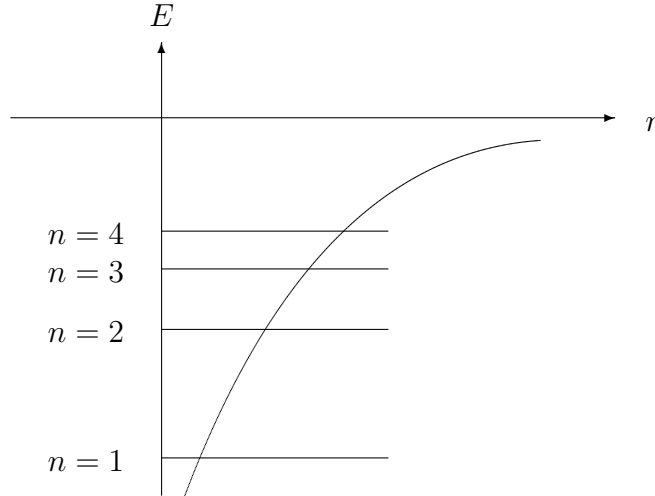
$$E = -\frac{Z^2 \mu e^4}{2\hbar^2 n^2}, \quad \text{or} \quad E = -\frac{Z^2 e^2}{2an^2}, \quad (45)$$

where $n = 1, 2, 3, \dots$, and $a = \frac{\hbar^2}{\mu e^2}$ is the *Bohr radius*.

These are the bound-state energy levels of hydrogen-like atoms responsible for the *discrete* nature of the absorption spectrum. In particular, the wavenumbers of the spectral lines are

$$\bar{\omega} = \frac{E_2 - E_1}{hc} = -\frac{Z^2 \mu e^4}{hc 2\hbar^2} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right).$$

The eigenvalues can be represented by the following diagram:



Degeneracy: Since the energy E depends only on the principal quantum number n , and the wave function ψ_{el} depends on n, l and m , there are n^2 possible states with the same energy.

States with the same energy are called *degenerate states*. The number of states with the same energy is the *degeneracy* of the energy level.

$$n=1, 2, 3, \dots$$

$$l=0, 1, 2, \dots, n-1 \quad \} \text{ these are } n \text{ states}$$

$$m=-l, -l+1, \dots, 0, 1, 2, \dots, l \quad \} \text{ these are } 2l + 1 \text{ states}$$

Exercise 38: Prove that the degeneracy of the energy level E_n is n^2 .

The complete hydrogen-like bound-state wave functions with quantum numbers n , l and m are,

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)P_l^m(\theta)\frac{1}{\sqrt{2\pi}}e^{im\phi},$$

where $P_l^m(\theta)$ are the *associated Legendre polynomials* (introduced in page 49), and $R_{nl}(r)$ are the *Laguerre associated polynomials*,

$$R_{nl}(r) = r^l e^{-\frac{zr}{na}} \sum_{j=0}^{n-l-1} b_j r^j, \quad \text{where } a \equiv \frac{\hbar^2}{\mu e^2} = 0.529177\text{\AA},$$

and,

$$b_{j+1} = \frac{2z}{na} \frac{j+l+1-n}{(j+1)(j+2l+2)} b_j.$$

Example 1: Consider the ground state wave function of the H atom with $n = 1, l = 0, m = 0$:

$$\boxed{R_{10}(r) = e^{-\frac{z}{a}r} b_0},$$

where, $b_0^2 = 1/\int_0^\infty dr r^2 e^{-\frac{2zr}{a}}$, and $b_0 = 2(\frac{z}{a})^{3/2}$.

Therefore,

$$\psi_{100}(r, \theta, \phi) = 2\left(\frac{z}{a}\right)^{3/2} \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2}} e^{-\frac{z}{a}r}.$$

Note: An alternative notation for wave functions with orbital quantum number $l = 0, 1, 2, \dots$ is

	s	p	d	f	$g\dots$
l	0	1	2	3	4...

Example 2: The possible wave functions with $n = 2$ are:

$$2s \quad 2p_0 \quad 2p_1 \quad 2p_{-1},$$

$$\psi_{200} \quad \psi_{210}, \quad \psi_{211} \quad \psi_{21-1},$$

Exercise 39: Show that,

$$\psi_{2s} = \frac{1}{\sqrt{\pi}} \left(\frac{z}{2a}\right)^{3/2} \left(1 - \frac{zr}{2a}\right) e^{-zr/2a}, \quad \psi_{2p_{-1}} = \frac{1}{8\sqrt{\pi}} \left(\frac{z}{a}\right)^{5/2} r e^{-zr/2a} \sin\theta e^{-i\phi},$$

$$\psi_{2p_0} = \frac{1}{\sqrt{\pi}} \left(\frac{z}{2a}\right)^{5/2} r e^{-zr/2a} \cos\theta, \quad \psi_{2p_1} = \frac{1}{8\sqrt{\pi}} \left(\frac{z}{a}\right)^{5/2} r e^{-zr/2a} \sin\theta e^{i\phi}.$$

Exercise 40: Compute the ionization energy of He^+ .

Exercise 41: Use perturbation theory to first order to compute the energies of states ψ_{210} , ψ_{211} , and ψ_{21-1} when a hydrogen atom is perturbed by a magnetic field $\vec{B} = B\hat{z}$, according to $\omega = -\beta\vec{L}\cdot\vec{B}$, where $\beta = \frac{e\hbar}{2mc}$. (The splitting of spectroscopic lines, due to the perturbation of a magnetic field, is called *Zeeman effect*).

Radial Distribution Functions

The probability of finding the electron in the region of space where r is between r to $r + dr$, θ

between θ to $\theta + d\theta$ and ϕ between ϕ and $\phi + d\phi$ is,

$$P = R^*(r)R(r)Y_l^m(\theta)^*Y_l^m(\theta)r^2\sin\theta drd\theta d\phi.$$

Therefore, the total probability of finding the electron with r between r and $r + dr$ is,

$$P^r(r) = \left[\int_0^\pi d\theta \int_0^{2\pi} d\phi Y_l^m(\theta)^*Y_l^m(\theta)\sin\theta \right] R^*(r)R(r)r^2 dr,$$

where $\int_0^\pi d\theta \int_0^{2\pi} d\phi Y_l^m(\theta)^*Y_l^m(\theta)\sin\theta = 1$.

Real Hydrogen-like Functions

Any linear combination of degenerate eigenfunctions of energy E is also an eigenfunction of the Hamiltonian with the same eigenvalue E . Certain linear combinations of hydrogen-like wavefunctions generate real eigenfunctions. For example, when $l = 1$,

$$\frac{1}{\sqrt{2}}(\psi_{n11} + \psi_{n1-1}) = R_{n1}(r)\sin\theta\cos\phi \equiv \psi_{P_{2x}},$$

$$\frac{1}{\sqrt{2}i}(\psi_{n11} - \psi_{n1-1}) = R_{n1}(r)\sin\theta\sin\phi \equiv \psi_{P_{2y}},$$

$$\psi_{210} \equiv \psi_{2P_z},$$

are real and mutually orthogonal eigenfunctions.

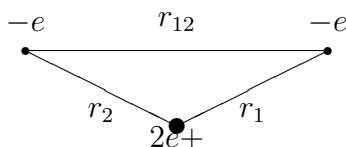
Function ψ_{2P_z} is zero in the xy plane, positive above such plane, and negative below it. Functions ψ_{2P_x} and ψ_{2P_y} are zero at the zy and xz planes, respectively. $\psi_{2P_{-1}}$ and ψ_{2P_1} are eigenfunctions of \hat{L}^2 with eigenvalue $2\hbar^2$. However, since $\psi_{2P_{-1}}$ and ψ_{2P_1} are eigenfunctions of \hat{L}_z with different eigenvalues (e.g., with eigenvalues \hbar and $-\hbar$, respectively), linear combinations ψ_{2P_x} , and ψ_{2P_y} , are eigenfunctions of \hat{L}^2 but not eigenfunctions of L_z .

Exercise 42: (A) What is the most probable value of r , for the ground state of a hydrogen atom? Such value is represented by r_M .

- (B) What is the total probability of finding the electron at a distance $r \leq r_M$?
- (C) Verify the orthogonality of functions $2P_x$, $2P_y$, and $2P_z$.
- (D) Verify that the ground state of the hydrogen atom is an eigenstate of \hat{H} , but that such state is not an eigenstate of \hat{T} , or \hat{V} .

22 Helium Atom

The helium atom is represented by the following diagram,



This diagram represents two electrons with charge $-e$, and a nucleus with charge $+2$.

The Hamiltonian of the Helium atom is,

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla_{r_1}^2 - \frac{2e^2}{r_1} - \frac{\hbar^2}{2\mu} \nabla_{r_2}^2 - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}.$$

Note that the term $\frac{e^2}{r_{12}}$ couples two one-electron hydrogenlike Hamiltonians. In order to find a solution to the eigenvalue problem,

$$\hat{H}\psi = E\psi,$$

we implement an approximate method. We first solve the problem by neglecting the coupling term. Then we consider such term to be a small perturbation, and we correct the initially zeroth-order eigenfunctions and eigenvalues by using perturbation theory.

Neglecting the coupling term, the Hamiltonian becomes,

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2\mu} \nabla_{r_1}^2 - \frac{2e^2}{r_1} - \frac{\hbar^2}{2\mu} \nabla_{r_2}^2 - \frac{2e^2}{r_2},$$

the sum of two independent one-electron Hamiltonians. The eigenfunctions of such Hamiltonian are,

$$\psi = R_{nl}(r_1)P_l^m(\theta_1)\frac{1}{\sqrt{2\pi}}e^{im\phi_1}R_{nl}(r_2)P_l^m(\theta_2)\frac{1}{\sqrt{2\pi}}e^{im\phi_2},$$

and the eigenvalues are,

$$E_{n_1n_2}^{(0)} = -\frac{z^2\mu e^4}{2\hbar^2n_1^2} - \frac{z^2\mu e^4}{2\hbar^2n_2^2}.$$

Exercise 43: Prove that,

$$\langle \psi_{100} | \frac{e^2}{r_{12}} | \psi_{100} \rangle = \frac{5}{8}e^2\frac{z}{a}.$$

In order to illustrate how to correct the zeroth order solutions by implementing perturbation theory, we compute the first order correction to the ground state energy as follows,

$$E = E_{11}^{(0)} + \langle \psi_{100} | \frac{e^2}{r_{12}} | \psi_{100} \rangle = -\frac{z^2\mu e^4}{\hbar^2} + \frac{5}{8}e^2\frac{z}{a}.$$

Alternatively, the variational method could be implemented to obtain better results with simple functions $\tilde{\psi}$, e.g., products of hydrogenlike orbitals with an effective nuclear charge z' :

$$\tilde{\psi} = A^2 e^{-\frac{z'}{a}(r_1+r_2)}.$$

According to the variational theorem, the expectation value $\langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle$ is always higher than the ground state energy. Therefore, the optimum coefficient z' minimizes the expectation value,

$$\tilde{E}(z') = \langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle, \quad \text{where}$$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla_{r_1}^2 - \frac{z'e^2}{r_1} - \frac{\hbar^2}{2\mu}\nabla_{r_2}^2 - \frac{z'e^2}{r_2} - \frac{(2-z')e^2}{r_1} - \frac{(2-z')e^2}{r_2} + \frac{e^2}{r_{12}}.$$

Computing the expectation value of \hat{H} analytically we obtain,

$$\tilde{E}(z') = -\frac{z'^2 e^2}{a} - 2A^2 \int dr e^{-\frac{z'2r}{a}} r^2 \frac{(2-z')}{r} e^2 + A^2 \int dr_1 \int dr_2 \frac{e^{-\frac{2z'}{a}(r_1+r_2)} r_2^2 e^2 r_1^2}{r_1 - r_2},$$

$$\tilde{E}(z') = -\frac{z'^2 e^2}{a} - 2z' \frac{(2-z')}{a} e^2 + \frac{5}{8} z' \frac{e^2}{a}.$$

Therefore, the optimum parameter z' is obtained as follows,

$$\frac{\partial \tilde{E}(z')}{\partial z'} = 0, \rightarrow z'_{\text{opt}} = 2 - \frac{5}{16}, \rightarrow \tilde{E}(z'_{\text{opt}}) = \left(2 - \frac{5}{16}\right)^2 \frac{e^2}{a} - 2 \left(2 - \frac{5}{16}\right) 2 \frac{e^2}{a} + \frac{5}{8} \left(2 - \frac{5}{16}\right) \frac{e^2}{a}.$$

23 Spin-Atom Wavefunctions

The description of atoms can be formulated to a very good approximation under the assumption that the total Hamiltonian depends only on spatial coordinates (and derivatives with respect to spatial coordinates), but *not* on spin variables. We can, therefore, separate the stationary-state wave function according to a product of spatial and spin wavefunctions.

Example 1: The spin-atom wavefunction of the hydrogen atom can be approximated as follows,

$$\psi_{el} = \psi(x, y, z)g(m_s),$$

where $g(m_s) = \alpha, \beta$, when $m_s = 1/2, -1/2$, respectively. Since the Hamiltonian operator is assumed to be independent of spin variables, it does not affect the spin function, and the eigenvalues of the system are the same as the energies found with a wave function that did not involve spin coordinates. Mathematically,

$$\hat{H}[\psi(x, y, z)g(m_s)] = g(m_s)\hat{H}\psi(x, y, z) = Eg(m_s)\psi(x, y, z).$$

The only consequence of modeling the hydrogen atom according to a *spin-atom wavefunction* is that the degeneracy of the energy levels is increased.

Example 2: The ground electronic state energy of the helium atom has been modeled according to the zeroth-order wave function $1S(1) 1S(2)$. In order to take spin into account we must

multiply such spatial wavefunction by a spin eigenfunction. Since each electron has two possible spin states, there are in principle four possible spin functions:

$$\alpha(1)\alpha(2), \quad \alpha(1)\beta(2), \quad \beta(1)\alpha(2), \quad \text{and} \quad \beta(1)\beta(2).$$

Functions $\alpha(1)\beta(2)$, and $\beta(1)\alpha(2)$, however, are not invariant under an electron permutation (i.e., these functions make a distinction between electron 1 and electron 2). Therefore, such functions are inadequate to describe the state of a system of *indistinguishable* quantum particles, such as electrons. Instead of working with functions $\alpha(1)\beta(2)$ and $\beta(1)\alpha(2)$, it is necessary to construct linear combinations of such functions, e.g.,

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) \pm \beta(1)\alpha(2)],$$

with correct exchange properties associated with indistinguishable particles,

$$\hat{P}_{12}\psi_{(1,2)} = \pm\psi_{(2,1)}.$$

The two linear combinations, together with functions $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$, form the basis of four normalized two-electron spin eigenfunctions of the helium atom.

24 Pauli Exclusion Principle

Pauli observed that relativistic quantum field theory requires that particles with *half-integer* spin ($s=1/2, 3/2, \dots$) must have *antisymmetric* wave functions and particles with *integer* spin ($s=0, 1, \dots$) must have *symmetric* wave functions. Such observation is usually introduced as an additional postulate of quantum mechanics: *The wave function of a system of electrons must be antisymmetric with respect to interchange of any two electrons.*

As a consequence of such principle is that *two electrons with the same spin cannot have the*

same coordinates, since the wavefunction must satisfy the following condition:

$$\psi_{(x_1, x_2)} = -\psi_{(x_2, x_1)},$$

and, therefore, $\psi_{(x_1, x_1)} = 0$. For this reason the principle is known as the *Pauli Exclusion Principle*.

Another consequence of the Pauli Principle is that since the ground state wave function of the He atom must also be anti-symmetric, and since the spatial part of the zeroth order wave function is symmetric, $\Psi = 1S(1)1S(2)$, then the spin wave function χ must be anti-symmetric,

$$\chi = \frac{1}{\sqrt{2}} \begin{vmatrix} \alpha(1) & \beta(1) \\ \alpha(2) & \beta(2) \end{vmatrix},$$

and the overall zeroth-order wave function becomes,

$$\psi = 1S(1)1S(2) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]. \quad (46)$$

Note that this anti-symmetric spin-atom wave function can be written in the form of the *Slater determinant*,

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1S(1)\alpha(1) & 1S(2)\beta(1) \\ 1S(1)\alpha(2) & 1S(2)\beta(2) \end{vmatrix}.$$

25 Lithium Atom

The spin factor affects primarily the *degeneracy* of the energy levels associated with the hydrogen and helium atoms. To a good approximation, the spin factors do not affect the energy levels of such atoms.

The lithium atom, however, has three electrons. An antisymmetric spin wave function of three electrons could in principle be written as the Slater determinant,

$$\chi = \frac{1}{\sqrt{6}} \begin{vmatrix} \alpha(1) & \beta(1) & \alpha(1) \\ \alpha(2) & \beta(2) & \alpha(2) \\ \alpha(3) & \beta(3) & \alpha(3) \end{vmatrix}. \quad (47)$$

Such Slater determinant, however, is equal to zero because two of the columns are equal to each other. This fact rules out the possibility of having a zero order wave function that is the Fock product of three hydrogenlike functions:

$$\psi^{(0)} = 1S(1) 1S(2) 1S(3) \quad (48)$$

Only if the construction of an antisymmetric spin wave function was possible, we could proceed in analogy to the Helium atom and compute the perturbation due to repulsive coupling terms as follows,

$$E^{(1)} = \langle \psi | \frac{e^2}{r_{12}} | \psi \rangle + \langle \psi | \frac{e^2}{r_{23}} | \psi \rangle + \langle \psi | \frac{e^2}{r_{13}} | \psi \rangle$$

where ψ is the product of hydrogenlike functions of Eq. (48).

Having ruled out such possibility, we construct the zeroth order ground-state wave function for lithium in terms of a determinant similar to Eq. (47), but where each element is a spin-orbital (i.e., a product of a one electron spatial orbital and one-electron spin function),

$$\psi^{(0)} = \frac{1}{\sqrt{6}} \begin{vmatrix} 1S(1)\alpha(1) & 1S(1)\beta(1) & 2S(1)\alpha(1) \\ 1S(2)\alpha(2) & 1S(2)\beta(2) & 2S(2)\alpha(2) \\ 1S(3)\alpha(3) & 1S(3)\beta(3) & 2S(3)\alpha(3) \end{vmatrix}, \quad (49)$$

where the third column includes the spatial orbital $2S$, instead of the orbital $1S$, because the Pauli exclusion principle rules out the possibility of having two electrons in the same spin-orbital. It is important to note that Eq. (49) is not simply a product of spatial and spin parts as for the H and He atoms. In contrast, the wave function of Li involves a linear combination of terms which are products of non-factorizable spatial and spin wavefunctions.

Exercise 44: Show that for the lithium atom, treating the electron-electron repulsion interaction \hat{H}_{rep} as a perturbation,

$$E^{(0)} = E_{1S}^{(0)} + E_{1S}^{(0)} + E_{2S}^{(0)},$$

and,

$$E^{(1)} = 2 \langle 1S(1)2S(2) | \frac{e^2}{r_{12}} | 1S(1)2S(2) \rangle + \langle 1S(1)1S(2) | \frac{e^2}{r_{12}} | 1S(1)1S(2) \rangle - \langle 1S(1)2S(2) | \frac{e^2}{r_{12}} | 2S(1)1S(2) \rangle .$$

26 Spin-Orbit Interaction

Although neglected up to this lecture, the interaction between the electron-spin and the orbital angular momentum must also be included in the atomic Hamiltonian. Such interaction is described according to the *spin-orbit Hamiltonian* defined as follows,

$$\hat{H}_{SO} = \frac{1}{2m_e c^2} \frac{1}{r} \left(\frac{\partial V}{\partial r} \right) \hat{L} \cdot \hat{S} = \xi \hat{L} \cdot \hat{S}, \quad (50)$$

where V is the Coulombic potential of the electron in the field of the atom. Note that the spin-orbit interaction is proportional to $\hat{L} \cdot \hat{S}$. A proper derivation of Eq. (50) requires a relativistic treatment of the electron which is beyond the scope of these lectures.

Note: A classical description of such interaction also gives a perturbation proportional to $\hat{L} \cdot \hat{S}$. This is because from the reference frame of the electron, the nucleus is a moving charge that generates a magnetic field B , proportional to \hat{L} . Such magnetic field interacts with the spin magnetic moment $m_s = -e/m_e \hat{S}$. Therefore, the interaction between B and m_s is proportional to $\hat{L} \cdot \hat{S}$. Unfortunately, however, the proportionality constant predicted by such classical model is *incorrect*, and a proper derivation requires a relativistic treatment of the electron as mentioned earlier in this section.

In order to compute the spin-orbit Hamiltonian of a many-electron atom, it is necessary to compute first an approximate effective potential V_i of each electron i in the total electric field of electrons and nuclear charges. Then, we can compute the sum over *all* electrons as follows,

$$\hat{H}_{SO} \approx \frac{1}{2m_e c^2} \sum_i \frac{1}{r_i} \frac{\partial V_i}{\partial r_i} \hat{L}_i \cdot \hat{S}_i = \sum_i \xi_i \hat{L}_i \cdot \hat{S}_i. \quad (51)$$

The correction of eigenfunctions and eigenvalues, due to the spin-orbit coupling, is usually computed according to perturbation theory after solving the atomic eigenvalue problem in the absence of the spin-orbit interaction. For example, the spin-orbit correction to the eigenvalue of state $|\Psi\rangle$ for a one-electron atom is,

$$E_{S.O.}^{(1)} \approx \langle \Psi | \xi \hat{L} \cdot \hat{S} | \Psi \rangle. \quad (52)$$

Note that the $L \cdot S$ product can be written in terms of J^2 , L^2 and S^2 as follows, $L \cdot S = \frac{1}{2}(J^2 - L^2 - S^2)$, because, $J^2 = J \cdot J = (L + S)(L + S) = L^2 + S^2 + 2L \cdot S$, and, since the unperturbed wave function is an eigenfunction of L^2 , S^2 and J^2 ,

$$L \cdot S |\psi\rangle = \frac{1}{2} \hbar^2 (J(J+1) - L(L+1) - S(S+1)) |\psi\rangle.$$

Therefore,

$$E_{S.O.} \approx \frac{1}{2} \hbar^2 \langle \xi \rangle [J(J+1) - L(L+1) - S(S+1)].$$

It is important to note that, due to the spin-orbit coupling, the total energy of a state depends on the value of the total angular momentum quantum number J . Furthermore, each of the energy levels is $(2J+1)$ times degenerate, as determined by the possible values of M_J . For example, when $L=1$, and $S=1/2$, then the possible values of J are $1/2$ and $3/2$, since $(J=L+S, L+S-1, \dots, L-S)$.

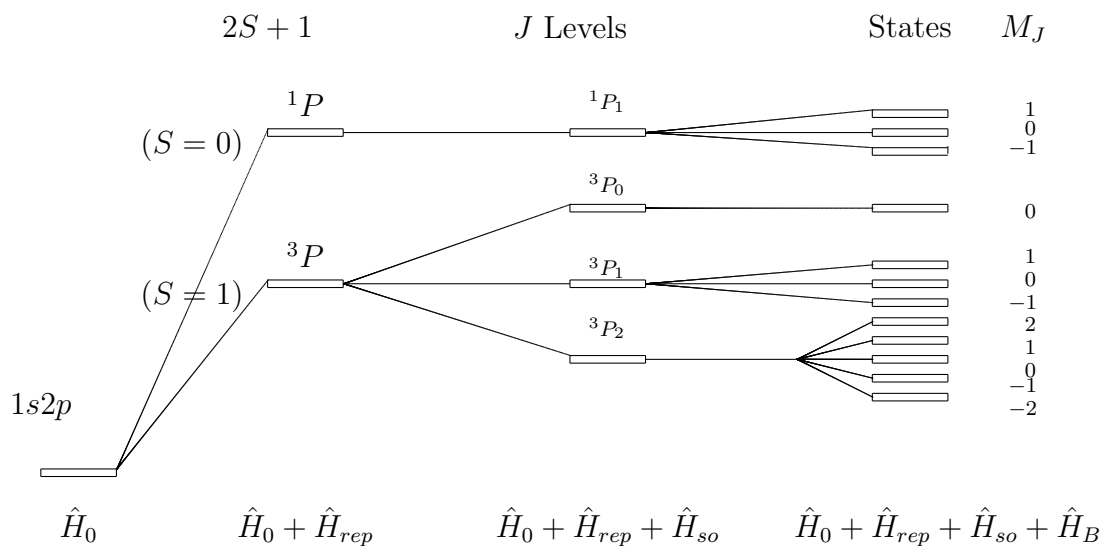
It is possible to remove the degeneracy of energy levels by applying an external magnetic field that perturbs the system as follows, $H_B = -m \cdot B$, where $m = m_L + m_S$, with $m_L = -\frac{e}{2m_e} L$, and $m_S = -\frac{e}{m_e} S$. The external perturbation is, therefore, described by the following Hamiltonian,

$$H_B = -\frac{e}{2m_e} (L + 2S) \cdot B = -\frac{e}{2m_e} (J + S) \cdot B.$$

The energy correction according to first-order perturbation theory is:

$$E_B = -\frac{e}{2m_e} B (\hbar M_J + \langle S_z \rangle) = ABM_J,$$

where $\langle S_z \rangle = \hbar M_J \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$ and A is a proportionality constant. Therefore, the perturbation of an external magnetic field splits energy level characterized by quantum number J into $2J+1$ energy sub-levels. These sub-levels correspond to different possible values of M_J , as described by the following diagram:



Exercise 45: (A). Calculate the energy of the spectroscopic lines associated with transitions $3S \rightarrow 3P$ for Na in the absence of an external magnetic field. (B). Calculate the spectroscopic lines associated with transitions $3S \rightarrow 3P$ for Na atoms perturbed by an external magnetic field B_z as follows:

$$\hat{H}_B = -\hat{m} \cdot B = \beta_e B \hbar^{-1} (\hat{J}_z + \hat{S}_z),$$

and $E_B = \langle \psi | \hat{H}_B | \psi \rangle = \beta_e B M_J g$, with $g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$.

27 Periodic Table

Previous sections of these lectures have discussed the electronic structure of H, He and Li atoms. The general approach implemented in those sections is summarized as follows. First, we *neglect the repulsive interaction between electrons* and write the zeroth order ground state wave functions as antisymmetrized products of spin-orbitals (Slater determinants), e.g.,

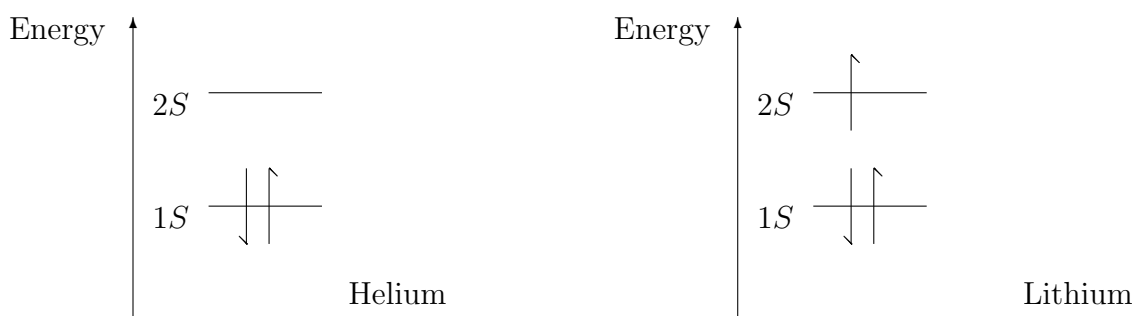
$$\psi_{He}^{gr} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1S(1)\alpha(1) & 1S(1)\beta(1) \\ 1S(2)\alpha(2) & 1S(2)\beta(2) \end{vmatrix} = 1S(1)1S(2) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)],$$

$$\psi_{Li}^{gr} = \frac{1}{\sqrt{6}} \begin{vmatrix} 1S(1)\alpha(1) & 1S(1)\beta(1) & 2S(1)\alpha(1) \\ 1S(2)\alpha(2) & 1S(2)\beta(2) & 2S(2)\alpha(2) \\ 1S(3)\alpha(3) & 1S(3)\beta(3) & 2S(3)\alpha(3) \end{vmatrix},$$

with zeroth order energies,

$$E_{He}^{(0)} = 2E(1S), \quad \text{and} \quad E_{Li}^{(0)} = 2E(1S) + E(2S),$$

represented by the following diagram:



It is important to note that these approximate wave functions are found by assuming that the electrons *do not interact with each other*. This is, of course, a very crude approximation. It is,

nonetheless, very useful because it is the underlying approximation for the construction of the periodic table. Approximate zeroth order wave functions can be systematically constructed for all atoms in the periodic table by considering the energy order of hydrogenlike atomic orbitals in conjunction with *Hund's Rules*.

Hund's First Rule: *Other things being equal, the state of highest multiplicity is the most stable.*

Hund's Second Rule: *Among levels of equal electronic configuration and spin multiplicity, the most stable level is the one with the largest angular momentum.*

These rules establish a distinction between the zeroth order wave functions of ground and excited electronic state configurations. For example, according to Hund's rules the lithium ground state wave function is,

$$\psi^{gr} = \frac{1}{\sqrt{6}} \begin{vmatrix} 1S(1)\alpha(1) & 1S(1)\beta(1) & 2S(1)\alpha(1) \\ 1S(2)\alpha(2) & 1S(2)\beta(2) & 2S(2)\alpha(2) \\ 1S(3)\alpha(3) & 1S(3)\beta(3) & 2S(3)\alpha(3) \end{vmatrix}, \quad (53)$$

and the first excited state wave function is,

$$\psi^{exc} = \frac{1}{\sqrt{6}} \begin{vmatrix} 1S(1)\alpha(1) & 1S(1)\beta(1) & 2P(1)\alpha(1) \\ 1S(2)\alpha(2) & 1S(2)\beta(2) & 2P(2)\alpha(2) \\ 1S(3)\alpha(3) & 1S(3)\beta(3) & 2P(3)\alpha(3) \end{vmatrix}.$$

Note that the energy order of hydrogenlike atomic orbitals, $E_n = -\frac{z^2 e^2}{2an^2}$, is not sufficient to distinguish between the two electronic configurations. According to such expression, orbitals 2p and 2s have the same energy E_2 . However, Hund's second rule distinguishes the ground electronic state as the one with higher angular momentum. This is verified by first order perturbation theory, since the perturbation energy of ψ^{exc} is higher than the perturbation energy computed with ψ^{gr} .

Exercise 46: Prove that according to first order perturbation theory, the energy difference ΔE

between the two states is

$$\Delta E(\psi^{gr} \rightarrow \psi^{exc}) = 2(J_{1S,2P} - J_{1S,2S}) - (K_{1S,2P} - K_{1S,2S}),$$

where $J_{\phi_1, \phi_2} = \langle \phi_1^{(i)} \phi_2^{(j)} | \frac{e}{r_{ij}} | \phi_1^{(i)} \phi_2^{(j)} \rangle \equiv$ Coulomb Integral,

and $K_{\phi_1, \phi_2} = \langle \phi_1^{(i)} \phi_2^{(j)} | \frac{e}{r_{ij}} | \phi_2^{(i)} \phi_1^{(j)} \rangle \equiv$ Exchange Integral.

Exercise 47: Use Hund's Rules to predict that the ground states of nitrogen, oxygen and fluorine atoms are 4S , 3P and 2P , respectively.

28 Problem Set (11/27/03)

Exercise 48: Use the variational approach to compute the ground state energy of a particle of mass m in the potential energy surface defined as follows, $V(x) = \lambda X^4$.

Hint: Use a Gaussian trial wave-function,

$$\phi(x) = \sqrt[4]{\frac{\alpha}{\pi}} \exp^{-\frac{\alpha}{2}x^2}.$$

From tables,

$$\int_{-\infty}^{\infty} dx x^4 e^{-\alpha x^2} = \frac{3}{4\alpha^2} \sqrt{\frac{\pi}{\alpha}}; \quad \int_{-\infty}^{\infty} dx e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}}; \quad \int_{-\infty}^{\infty} dx x^2 e^{-\alpha x^2} = \frac{1}{2\alpha} \sqrt{\frac{\pi}{\alpha}}.$$

Exercise 49: Compute the eigenvalues and normalized eigenvectors of $\sigma = \sigma_y + \sigma_z$, where,

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Exercise 50: Construct two excited state wavefunctions of He that obey the Pauli Exclusion

principle, with one electron in a 1S orbital and the other electron in the 2S orbital. Explain the symmetry of spin and orbital wave-functions?

Exercise 51: Consider a spin 1/2 represented by the spinor,

$$\chi = \begin{pmatrix} \cos\alpha \\ \sin\alpha \quad e^{i\beta} \end{pmatrix}.$$

What is the probability that a measurement of S_y would yield the value $-\frac{\hbar}{2}$ when the spin is described by χ ?

29 Hartree Self-Consistent Field Method

The Hartree Self-Consistent Field (SCF) Method is a variational approach for computing the Fock product,

$$\Phi = g_1(r_1, \theta_1, \phi_1)g_2(r_2, \theta_2, \phi_2)\dots g_n(r_n, \theta_n, \phi_n),$$

that minimizes the variational integral,

$$I = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}.$$

Functions $g_i(r_i, \theta_i, \phi_i)$ are one electron functions characterized by a set of variational parameters (e.g., the effective nuclear charge, when such functions are defined as hydrogenlike orbitals). The initial guess of the n-electron product function,

$$\Phi = S_1(r_1, \theta_1, \phi_1)S_2(r_2, \theta_2, \phi_2)\dots S_n(r_n, \theta_n, \phi_n), \quad (\text{Fock Product}),$$

is used to compute the potential energy,

$$V_1(r_1, \theta_1, \phi_1) = \sum_{j=2}^n Q_j \int \frac{\rho_j}{r_{1j}} d\sigma_j - \frac{ze^2}{r_1},$$

where $Q_1 = -e$ and $\rho_j = -e|S_j|^2$. Then, it is assumed that the effective potential acting on an electron can be adequately described by the *average* of the potential $V_1(r_1, \theta_1, \phi_1)$ over angles θ and ϕ ,

$$V_1(r_1) = \frac{1}{4\pi} \int d\theta_1 \int d\phi_1 \sin\theta_1 V_1(r_1, \theta_1, \phi_1).$$

Such potential function is used to solve the one-electron Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 + V_1(r_1) \right] t_1(1) = \epsilon_1 t_1(1),$$

according to the variational approach. The eigenfunctions $t_1(1)$ are improved version of the initially guessed functions S_1 . The procedure is then repeated, after replacing the *initial* trial function ϕ by the *improved* trial wavefunction $\tilde{\phi} = t_1 S_2 \dots S_n$, and t_2 is obtained as an improved version of S_2 . The procedure is repeated to obtain t_3 , etc., until S_n is replaced by t_n . The whole procedure is iterated (i.e., starting with $t_1 \dots$, etc.) until there is no further change from one iteration to the next one. The converged wave function gives the Hartree SCF solution of the eigenvalue problem with energy,

$$E = \sum_i \epsilon_i - \sum_i \sum_{j>i} J_{ij}.$$

The last term in this equation involves the Coulombic integrals J_{ij} and discounts all of the interactions that have been counted twice.

30 Hartree-Fock Self-Consistent Field Method

The Hartree-Fock Self-Consistent Field Method is similar to the Hartree SCF Method, but takes the antisymmetry property into account by writing the trial wave function as a Slater determinant of variational spin-orbitals,

$$\Phi = \frac{1}{\sqrt{n!}} \begin{vmatrix} 1S(1)\alpha(1) & 1S(1)\beta(1) & \dots \\ \dots & \dots & \dots \\ 1S(n)\alpha(n) & 1S(n)\beta(n) & \dots \end{vmatrix},$$

where typical basis functions for the spatial orbitals 1S, 2S, ..., etc., are linear combinations of Gaussians, or Slater type orbitals $r^{n-1}e^{-\xi r/a_0}Y_l^m$.

Configuration Interaction

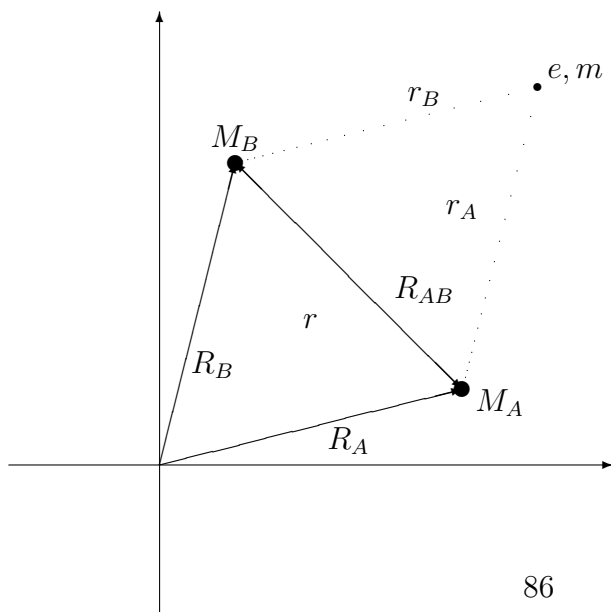
Improvement over the one-determinant trial wave function can be achieved by using a trial wave function that involves a linear combination of Slater determinants. This method is known as *configuration interaction*. The energy correction over the Hartree-Fock energy,

$$E_{cor} = E - E_{HF},$$

is known as *correlation energy*.

31 LCAO Method: H_2^+ Molecule

The H_2^+ molecule can be represented by the following diagram:



where A and B represent two hydrogen nuclei and e represents the electron. The Hamiltonian of the system is, **R1(376)**

$$\hat{H} = -\frac{\hbar^2}{2M_A} \nabla_{R_A}^2 - \frac{\hbar^2}{2M_B} \nabla_{R_B}^2 + H_{el}, \quad (54)$$

where,

$$\hat{H}_{el} = -\frac{\hbar^2}{2m} \nabla_r^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R_{AB}}. \quad (55)$$

This is another three-body Hamiltonian, similar to the Helium atom Hamiltonian, where instead of having two electrons and one nucleus we have two nuclei and one electron. In order to compute the eigenstates, we assume that the kinetic energy of the nuclei can be neglected when compared to the other terms in the Hamiltonian (Born-Oppenheimer approximation). The electronic energy is computed at various internuclear distances R_{AB} , by considering that the term $\frac{e^2}{R_{AB}}$, in Eq. (55) is a constant factor parametrized by R_{AB} . (In practice, this constant factor is ignored when solving the eigenvalue problem, since it can be added at the end of the calculation).

According to the linear combination of atomic orbitals (LCAO) method, a convenient trial state for H_2^+ can be written as follows,

$$|\Psi\rangle = C_A |\phi_A\rangle + C_B |\phi_B\rangle, \quad (\text{compare this equation with Eq. (21)})$$

where $|\phi_A\rangle$, and $|\phi_B\rangle$, are 1S atomic orbitals of atoms A and B, respectively.

According to the variational theorem, the optimum coefficients C_A and C_B can be found by minimizing the expectation value of the energy,

$$\langle E \rangle = \frac{\langle \psi | \hat{H}'_{el} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{C_A^2 H_{AA} + 2C_A C_B H_{AB} + C_B^2 H_{BB}}{C_A^2 S_{AA} + 2C_A C_B S_{AB} + C_B^2 S_{BB}},$$

with respect to C_A and C_B . Here, $H_{jk} = \langle \phi_j | \hat{H}'_{el} | \phi_k \rangle$, $S_{jk} = \langle \phi_j | \phi_k \rangle$, and

$$\hat{H}'_{el} = -\frac{\hbar^2}{2m} \nabla_r^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B}.$$

Exercise 52: Show that the condition,

$$\left(\frac{\partial \langle E \rangle}{\partial C_A} \right)_{C_B} = 0 \text{ implies } C_A(H_{AA} - \langle E \rangle) + C_B(H_{AB} - S_{AB} \langle E \rangle) = 0, \text{ and}$$

$$\left(\frac{\partial \langle E \rangle}{\partial C_B} \right)_{C_A} = 0 \text{ implies } C_A(H_{AB} - S_{AB} \langle E \rangle) + C_B(H_{BB} - \langle E \rangle) = 0, \text{ when } \langle \phi_j | \phi_j \rangle = 1.$$

These equations are called *secular equations* and have a nontrivial solution (i.e., a solution different from the trivial solution $C_A = 0, C_B = 0$), when the determinant of the expansion coefficients vanishes, i.e.,

$$\begin{vmatrix} H_{AA} - \langle E \rangle & H_{AB} - S_{AB} \langle E \rangle \\ H_{BA} - S_{BA} \langle E \rangle & H_{BB} - \langle E \rangle \end{vmatrix} = 0,$$

This determinant is called the *secular determinant*.

Since $|\phi_A\rangle$ and $|\phi_B\rangle$ are 1S orbitals, $H_{AA} = H_{BB}$, and $S_{AB} = S_{BA} = S$. Therefore,

$$(H_{AA} - \langle E \rangle)^2 - (H_{AB} - S \langle E \rangle)^2 = 0,$$

and

$$E_{\pm} = \frac{H_{AA} \pm H_{AB}}{1 \pm S}.$$

Substituting $\langle E \rangle_{\pm}$ in the secular equations we obtain,

$$C_{A\pm} = \pm C_{B\pm}.$$

Therefore,

$$\psi_+ = C_{A+}(\phi_A + \phi_B), \text{ where } C_{A+} = \frac{1}{\sqrt{2+2S}},$$

$$\psi_- = C_{A-}(\phi_A - \phi_B), \text{ where } C_{A-} = \frac{1}{\sqrt{2-2S}}.$$

The strategy followed in this section for solving the eigenvalue problem of H_2^+ can be summarized as follows:

1. Expand the solution $|\Psi\rangle$ according to a linear combination of atomic orbitals (LCAO).
2. Obtain a set of n secular equations according to the variational approach.

3. Solve the secular determinant by finding the roots of the characteristic equation, a polynomial of degree n in E .
4. Substitute each root into the secular equations and find the eigenvectors (e.g., the expansion coefficients in the LCAO) that correspond to such root.

The energies $\langle E \rangle_{\pm}$ are functions of H_{AA} , H_{AB} and S . The integral H_{AA} is defined as the sum of the energy of an electron in a 1S orbital and the attractive energy of the other nucleus:

$$H_{AA} = \int d\tau \phi_A^* \left[-\frac{\hbar^2}{2m} \nabla_r^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} \right] \phi_A = E_{1S}(H) - \int d\tau \phi_A^* \frac{e^2}{r_B} \phi_A. \quad (56)$$

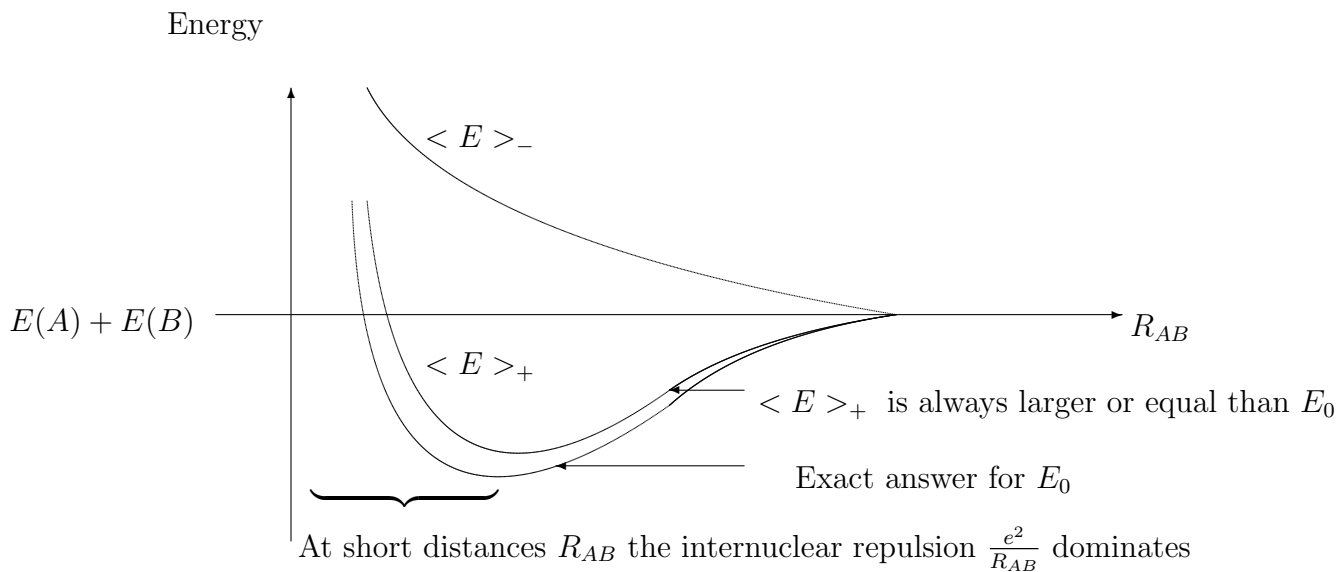
As the nuclei A and B are brought closer together, the second term in Eq. (56) (i.e., the term $\int d\tau \phi_A^* \frac{e^2}{r_B} \phi_A$) tends to make the energy of H_2^+ more negative, increasing the stability of the molecule. The term $\frac{e^2}{R_{AB}}$ is responsible for the repulsion between nuclei and increases monotonically as the two nuclei get closer together, counteracting the stabilization caused by $-\frac{e^2}{r_B}$. Therefore, the sum $H_{AA} + \frac{e^2}{R_{AB}}$ is not responsible for the stabilization of the system as the nuclei are brought closer together.

The integral H_{AB} defined as follows,

$$H_{AB} = \int d\tau \phi_A^* \left(-\frac{\hbar^2}{2m} \nabla_r^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} \right) \phi_B, \quad (57)$$

is called *resonance integral* and takes into account the fact that the electron is not restricted to any of the two 1S atomic orbitals, but it can rather be *exchanged* between the two orbitals.

At large values of R_{AB} , the resonance integral H_{AB} goes to zero. Decreasing R_{AB} , H_{AB} becomes more negative and stabilizes the molecule relative to the asymptotically separated atoms. The eigenvalues $\langle E \rangle_{\pm}$ can be represented as a function of R_{AB} by the following diagram:



Note that $\langle E \rangle_+$ is lower than $\langle E \rangle_-$ because H_{AA} and H_{AB} are negative.

In analogy to the variational approach implemented to study the Helium atom, one could further improve the variational solution of H_2^+ by optimizing the exponents ξ (e.g., effective nuclear charges) in the functions that represent ϕ_A and ϕ_B ,

$$\phi_{A/B} = \frac{\left(\frac{\xi}{2a}\right)^{3/2}}{\sqrt{\pi}} e^{-\frac{\xi r_{A/B}}{2a}}. \quad (58)$$

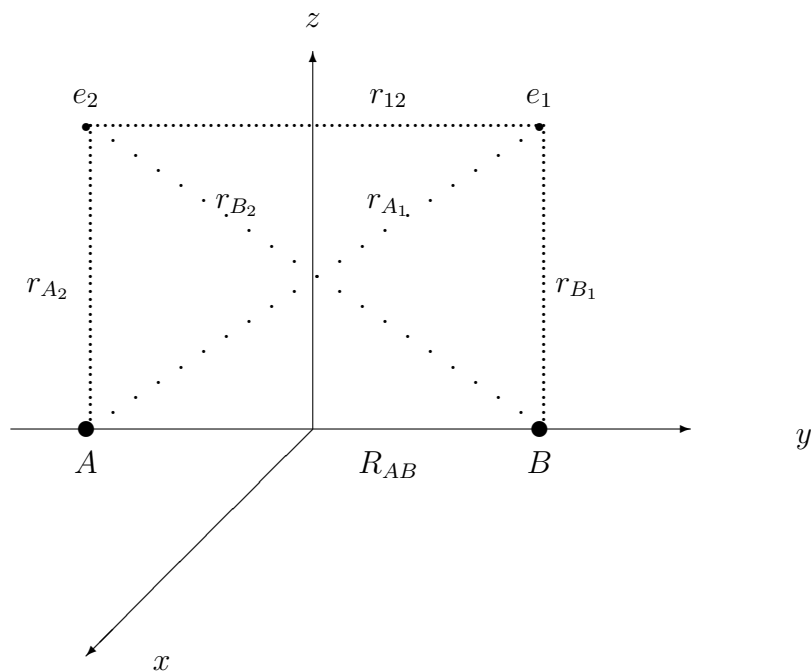
Such variational correction of the effective nuclear charge is known as *scaling*.

Exercise 53: According to the quantum mechanical description of H_2^+ explain:

- (1) Why do molecules form? What is a chemical bond?
- (2) Consider state $\psi_+ = (2 + 2S)^{-1/2}(\chi_A + \chi_B)$ where nucleus A is at $R_A = (\frac{R}{2}, 0, 0)$ and nucleus B is at $R_B = (-\frac{R}{2}, 0, 0)$. Compute $\psi^*\psi$ at the coordinate $(0,0,0)$, and compare such probability density to the sum of probability amplitudes due to ϕ_A and ϕ_B .

32 H₂ Molecule

The H₂ molecule can be represented by the following diagram:



The diagram includes two electrons, represented by e_1 and e_2 , and two protons A and B . The Hamiltonian of the system is,

$$\hat{H} = -\frac{\hbar^2}{2M_A} \nabla_{R_A}^2 - \frac{\hbar^2}{2M_B} \nabla_{R_B}^2 + \hat{H}_{el},$$

where

$$\hat{H}_{el} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{r_{A1}} - \frac{e^2}{r_{B1}} - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B2}} + \frac{e^2}{r_{12}} + \frac{e^2}{R_{AB}}.$$

In analogy to the He atom, it is possible to identify one-electron Hamiltonians (i.e., associated with electrons 1 and 2),

$$H_2^+(1) = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{r_{A1}} - \frac{e^2}{r_{B1}},$$

and,

$$H_2^+(2) = -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B2}}.$$

A zeroth order solution is obtained by neglecting the repulsion between electrons. Since $\frac{e^2}{R_{AB}}$ contributes only with a constant value to the energy (e.g., a constant parametrized by R_{AB}), we can make use of the theorem of separation of variables and obtain the solution of the eigenvalue problem,

$$\hat{H} | \psi \rangle = E | \psi \rangle,$$

as the product

$$| \psi \rangle = A | \Phi_1 \rangle | \Phi_2 \rangle, \quad (59)$$

where $| \Phi_1 \rangle$ and $| \Phi_2 \rangle$ are eigenstates of the H_2^+ Hamiltonian and A is the anti-symmetrizing spin wave function,

$$A = \frac{1}{N\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)].$$

Note that the hydrogen molecule occupies the same place in the theory of molecular electronic structure as the helium atom in the theory of atomic electronic structure. Therefore, the correction due to electronic repulsion can be calculated according to first order perturbation theory as follows,

$$E = 2E_{H_2^+}(R_{AB}) + \langle \psi | \frac{e^2}{r_{12}} | \psi \rangle - \frac{e^2}{R_{AB}}. \quad (60)$$

Note that the last term discounts the repulsion between nuclei that has been over-counted.

The equilibrium distance, $R_{AB}^{(eq)}$, is obtained by minimizing E with respect to R_{AB} . Substituting such value into Eq. (60), we obtain the minimum energy of the H_2 molecule.

The complete ground state of H_2 is described as follows,

$$\psi = \frac{1}{N\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] [1S_A(1)1S_A(2) + 1S_A(1)1S_B(2) + 1S_B(1)1S_A(2) + 1S_B(1)1S_B(2)], \quad (61)$$

where N is a normalization factor, obtained by substituting $| \Phi_1 \rangle$ and $| \Phi_2 \rangle$ in Eq. (59), by the ground state wave function of H_2^+ ,

$$\Phi_j = \frac{1}{\sqrt{N}} [1S_A(j) + 1S_B(j)].$$

According to Eq. (61), the probability of finding both electrons close to nucleus A (i.e., the probability of finding the electronic configuration $H_A^- H_B^+$), is determined by the square of the expansion coefficient associated with the term $1S_A(1)1S_A(2)$. Analogously, the probability of finding both electrons close to nucleus B is proportional to the square of the expansion coefficient associated with the term $1S_B(1)1S_B(2)$. Therefore, terms $1S_A(1)1S_A(2)$, $1S_B(1)1S_B(2)$ describe ionic configurations, while terms $1S_A(1)1S_B(2)$ and $1S_B(1)1S_A(2)$ describe covalent structures. Unfortunately, the LCAO wavefunction, introduced by Eq. (61), predicts the same probability for ionic and covalent configurations, $H_A^+ H_B^-$, $H_A^- H_B^+$, and $H_A H_B$, respectively. This is quite unsatisfactory since it is contrary to the chemical experience. The LCAO model predicts that upon dissociation half of the H_2 molecules break into ions H^- and H^+ . Contrary to such prediction, the H_2 molecule dissociates almost always into two hydrogen atoms.

Heitler-London(HL) Method:

The *Heitler-London approach* aims to correct the shortcomings of the LCAO description by neglecting the ionic terms altogether. Therefore, the HL wave function of H_2 includes only covalent terms as follows,

$$\psi_{HL} = \frac{1}{N'\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] [1S_A(1)1S_B(2) + 1S_B(1)1S_A(2)].$$

This wave function gives a better description of the energy as a function of R_{AB} and predicts the proper asymptotic behavior at large internuclear distances.

Exercise 54: Prove that, according to the HL approach,

$$E = \frac{J + K}{1 + S^2},$$

with

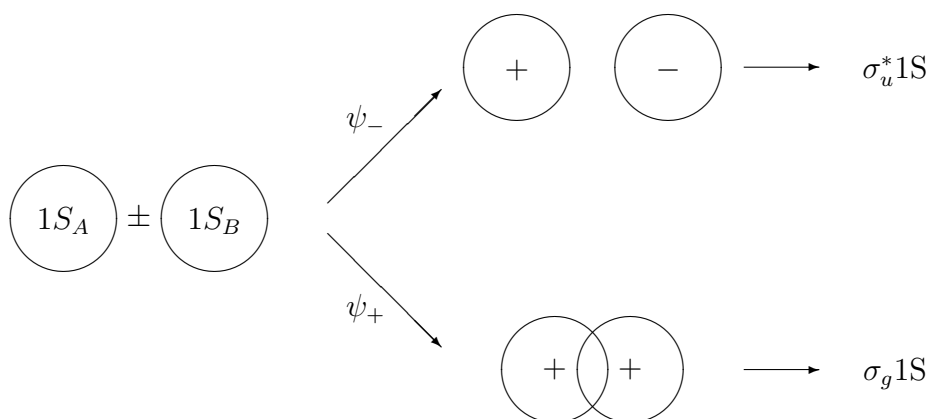
$$J = \langle 1S_A(1)1S_B(2) | H | 1S_A(1)1S_B(2) \rangle,$$

and

$$K = \langle 1S_A(1)1S_B(2) | H | 1S_B(1)1S_A(2) \rangle.$$

33 Homonuclear Diatomic Molecules

Other *homonuclear diatomic molecules* (e.g., Li_2 , O_2 , He_2 , F_2 , N_2 , ...) can be described according to the LCAO approach introduced with the study of the H_2^+ molecule. A general feature of the LCAO method is that a combination of two atomic orbitals on different centers gives two molecular orbitals (MO). One of these molecular orbitals is called *bonding* and the other one is called *antibonding*. The bonding state is more stable than the system of infinitely separated atomic orbitals. On the other hand, the antibonding state is less stable than the isolated atomic orbitals. The description of the H_2^+ molecule discussed in previous sections can be summarized by the following diagram:



This diagram introduces the nomenclature of states of homonuclear diatomic molecules, which is determined by the following aspects:

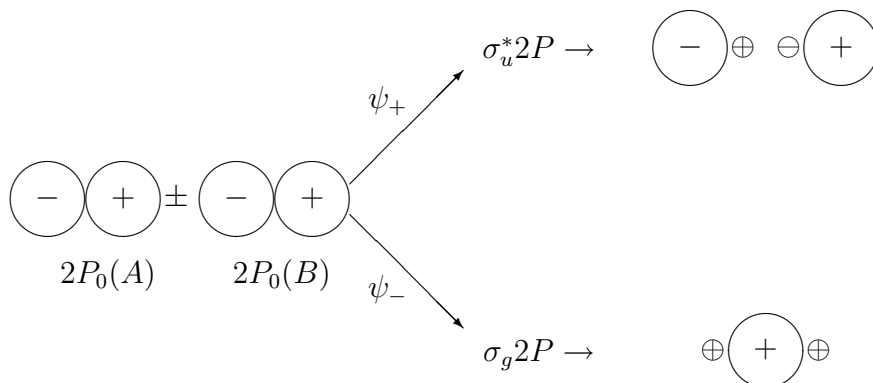
1. Nature of the atomic orbitals in the linear combination (e.g., 1S orbitals in the study of the H_2^+ molecules).

2. Eigenvalue of \hat{L}_z , with z the internuclear axis (e.g., such eigenvalue is zero for the H_2^+ molecule and, therefore, the orbital is called σ).

3. Eigenvalue of the inversion operator through the center of the molecule (e.g., g when the eigenvalue is 1, and u when the eigenvalue is -1).

4. Stability with respect to the isolated atoms (e.g., an asterisk indicates that the state is unstable relative to the isolated atoms).

Other homonuclear diatomic molecules involve linear combinations of p orbitals. Such linear combinations give rise to σ type orbitals when there is no component of the angular momentum in the bond axis (e.g., we choose the bond axis to be the z axis). An example of such linear combination is represented by the following diagram:



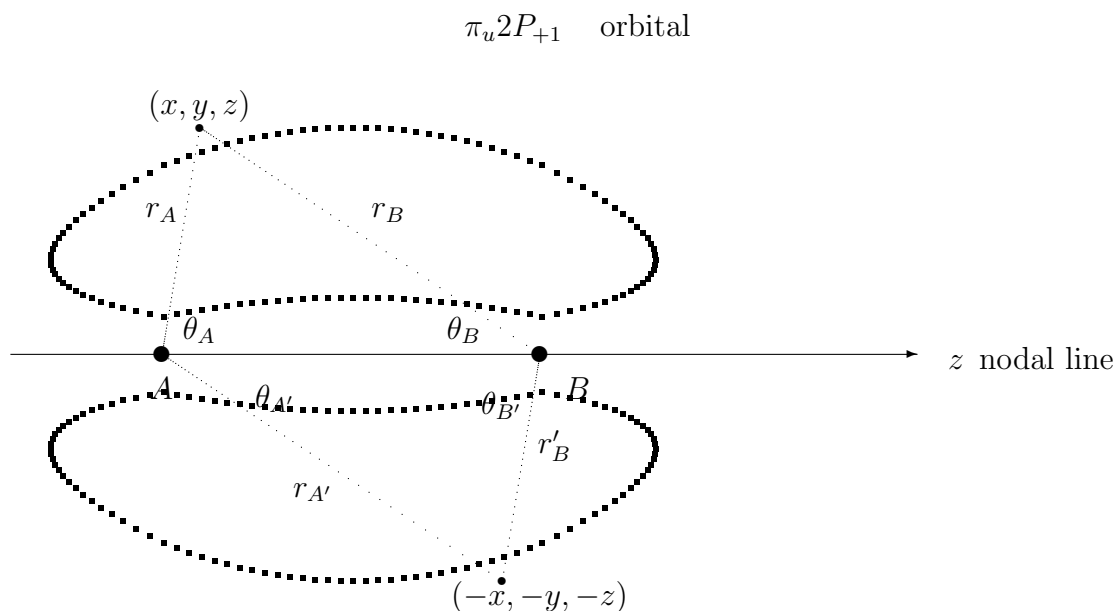
In order to classify molecular states according to eigenvalues of \hat{L}_z , we make linear combinations of eigenfunctions of \hat{L}_z with common eigenvalues. There are four possible states:

$$\begin{aligned} m=1: & \quad 2P_{+1}(A) \pm 2P_{+1}(B), & \quad \overbrace{\pi_u 2P_{+1}}^{\oplus}, \overbrace{\pi_g^* 2P_{+1}}^{\ominus}, \\ m=-1: & \quad 2P_{-1}(A) \pm 2P_{-1}(B), & \quad \pi_u 2P_{-1}, \pi_g^* 2P_{-1}. \end{aligned}$$

All of these linear combinations are π states, because $\lambda = |m| = 1$ for all of them. In order to justify their symmetry properties with respect to inversion we analyze the following particular case,

$$\pi_u 2P_{+1} = 2P_{+1}(A) + 2P_{+1}(B) = \frac{1}{8\sqrt{\pi}} \left(\frac{z}{a}\right)^{5/2} (e^{i\phi_A} e^{-\frac{zr_A}{2a}} r_A \sin\theta_A + e^{i\phi_B} e^{-\frac{zr_B}{2a}} r_B \sin\theta_B),$$

which is represented by the following diagram:



This diagram shows that under inversion through the origin, coordinates are transformed as follows,

$$\begin{aligned} r_A &\rightarrow r_B, & \theta_A &\rightarrow \theta_B, \\ r_B &\rightarrow r_A, & \theta_B &\rightarrow \theta_A, \end{aligned}$$

$$\phi_A = \phi_B = \phi,$$

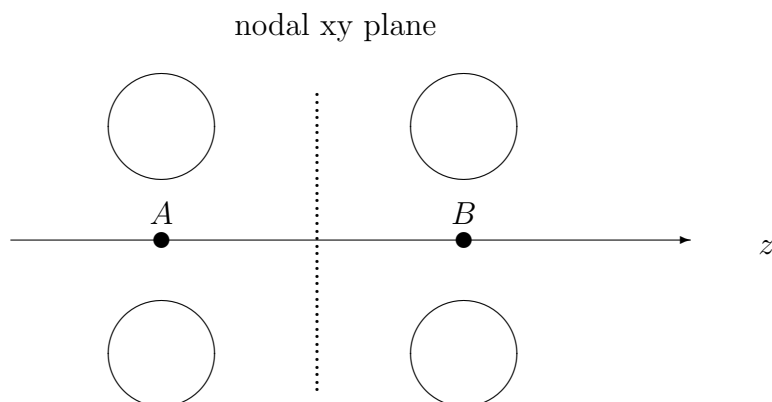
$$\phi \rightarrow \phi + \pi,$$

$$e^{i(\phi+\pi)} = e^{i\phi} e^{i\pi} = -e^{i\phi}, \text{ because } e^{i\pi} = \underbrace{\text{Cos}\pi}_{-1} + i \underbrace{\text{Sin}\pi}_0.$$

The states constructed with orbitals P_{-1} differ, relative to those constructed with orbitals p_{+1} , only in the sign of phase ϕ introduced by the following expression,

$$\pi_g^* 2P_{+1} = \frac{1}{8\sqrt{\pi}} \left(\frac{z}{a}\right)^{5/2} e^{i\phi} \left(e^{-\frac{zr_A}{2a}} r_A \sin\theta_A + e^{-\frac{zr_B}{2a}} r_B \sin\theta_B \right).$$

This function has a nodal xy plane and is described by the following diagram:



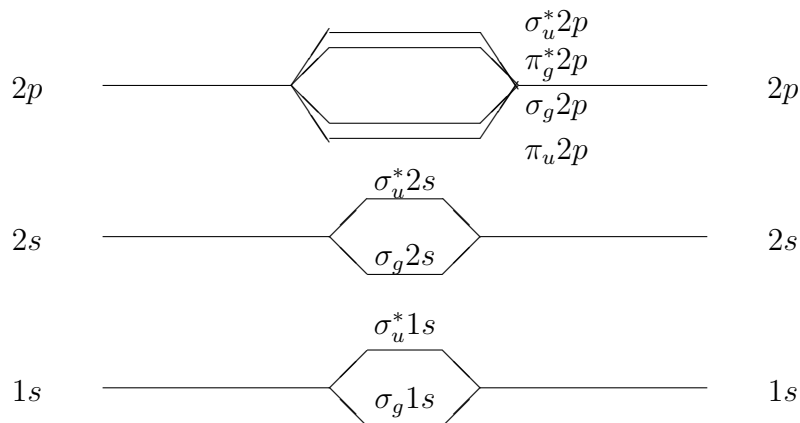
Since atomic orbitals $2p_x$, and $2p_y$ are linear combinations of atomic orbitals $2p_{+1}$ and $2p_{-1}$ molecular orbitals $\pi_u 2p_{+1}$ and $\pi_u 2p_{-1}$ can be combined to construct molecular orbitals $\pi_u 2p_x$, and $\pi_u 2p_y$ as follows,

$$\pi_u 2p_x = 2p_x(A) + 2p_x(B),$$

$$\pi_u 2p_y = 2p_y(A) + 2p_y(B).$$

Note, however, that molecular orbitals $\pi_u 2p_x$, and $\pi_u 2p_y$ are not eigenfunctions of \hat{L}_z .

The order of increasing energy for homonuclear diatomic orbitals is described by the following diagram:



The electronic structure of homonuclear diatomic molecules can be approximated to zeroth order by filling up the unperturbed states according to the Pauli exclusion principle. However, we should always keep in mind that we are using the H_2^+ molecular orbitals (i.e., the unperturbed states) and, therefore, we are neglecting the repulsive interaction between electrons.

This is the same kind of approximation implemented in the construction of zeroth order wave functions of atoms according to hydrogenlike atomic orbitals, where the repulsion energy between electrons was disregarded and the electronic configuration was constructed by filling up hydrogenlike atomic orbitals according to the Pauli exclusion principle.

Exercise 55:

- (A) Predict the multiplicity of the ground state of O_2 .
- (B) Show that the ground electronic state of C_2 is a singlet.

34 Conjugated Systems: Organic Molecules

The Hamiltonian of a molecule containing n electrons and N nuclei can be described according to the Born-Oppenheimer approximation as follows,

$$\hat{H}_{el} = \sum_{i=1}^n \left(-\frac{\hbar^2}{2m_i} \nabla_{r_i}^2 - \sum_{j=1}^N \frac{z_j e^2}{r_{ji}} \right) + \sum_i^n \sum_{k>i}^n \frac{e^2}{r_{ik}}.$$

This Hamiltonian includes terms that describe both π and σ electrons. However, the distinctive chemistry of conjugated organic molecules is usually relatively independently of σ -bonds, and rather correlated with the electronic structure of π -electrons. For example, the spectroscopy of conjugated organic molecules, as well as ionization potentials, dipole moments and reactivity, can be described at least qualitatively by the electronic structure of the π -electron model. Therefore, we make the approximation that the solution of the eigenvalue problem of a conjugated system can be factorized as follows,

$$\psi = \hat{A} \psi_\sigma \psi_\pi,$$

where \hat{A} is an antisymmetrization operator upon exchange of σ and π electrons.

The potential due to the nuclei and the average field due to σ electrons, can be described by the following Hamiltonian:

$$\hat{H}_\pi = \sum_{i=1}^{n_\pi} \hat{h}_{core}(i) + \sum_{i=1}^{n_\pi} \sum_{k>i}^{n_\pi} \frac{e^2}{r_{ik}}, \quad (62)$$

where \hat{h}_{core} includes kinetic energy of π electrons, interaction of π electrons with σ electrons, and shielding of nuclear charges. An approximate solution can be obtained by disregarding the repulsion between π electrons in Eq. (62), and by approximating the Hamiltonian of the system as follows,

$$\hat{H}_\pi^{(0)} \approx \sum_{i=1}^{n_\pi} H_{\text{eff}}(i), \quad \text{where} \quad \hat{H}_{\text{eff}}(j) = -\frac{\hbar^2}{2m_j} \nabla_{r_j}^2 - \sum_{k=1}^N \frac{z'_k e^2}{r_{kj}}. \quad (63)$$

The effective nuclear charge z'_k incorporates the average screening of nuclear charges due to σ and π electrons.

Since $\hat{H}_{\text{eff}}(j)$ depends *only* on coordinates of electron j , we can implement the separation of variables method and solve the eigenvalue problem,

$$\hat{H}_{\pi}^{(0)}|\psi_{\pi}\rangle = E_{\pi}|\psi_{\pi}\rangle,$$

according to the factorizable solution $|\psi_{\pi}\rangle = \prod_{j=1}^{n_{\pi}} |\phi_j\rangle$, where,

$$\hat{H}_{\text{eff}}(j) |\phi_j\rangle = \epsilon_j |\phi_j\rangle. \quad (64)$$

The energy E_{π} is obtained by using the Pauli exclusion principle to fill up the molecular orbitals, after finding the eigenvalues ϵ_j .

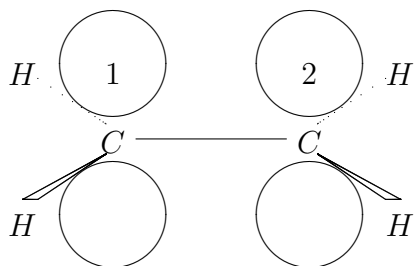
Eq. (63) is solved by implementing the variational method, assuming that $|\phi_j\rangle$ can be written according to a linear combination of atomic orbitals,

$$|\phi_j\rangle = \sum_{k=1}^N C_{jk} |\chi_k\rangle,$$

where $|\chi_k\rangle$ represents a $2p_z$ orbital localized in atom k and the sum extends over all atoms in the conjugated system.

Example:

Consider the ethylene molecule represented by the following diagram:



The diagram shows σ bonds in the equatorial plane of the molecule, and π orbitals 1 and 2 that are perpendicular to such plane.

The LCAO for ethylene is,

$$|\phi_j\rangle = c_{j1} |\chi_1\rangle + c_{j2} |\chi_2\rangle. \quad (65)$$

Therefore, the secular equations can be written as follows,

$$(H_{11} - S_{11}\epsilon_j) c_{j1} + (H_{12} - S_{12}\epsilon_j) c_{j2} = 0,$$

$$(H_{21} - S_{21}\epsilon_j) c_{j1} + (H_{22} - S_{22}\epsilon_j) c_{j2} = 0.$$

Hückel Method:

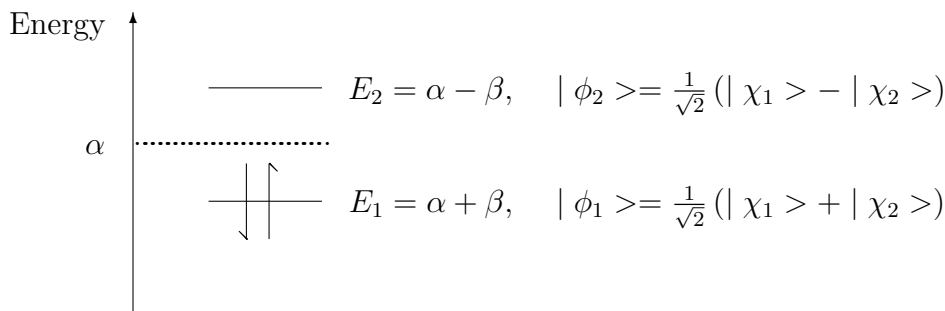
The Hückel Method is a semi-empirical approach for solving the secular equations. The method involves making the following assumptions:

1. $H_{kk} = \alpha$, where α is an empirical parameter (*vide infra*).
2. $H_{jk} = \beta$, when $j = k \pm 1$; and $H_{jk} = 0$, otherwise. The constant β is also an empirical parameter (*vide infra*).
3. $S_{jk} = 1$, when $k = j \pm 1$; and $S_{jk} = 0$, otherwise.

According to the Hückel model, the secular determinant becomes,

$$\begin{vmatrix} \alpha - \epsilon_j & \beta \\ \beta & \alpha - \epsilon_j \end{vmatrix} = 0.$$

Therefore, the eigenvalues of the secular determinant are $\epsilon_j = \alpha \pm \beta$ and can be represented by the following diagram:



$$E_\pi = 2E_1 = 2\alpha + 2\beta, \quad |\phi_\pi\rangle = \frac{1}{\sqrt{2}}(|\phi_1(1)\rangle + |\phi_1(2)\rangle) (\alpha\beta - \beta\alpha).$$

The energy difference between ground and excited states is $\Delta E = E_2 - E_1 = -2\beta$. Parameter β is usually chosen to make ΔE coincide with the peak of the experimental absorption band of the molecule.

35 Empirical Parameterization of Diatomic Molecules

The main features of chemical bonding by electron pairs are properly described by the HL model of H_2 (see page 91). According to such model, the covalent bond is described by a singlet state,

$${}^1\psi_{HL} = N_1[\alpha(1)\beta(2) - \beta(1)\alpha(2)][\chi_A(1)\chi_B(2) + \chi_A(2)\chi_B(1)],$$

with energy

$${}^1E_+ = \langle {}^1\psi_{HL} | H | {}^1\psi_{HL} \rangle = \frac{J + K}{1 + S^2},$$

where $H = h(1) + h(2) + e^2/r_{12}$, with

$$h(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}},$$

$$h(2) = -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}},$$

$$J = \langle \chi_A(1)\chi_B(2) | H | \chi_A(1)\chi_B(2) \rangle \quad \text{Coulomb integral}$$

$$K = \langle \chi_A(1)\chi_B(2) | H | \chi_A(2)\chi_B(1) \rangle \quad \text{Exchange integral}$$

$$S^2 = \langle \chi_A(1)\chi_B(2) | \chi_A(2)\chi_B(1) \rangle .$$

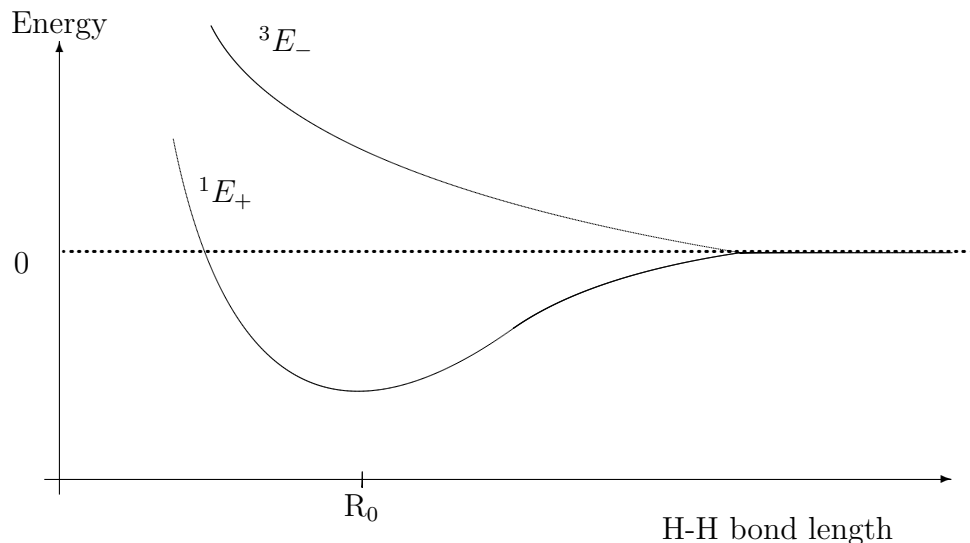
Similarly, the triplet state is described as follows,

$${}^3\psi_{HL} = N_3[\chi_A(1)\chi_B(2) - \chi_B(1)\chi_A(2)] \begin{cases} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \end{cases} ,$$

and has energy

$${}^3E_- = \frac{(J - K)}{(1 - S^2)} .$$

The energies of the singlet and triplet states are parametrized by the internuclear H-H distance and can be represented by the following diagram,



The energies 1E and 3E can be approximated by the following analytical functions:

$${}^1E_+ \approx D [e^{-2a(R-R_0)} - 2e^{-a(R-R_0)}] \equiv M(R),$$

$${}^3E_- \approx \frac{D}{2} [e^{-2a(R-R_0)} + 2e^{-a(R-R_0)}] \equiv M^*(R).$$

Parameters D and a can be obtained by fitting $M(R)$ to the actual (experimental or ab-initio) ground state potential energy surface. Such parametrization allows us to express the Coulombic and Resonance integrals J and K in terms of available experimental (or ab initio) data as follows,

$$J \approx \frac{1}{2} [(M + M^*) + S^2(M - M^*)],$$

$$K \approx \frac{1}{2} [(M - M^*) + S^2(M + M^*)].$$

This parametrization of Hamiltonian matrix elements illustrates another example of *semi-empirical parametrization* that can be implemented by using readily available experimental information (remember that in the previous section we described the semiempirical parametrization of the Hückel model according to the absorption spectrum of the molecule).

The covalent nature of the chemical bond significantly changes when one of the two atoms in the molecule is substituted by an atom of different electronegativity. Under those circumstances, the wave function should include ionic terms, e.g.,

$${}^1\psi_A^{ion} = \tilde{N}\chi_A(1)\chi_A(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)],$$

and

$${}^1\psi_B^{ion} = \tilde{N}\chi_B(1)\chi_B(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)].$$

The complete wave function (with both covalent and ionic terms) can be described as follows,

$\psi = C_1\psi_1 + C_2\psi_2$, where the covalent wave function is

$$\psi_1 = [\alpha(1)\beta(2) - \beta(1)\alpha(2)](\chi_A(1)\chi_B(2) + \chi_A(2)\chi_B(1)),$$

and the ionic wave function is

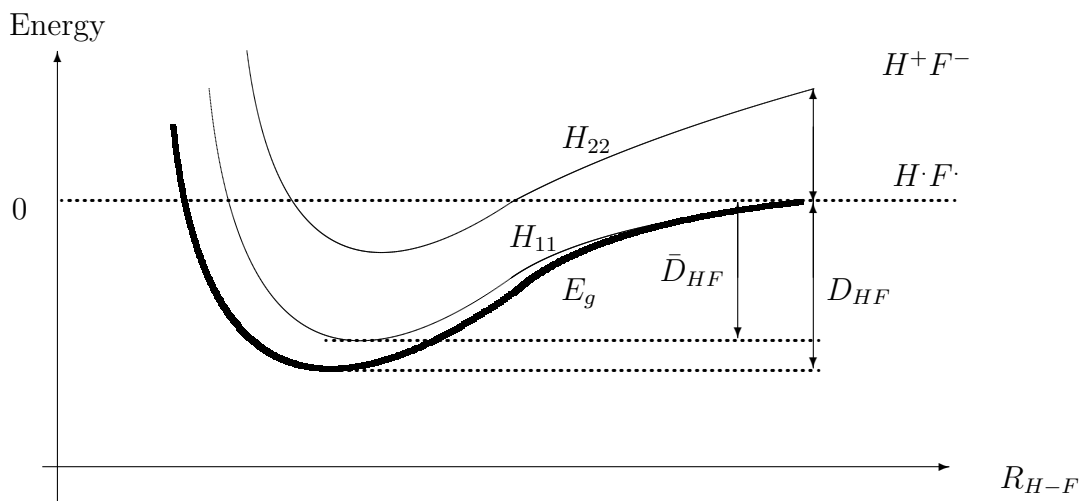
$$\psi_2 = [\alpha(1)\beta(2) - \beta(1)\alpha(2)][\chi_A(1)\chi_A(2)\xi_1 + \chi_B(1)\chi_B(2)(1 - \xi_1)],$$

where the parameter ξ_1 is determined by the relative electronegativity of the two atoms. For example, consider the HF molecule. For such molecule $\xi_1 = 1$, A represents the F atom, and B represents the H atom (i.e., due to the electronegativity difference between the two atoms, the

predominant ionic configuration is H^+F^-). Therefore, the ground state energy E_g is obtained as the lowest eigenvalue of the secular equation,

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} = 0. \quad (66)$$

Here we have neglected S_{12} , assuming that such approximation can be partially corrected according to the parametrization of H_{12} . The semiempirical parametrization strategy can be represented by the following diagram:



This diagram represents the following curves:

$H_{11} = \bar{M} = \bar{D}[e^{-2a(R-R_0-\delta)} - 2e^{-a(R-R_0-\delta)}]$ is a covalent state represented by a Morse potential \bar{M} .

$H_{22} = I - EA - \frac{332}{R} + Ae^{-bR} + CR^{-9}$, is the potential energy surface of the ionic state, where the difference between the H ionization energy and the F electron affinity, I-EA, corresponds to the energy of forming the ion pair $H^+ F^-$. The term $-\frac{332}{R}$ is the Coulombic interaction and $Ae^{-bR} + CR^{-9}$ is the short range repulsive potential.

The ground state potential energy surface $E_g = M = D[e^{-2a(R-R_0)} - 2e^{-a(R-R_0)}]$ is represented by a Morse potential M . Parameters D and R_0 can be obtained from the experimental bond-energy and bond-length. The parameter a can be adjusted to reproduce the vibrational frequency of the diatomic molecule. The parameter $\bar{D}_{HF} = \sqrt{D_{HH}D_{FF}}$ and $\delta = 0.05\text{\AA}$. Parameters A and C are adjusted so that the minimum energy of H_{22} corresponds to the H-F bond-length (i.e., the sum of ionic radii of H and F). This empirical parametrization allows us to solve Eq. (66) for H_{12} ,

$$H_{12} = \sqrt{(H_{11} - M)(H_{22} - M)},$$

and obtain the Hamiltonian matrix elements in terms of empirical parameters.

Conclusion: Potential energy surfaces parametrized by a few empirical parameters are able to describe bonding properties of molecules associated with atoms of different electronegativity.

Dipole Moment

The dipole moment is one of the most important properties of molecules and can be computed as follows,

$$\mu_g = \langle \psi_g | \hat{\mu} | \psi_g \rangle,$$

where

$$\hat{\mu} = - \sum_i e r_i + \sum_j e z_j R_j.$$

The first term of this equation involves electronic coordinates r_i and the second term involves nuclear coordinates R_j .

For example, the dipole moment of HF can be computed as follows,

$$\mu_g = C_1^2 \underbrace{\langle \psi_1 | \hat{\mu} | \psi_1 \rangle}_0 + C_2^2 \underbrace{\langle \psi_2 | \hat{\mu} | \psi_2 \rangle}_{eR_0} + 2C_1C_2 \underbrace{\langle \psi_1 | \hat{\mu} | \psi_2 \rangle}_0,$$

since ψ_1 represents a covalent state and the overlap between ψ_1 and ψ_2 is assumed to be negligible.

The dipole moment is usually reported in Debye units, where 4.803 Debye is the dipole moment of two charges of 1 a.u. with opposite sign and separated by 1 Å, from each other.

Exercise 56: Evaluate the dipole moment for HF using the following parameters for the semiempirical model of HF potential energy surfaces (energies are expressed in kcal/mol, and distances in Å),

$$\begin{aligned} D=134; & \quad \bar{D}=61; & \quad R_0=0.92; & \quad a=2.27; \\ A=640; & \quad b=2.5; & \quad C=20; & \quad I=313; & \quad EA=83. \end{aligned}$$

Polarization

The electric field of an external charge z located at coordinate R_0 along the axis of the molecule does not affect the energy of the covalent state H_{11} , but affects the energy of the ionic state H_{22} as follows,

$$H'_{22} = H_{22} + \frac{ze}{R_{H^+C}} - \frac{ze}{R_{F-C}}.$$

Therefore, the presence of an external charge perturbs the ground state energy of the molecule. Such perturbation can be computed by re-diagonalizing Eq. (66), using H'_{22} instead of H_{22} . Solving for the ground state energy we obtain,

$$E'_g = \frac{1}{2} [(H'_{22} + H_{11}) - ((H'_{22} - H_{11}) + 4H_{12}^2)^{1/2}].$$

Exercise 57:

(1) Plot E'_g , as a function of the internuclear distance R , for the HF molecule in the presence of an external charge located in the axis of the molecule at 10 Å, to the left of the F atom.

(2) Compare your results with the analog Gaussian98 calculation by using the *scan* keyword.
Hint: The Gaussian98 input file necessary to scan the ground state potential energy surface of H_2 is described as follows,

```
#hf/6-31G scan  
  
potential scan for H2  
  
0 1  
H  
H 1 R  
  
R 0.9 5 0.1
```

This input file scans the potential energy of H_2 by performing single point calculations at 5 internuclear distances. The output energies are represented by the following diagram:

