Introductory Quantum Chemistry

Chem 570a: Lecture Notes

Prof. Victor S. Batista

Room: Sterling Chemistry Laboratories (SCL) 19

Tuesdays and Thursdays 9:00 – 10:15 am

Yale University - Department of Chemistry

Contents

1 Syllabus

The goal of this course is to introduce fundamental concepts of *Quantum Mechanics* with emphasis on Quantum Dynamics and its applications to the description of molecular systems and their interactions with electromagnetic radiation. Quantum Mechanics involves a *mathematical formulation* and a *physical interpretation*, establishing the correspondence between the mathematical elements of the theory (e.g., functions and operators) and the elements of reality (e.g., the observable properties of real systems).[1] The presentation of the theory will be mostly based on the so-called *Orthodox Interpretation*, developed in Copenhagen during the first three decades of the 20th century. However, other interpretations will be discussed, including the 'pilot-wave' theory first suggested by Pierre De Broglie in 1927 and independently rediscovered by David Bohm in the early 1950's.

Textbooks: The official textbook for this class is:
R1: Levine, Ira N. Quantum Chemistry; 5th Edition; Pearson/Prentice Hall; 2009.
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),
All these references are 'on-reserve' at the Kline science library.
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.
Useful search engines for mathematical and physical concepts can be found at
http://scienceworld.wolfram.com/physics/ and http://mathworld.wolfram.com/
The lecture notes are posted online at: (http://ursula.chem.yale.edu/∼batista/classes/vvv/v570.pdf)

Grading: Grading and evaluation is the same for both undergraduate and graduate students. The mid-terms will be on 10/12 and 11/07. The date for the Final Exam is determined by Yale's calendar of final exams. Homework includes exercises and computational assignments due one week after assigned.

Contact Information and Office Hours: Prof. Batista will be glad to meet with students at SCL 115 as requested by the students via email to victor.batista@yale.edu, or by phone at (203) 432-6672.

[1] Old Story: Heisenberg and Schrödinger get pulled over for speeding. The cop asks Heisenberg "Do you know how fast you were going?" Heisenberg replies, "No, but we know exactly where we are!" The officer looks at him confused and says "you were going 108 miles per hour!" Heisenberg throws his arms up and cries, "Great! Now we're lost!" The officer looks over the car and asks Schröinger if the two men have anything in the trunk. "A cat," Schrödinger replies. The cop opens the trunk and yells "Hey! This cat is dead." Schrödinger angrily replies, "Well he is now."

2 The Fundamental Postulates of Quantum Mechanics

Quantum Mechanics can be formulated in terms of 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. To keep the notation as simple as possible, expressions are written for a 1-dimensional system. The generalization to many dimensions is usually straightforward.

$\boxed{Postulate\ 1}$: *Any system in a pure state can be described by a wave-function , $\psi(t,x)$, where t is a parameter representing the time and x represents the coordinates of the system. Such a function $\psi(t,x)$ must be continuous, single valued and square integrable.*
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, first realized by Max Born.* [2]

$\boxed{Postulate\ 2}$: 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: *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,*

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

[2] Note that this probabilistic interpretation of ψ has profound implications to our understanding of reality. It essentially reduces the objective reality to $P(t,x)$. All other properties are no longer independent of the process of measurement by the observer. A. Pais' anecdote of his conversation with A. Einstein while walking at Princeton emphasizes the apparent absurdity of the implications: [Rev. Mod. Phys. 51, 863914 (1979), p. 907]: 'We often discussed his notions on objective reality. I recall that during one walk Einstein suddenly stopped, turned to me and asked whether I really believed that the moon exists only when I look at it.'

where the asterisk represents the complex conjugate.

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.
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 $\int dx\phi_m^*\phi_n = 0$.

$\boxed{Postulate\ 3}$**:** *The only possible experimental results of a measurement of an observable are the eigenvalues of the operator that corresponds to such observable.*

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

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

$\boxed{Postulate\ 5}$**:***The evolution of $\psi(x,t)$ in time is described by the time-dependent Schrödinger 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, $E = \frac{p^2}{2m} + V(x)$.

Expansion Postulate: **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*.
Note that $\bar{A} = \sum_j C_j C_j^* a_j$, when $\psi(x) = \sum_j C_j\phi_j(x)$,

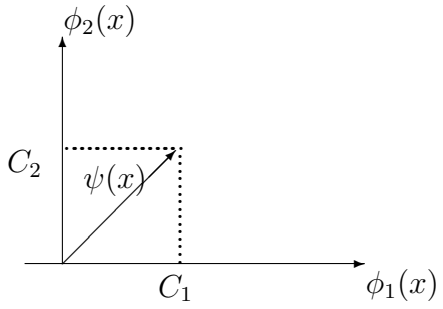
$$\hat{A}\phi_j(x) = a_j\phi_j(x), \quad \text{and} \qquad \int dx\phi_j(x)^*\phi_k(x) = \delta_{jk}.$$

This is because the eigenvalues a_j are the only possible experimental results of measurements of $\hat{A}$ (according to Postulate 3), and the expectation value $\bar{A}$ is the average value of many measurements of $\hat{A}$ when the system is described by the expansion $\psi(x) = \sum_j C_j\phi_j(x)$ (Postulate 4). Therefore, the product $C_jC_j^*$ 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., $\Psi(x) = C_1\phi_1(x) + C_2\phi_2(x) + \ldots$). 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 $\phi_2(x)$.

3 Continuous Representations

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 $\delta(x_0 - x)$ thus define a continuous representation (the so-called 'coordinate representation') for which

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

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

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

When combined with postulates 3 and 4, the definition of the expansion coefficients $C_{x_0} = \psi(x_0)$ implies that 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, eigenstates $\phi(\alpha, x)$ with a continuum spectrum of eigenvalues α define continuous representations,

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

with $C_\alpha = \int dx \phi(\alpha, x)^* \psi(x)$. Delta functions and the plane waves are simply two particular examples of basis sets with continuum spectra.

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)**

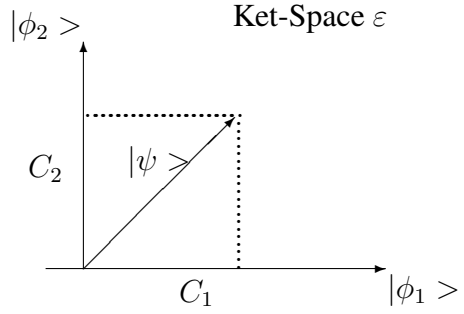
4 Vector Space

Vector-Ket Space ε: The vector-ket space is introduced to represent states in a convenient space of *vectors* $|\phi_j>$, 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 $|\psi>$ 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 $|\psi>$ such that,

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

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



Note that the expansion coefficients C_j depend only on the kets $|\ \psi_j>$ 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,

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

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 $|\psi>$ we define a linear functional $<\psi|$, called *bra-vector*, as follows:

$$<\psi|(|\phi>) = \int dx \psi^*(x)\phi(x).$$

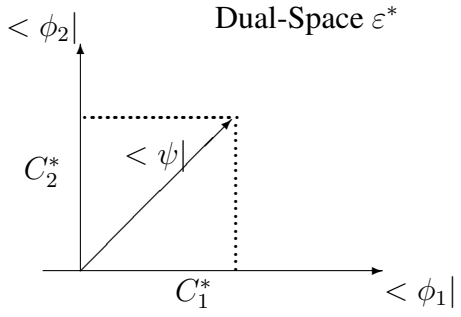
Note that functional $< \psi|$ is linear because the scalar product is a linear functional. Therefore,

$$< \psi|(a|\phi > +b|f >) = a < \psi|(|\phi >) + b < \psi|(|f >).$$

Note: For convenience, we will omit parenthesis so that the notation $< \psi|(|\phi >)$ will be equivalent to $< \psi||\phi >$. 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,

$$< \psi||\phi >=< \psi|\phi > .$$

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



where C_j^* is the projection of $< \psi \mid$ along $< \phi_j \mid$.

Projection Operator and Closure Relation
Given a ket $\mid \psi >$ in a certain basis set $|\phi_j >$,

$$|\psi >= \sum_j C_j|\phi_j >, \tag{1}$$

where $< \phi_k|\phi_j >= \delta_{kj}$,

$$C_j =< \phi_j|\psi > . \tag{2}$$

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

$$|\psi >= \sum_j |\phi_j >< \phi_j|\psi > . \tag{3}$$

From Eq.(3), it is obvious that

$$\sum_j |\phi_j >< \phi_j| = \hat{1}, \qquad Closure\ Relation$$

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

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

$$\hat{P}_j|\psi >=< \phi_j|\psi > |\phi_j > .$$

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 $< \phi_j|\phi_j >= 1$.

4.1 Exercise 1

Prove that

$$i\hbar\frac{\partial \hat{P}_j}{\partial t} = [\hat{H}, \hat{P}_j],$$

where $[\hat{H}, \hat{P}_j] = \hat{H}\hat{P}_j - \hat{P}_j\hat{H}$.

Continuity Equation

4.2 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:

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

5 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:

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

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,

$$\frac{i\hbar}{f(t)}\frac{\partial f(t)}{\partial t} = E \Rightarrow f(t) = f(0)\text{exp}(-\frac{i}{\hbar}Et),$$

$$-\frac{\hbar^2}{2m\phi(x)}\frac{\partial^2\phi(x)}{\partial x^2} + V(x) = E \Rightarrow \boxed{\hat{H}\phi(x) = E\phi(x)}.$$

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,

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

and

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

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

5.1 Exercise 3

Prove that $\hat{H}$ is a Hermitian operator.

5.2 Exercise 4

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

5.3 Exercise 5

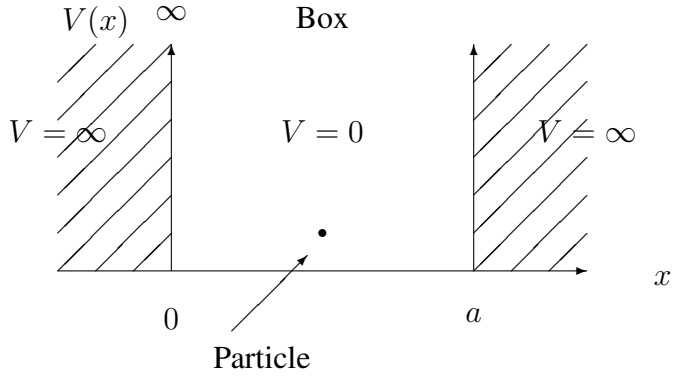
Prove that if two hermitian operators $\hat{Q}$ and $\hat{P}$ satisfy the equation $\hat{Q}\hat{P} = \hat{P}\hat{Q}$, i.e., if P and Q commute (*vide infra*), the product operator $\hat{Q}\hat{P}$ is also hermitian.
Since $\hat{H}$ is hermitian, E is a real number $\Rightarrow E = E^*$ (see Property 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.

6 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

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

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

$$-\frac{\hbar^2}{2m}\frac{\partial}{\partial x^2}\Phi(x) = E\Phi(x), \qquad \Rightarrow \qquad \Phi(x) = A\,\text{Sin}(K\,x). \tag{6}$$

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

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

and determine the energy associated with $\Phi(x)$ inside the box as follows. From Eq. (6), we obtain:
$\frac{\hbar^2}{2m}AK^2 = EA, \quad$ and, $\quad \Phi(a) = A\text{Sin}(K\,a) = 0,$
$\Rightarrow \qquad Ka = n\pi, \quad$ with $\quad n = 1, 2, ... \qquad \Rightarrow$
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,

$$E = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2}, \qquad \text{with } \; n = 1,\; 2,\; ...$$

e.g.,

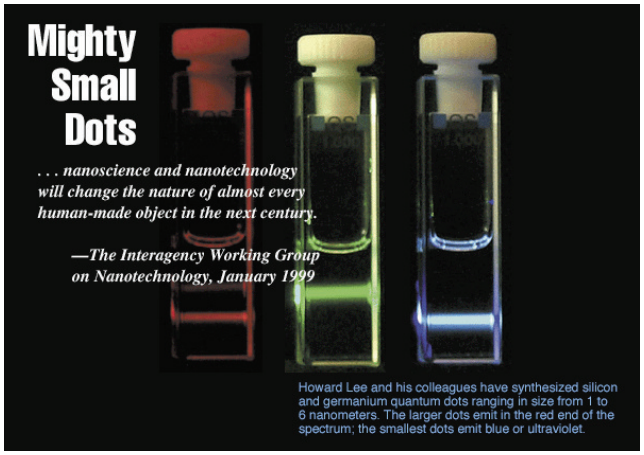
$$E(n = 1) = \frac{\hbar^2}{2m}\frac{\pi^2}{a^2},$$

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

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).

6.1 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 λ_{MAX}=268nm.
(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.

7 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.

7.1 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.
Note: Mathematically, we see that the momentum and position operators do not commute simply because $\hat{p} = -i\hbar\partial/\partial x$, so $\hat{p}x = -i\hbar(1+x\partial/\partial x)$ is not the same as $x\hat{p} = -i\hbar x\partial/\partial x$. Conceptually, it means that one cannot measure the position without affecting the state of motion since measuring the position would perturb the momentum. To measure the position of a particle it is necessary to make it leave a mark on a sensor/detector (*e.g.*, a piece chalk needs to leave a mark on the blackboard to report its position). That process unavoidably slows it down, affecting its momentum.

8 Uncertainty Relations

The goal of this section is to show that the uncertainties $\Delta A = \sqrt{< (\hat{A} - < \hat{A} >)^2 >}$ and $\Delta B = \sqrt{< (\hat{B} - < \hat{B} >)^2 >}$, of any pair of hermitian operators $\hat{A}$ and $\hat{B}$, satisfy the uncertainty relation:**R3(437)**

$$(\Delta A)^2(\Delta B)^2 \geq \frac{1}{4} < i[A, B] >^2 . \tag{7}$$

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

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}. \tag{8}$$

Proof:
$\hat{U} \equiv \hat{A} - < A >$, $\quad \phi(\lambda, x) \equiv (\hat{U} + i\lambda\hat{V})\Phi(x)$,
$\hat{V} \equiv \hat{B} - < B >$, $\quad I(\lambda) \equiv \int dx\phi^*(\lambda, x)\phi(\lambda, x) \geq 0$,

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

$$I(\lambda) =< \Phi|U^2|\Phi > +\lambda^2 < \Phi|V^2|\Phi > -i\lambda < \Phi|UV - VU|\Phi >\geq 0, \tag{9}$$

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

$$2\lambda(\Delta B)^2 = i < [A, B] >, \qquad => \qquad \lambda = \frac{i < [A, B] >}{2(\Delta B)^2}.$$

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

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

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

8.1 Exercise 8

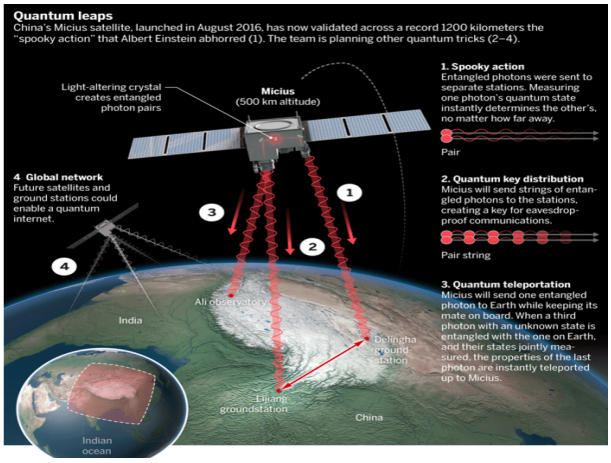
Compute $< X >$, $< P >$, ΔX and ΔP for the particle in the box in its minimum energy state and verify that ΔX and ΔP satisfy the uncertainty relation given by Eq. (7)?

8.2 EPR Paradox

Gedankenexperiments (*i.e.*, thought experiments) have been proposed to determine "hidden" variables. The most famous of these proposals has been the Einstein-Podolski-Rosen (EPR) *gedanken-experiment* [*Phys. Rev.* (1935) **47**:777-780] , where a system of 2 particles is initially prepared with total momentum p_t. At a later time, when the two particles are far apart from each other, the position x_1 is measured on particle 1 and the momentum p_2 is measured on particle 2. The paradox is that the momentum of particle 1 could be obtained from the difference $p_1 = p_t - p_2$. Therefore, the coordinate x_1 and momentum p_1 of particle 1 could be determined with more precision than established as possible by the uncertainty principle, so long as the separation between the two particles could prevent any kind of interaction or disturbance of one particule due to a measurement on the other.

The origin of the paradox is the erroneous assumption that particles that are far apart from each other cannot maintain instantaneous correlations. However, quantum correlations between the properties of distant noninteracting systems *can* be maintained, as described by Bohm and Aharonov [*Phys. Rev.* (1957) **108**:1070-1076] for the state of polarization of pairs of correlated photons. Within the Bohmian picture of quantum mechanics, these quantum correlations are established by the quantum potential $V_Q(q)$, even when the particles are noninteracting (*i.e.*, $V(q) = 0$).

Quantum correlations between distant noninteracting photons were observed for the first time by Aspect and co-workers in 1982 [*Phys. Rev. Lett.* (1982) **49**:91-94] , 47 years after the EPR paradox was presented. These quantum correlations constitute the fundamental physics exploited by *teleportation* (*i.e.*, the transmission and reconstruction of quantum states over arbitrary large distances) [*Nature* (1997) **390**:575-579] and *ghost imaging* (*i.e.*, a technique where the object and the image system are on separate optical paths) [*Am. J. Phys.* (2007) **75**:343-351] . Most recently, a 'spooky action at a distance' record of 1,203 kilometers has been demonstrated in preparation for quantum communication through the internet.



9 Exercise 9

9.1 Copenhagen Interpretation:

Describe the Copenhagen (probabilistic) formulation of Quantum Mechanics and show that a consequence of Postulates 1 and 4 is that $P(t,x) = \psi^*(t,x)\psi(t,x)dx$ represents the probability of observing the system described by $\psi(x,t)$ between x and $x+dx$ at time t.

9.2 Feynman Interview:

Watch Feynman talking about Quantum Mechanics at the (Interview) and comment on his observations in the context of the postulates of Quantum Mechanics.

9.3 Momentum Operator:

Show that the momentum operator must be defined as

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}, \tag{10}$$

and the eigenfunction of the momentum operator with eigenvalue p_j as a plane wave

$$\langle x|p_j\rangle = \frac{e^{\frac{i}{\hbar}p_j x}}{\sqrt{2\pi\hbar}}, \tag{11}$$

since

$$\hat{p}\delta(p-p_j) = p_j\delta(p-p_j). \tag{12}$$

Hint: Use the integral form of Dirac's delta function: $\delta(p-p_j) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dx e^{\frac{i}{\hbar}x(p-p_j)}$.

9.4 EPR Paradox:

In 1935, Einstein, Podolsky, and Rosen proposed a thought experiment where two systems that interact with each other are then separated so that they presumably interact no longer. Then, the position or momentum of one of the systems is measured, and due to the known relationship between the measured value of the first particle and the value of the second particle, the observer is aware of the value in the second particle. A measurement of the second value is made on the second particle, and again, due to the relationship between the two particles, this value can then be known in the first particle. This outcome seems to violate the uncertainty principle, since both the position and momentum of a single particle would be known with certainty.

Explain what is wrong with this paradox.

9.5 Schrödinger's cat paradox:

A cat is placed in a steel box along with a Geiger counter, a vial of poison, a hammer, and a radioactive substance. When the radioactive substance decays, the Geiger detects it and triggers the hammer to release the poison, which subsequently kills the cat. The radioactive decay is a random process, and there is no way to predict when it will happen. The atom exists in a state known as a superposition both decayed and not decayed at the same time.

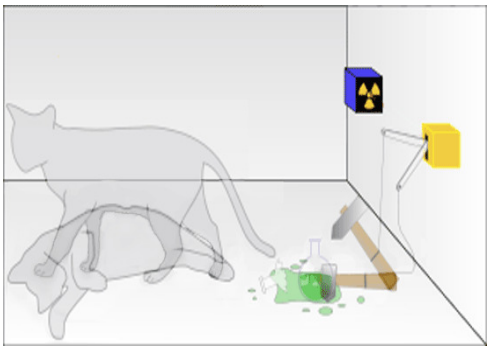
Until the box is opened, an observer doesn't know whether the cat is alive or dead because the cat's fate is intrinsically tied to whether or not the atom has decayed and the cat would, as Schrödinger put it, be "living and dead ... in equal parts" until it is observed.

In other words, until the box was opened, the cat's state is completely unknown and therefore, the cat is considered to be both alive and dead at the same time until it is observed.

The obvious contradiction is that the cat can not be both dead and alive, so there must be a fundamental flaw of the paradox or of the Copenhagen interpretation. Explain what aspect of the Copenhagen interpretation of quantum mechanics is questioned by this gedanken experiment and what is wrong with the paradox.

10 Heisenberg Representation

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 numerical and approximate methods (e.g., *perturbation methods* and *variational methods*).

In this section, we describe the matrix representation, introduced by Heisenberg, which is most useful for numerical methods to solve the eigenvalue problem,**R4(124) R3(240)**

$$\hat{H}|\psi_l\rangle = E_l|\psi_l\rangle, \tag{13}$$

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

$$|\psi_l\rangle = \sum_j C_l^{(j)}|\phi_j\rangle, \tag{14}$$

where $C_l^{(j)} = \langle\phi_j|\psi_l\rangle$, and $\langle\phi_j|\phi_k\rangle = \delta_{jk}$. Substituting Eq. (14) into Eq. (13) we obtain:

$$\sum_j \hat{H}|\phi_j\rangle C_l^{(j)} = \sum_j E_l C_l^{(j)}|\phi_j\rangle.$$

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

$$\sum_j \langle\phi_k|\hat{H}|\phi_j\rangle C_l^{(j)} = \sum_j E_l\langle\phi_k|\phi_j\rangle C_l^{(j)}, \tag{15}$$

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

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

$$\begin{array}{lll} (k=1) & \rightarrow & \begin{cases} H_{11}C_l^{(1)} + H_{12}C_l^{(2)} + H_{13}C_l^{(3)} + ... + H_{1n}C_l^{(n)} = E_l C_l^{(1)} + 0C_l^{(2)} + ... + 0C_l^{(n)}, \\ H_{21}C_l^{(1)} + H_{22}C_l^{(2)} + H_{23}C_l^{(3)} + ... + H_{2n}C_l^{(n)} = 0C_l^{(1)} + E_l C_l^{(2)} + ... + 0C_l^{(n)}, \\ ... \\ H_{n1}C_l^{(1)} + H_{n2}C_l^{(2)} + H_{n3}C_l^{(3)} + ... + H_{nn}C_l^{(n)} = 0C_l^{(1)} + 0C_l^{(2)} + ... + E_l C_l^{(n)}, \end{cases} \\ (k=2) & \rightarrow & \\ & ... & \\ (k=n) & \rightarrow & \end{array} \tag{16}$$

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

$$\begin{bmatrix} H_{11} & H_{12} & ... & H_{1n} \\ H_{21} & H_{22} & ... & H_{2n} \\ ... & & & \\ H_{n1} & H_{n2} & ... & H_{nn} \end{bmatrix} \begin{bmatrix} C_l^{(1)} \\ C_l^{(2)} \\ ... \\ C_l^{(n)} \end{bmatrix} = \begin{bmatrix} E_l & 0 & ... & 0 \\ 0 & E_l & ... & 0 \\ ... & & & \\ 0 & 0 & ... & E_l \end{bmatrix} \begin{bmatrix} C_l^{(1)} \\ C_l^{(2)} \\ ... \\ C_l^{(n)} \end{bmatrix}. \tag{17}$$

This is the *Heisenberg representation* of the eigenvalue problem introduced by Eq. (13). According to the *Heisenberg representation*, also called *matrix representation*, the *ket* $|\psi_l\rangle$ is represented by the *vector* C_l, with components $C_l^{(j)} = \langle \phi_j | \psi_l \rangle$, with $j = 1, ..., n$, 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,

$$\langle \psi_l | H | \psi_l \rangle = \sum_j \sum_k C_l^{(k)*} \langle \phi_k | \hat{H} | \phi_j \rangle C_l^{(j)},$$

can be written in the matrix representation as follows,

$$\langle \psi_l | H | \psi_l \rangle = C_l^\dagger \mathbf{H} C_l = \begin{bmatrix} C_l^{(1)*} & C_l^{(2)*} & ... & C_l^{(n)*} \end{bmatrix} \begin{bmatrix} H_{11} & H_{12} & ... & H_{1n} \\ H_{21} & H_{22} & ... & H_{2n} \\ ... & & & \\ H_{n1} & H_{n2} & ... & H_{nn} \end{bmatrix} \begin{bmatrix} C_l^{(1)} \\ C_l^{(2)} \\ ... \\ C_l^{(n)} \end{bmatrix}.$$

Note:
(1) It is important to note that according to the matrix representation the *ket-vector* $|\psi_l\rangle$ is represented by a column vector with components $C_l^{(j)} = \langle \phi_j | \psi_l \rangle$, and the *bra-vector* $\langle \psi_l |$ is represented by a *row vector* with components $C_l^{(j)*}$.
(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 $\mathbf{H}$.
(3) Finally, we note that the matrix of column eigenvectors $\mathbf{C}$ satisfy the equation, $\mathbf{HC} = \mathbf{CE}$, where $\mathbf{E}$ is the diagonal matrix of eigenvalues:

$$\begin{bmatrix} H_{11} & H_{12} & ... & H_{1n} \\ H_{21} & H_{22} & ... & H_{2n} \\ ... & & & \\ H_{n1} & H_{n2} & ... & H_{nn} \end{bmatrix} \begin{bmatrix} C_1^{(1)} & C_2^{(1)} & \cdots & C_n^{(1)} \\ C_1^{(2)} & C_2^{(2)} & \cdots & C_n^{(2)} \\ ... & ... & ... & ... \\ C_1^{(n)} & C_2^{(n)} & \cdots & C_n^{(n)} \end{bmatrix} = \begin{bmatrix} C_1^{(1)} & C_2^{(1)} & \cdots & C_n^{(1)} \\ C_1^{(2)} & C_2^{(2)} & \cdots & C_n^{(2)} \\ ... & ... & ... & ... \\ C_1^{(n)} & C_2^{(n)} & \cdots & C_n^{(n)} \end{bmatrix} \begin{bmatrix} E_1 & 0 & ... & 0 \\ 0 & E_2 & ... & 0 \\ ... & & & \\ 0 & 0 & ... & E_n \end{bmatrix}. \tag{18}$$

11 Fourier Grid Hamiltonian

The goal of this section is to introduce the Fourier grid Hamiltonian (FGH),

$$\begin{aligned} H(j,j') &= V(x_j)\langle x_j|x_j'\rangle + \frac{\Delta x \Delta p}{2\pi\hbar}\sum_{k=1}^{n_p} e^{\frac{i}{\hbar}(x_{j'}-x_j)p_k}\frac{p_k^2}{2m}, \\ &= V(x_j)\delta_{jj'} + \frac{\Delta x \Delta p}{2\pi\hbar}\sum_{k=1}^{n_p} e^{\frac{i}{\hbar}(x_{j'}-x_j)p_k}\frac{p_k^2}{2m}, \end{aligned} \tag{19}$$

as described by Marston and Balint-Kurti [*J. Chem. Phys.* (1989) **91**:3571-3576] . We write the Hamiltonian as a matrix in the representation of equally spaced delta functions $\delta(x - x_j)$, with coordinates

$$x_j = (j - n_x/2)\Delta_x, \tag{20}$$

where $\Delta_x = (x_{max} - x_{min})/n_x$ and j = 1–n_x, and momenta $p_k = \Delta p(k - n_p/2)$ with $\Delta p = 2\pi/(x_{max} - x_{min})$. Equation (19) is derived by writing the kinetic energy in the basis of plane waves, as follows:

$$\begin{aligned} \langle x_l|\hat{T}|x_j\rangle &= \langle x_l|\frac{\hat{p}^2}{2m}|x_j\rangle, \\ &= \int dp \int dp' \langle x_l|p'\rangle\langle p'|\frac{\hat{p}^2}{2m}|p\rangle\langle p|x_j\rangle, \\ &= \int dp \int dp' \langle x_l|p'\rangle\frac{p^2}{2m}\langle p'|p\rangle\langle p|x_j\rangle, \\ &= \int dp \langle x_l|p\rangle\frac{p^2}{2m}\langle p|x_j\rangle = \frac{\Delta x}{2\pi\hbar}\int dp e^{\frac{i}{\hbar}(x_l-x_j)p}\frac{p^2}{2m}, \\ &= \frac{\Delta x \Delta p}{2\pi\hbar}\sum_{k=1}^{n_p} e^{\frac{i}{\hbar}(x_l-x_j)p_k}\frac{p_k^2}{2m}, \end{aligned} \tag{21}$$

since the identity operator is $\mathbf{I} = \sum_j |x_j\rangle\Delta x\langle x_j|$, in the discretized version of the delta function representation, and $\Delta x\langle x_j|x_k\rangle = \delta_{jk}$.

11.1 Computational Problem FGH

Write a program to solve the time independent Schrödinger equation by using the FGH method and apply it to find the first 5 eigenvalues and eigenfunctions of the particle in the box with $m = a = 1$. Compare your numerical and analytical solutions. Modify the potential to obtain the analogous eigenstates for the Harmonic oscillator introduced by Eq. (28) with $m = 1$ and $\omega = 1$. Verify that the eigenvalues are $E(\nu) = (1/2 + \nu)\hbar\omega$, $\nu = 0$–4.

The link (http://ursula.chem.yale.edu/∼batista/classes/vvv/pbox.m) provides a Matlab solution to the FGH computational assignment.

The link http://ursula.chem.yale.edu/∼batista/classes/vvv/M1.pdf provides a Matlab tutorial with a detailed explanation of the solution to the computational assignment, prepared by Dr. Videla.

The link (http://ursula.chem.yale.edu/∼batista/classes/vvv/hbox.m) provides the corresponding Matlab solution to the harmonic well potential.

The link (http://ursula.chem.yale.edu/∼batista/classes/vvv/2DFGH.tar) provides the corresponding Matlab solution to the 2-dimensional harmonic well potential.

12 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,

$$< \psi|\hat{H}|\psi > \geq E_0,$$

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 $\hat{H}$.

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

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 $< \psi|\hat{H}|\psi >$ with respect to the expansion coefficients. The link (http://ursula.chem.yale.edu/∼batista/classes/vvv/VT570.tar) , provides a Matlab implementation of the variational method as applied to the calculation of the ground and excited states of a harmonic well.

The link http://ursula.chem.yale.edu/∼batista/classes/vvv/M2.pdf , provides a detailed description of the solution to the computational assignment, prepared by Dr. Pablo Videla.

13 Digital Grid-Based Representations

The standard formulation of quantum mechanics, presented in previous sections, relies upon the tools of *calculus* (*e.g.*, derivatives, integrals, etc.) and involves equations and operations with infinitesimal quantities as well as states in Hilbert-space (the infinite dimensional space of functions L^2). The equations, however, seldom can be solved analytically. Therefore, computational solutions are necessary. However, computers can not handle infinite spaces since they have only limited memory. In fact, all they *can* do is to store and manipulate discrete arrays of numbers. Therefore, the question is: how can we represent continuum states and operators in the space of memory of digital computers?

In order to introduce the concept of a *grid-representation*, we consider the state,

$$\Psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{\alpha}{2}(x-x_0)^2 + ip_0(x-x_0)}, \tag{22}$$

which can be expanded in the infinite basis set of delta functions $\delta(x-x')$ as follows,

$$\Psi_0(x) = \int dx' c(x') \delta(x-x'), \tag{23}$$

where $c(x') \equiv \langle x'|\Psi_0\rangle = \Psi_0(x')$. All expressions are written in atomic units, so $\hbar = 1$.

Note that in a discrete representation, $\Psi_0(x) = \Delta \sum c_j g_j(x)$, where $c_j = \langle g_j|\Psi_0\rangle$. So, the particular representation with $g_j(x) = \delta(x-x_j)$ gives $c_j = \int dx \delta(x-x_j)\Psi(x) = \Psi_0(x_j)$. Therefore, $\Psi_0(x) = \sum \Psi_0(x_j)\delta(x-x_j)$.

A grid-based representation of $\Psi_0(x)$ can be obtained, in the coordinate range $x = (x_{min}, x_{max})$, by discretizing Eq. (23) as follows,

$$\Psi_0(x) = \Delta \sum_{j=1}^{n} c_j \delta(x-x_j), \tag{24}$$

where the array of numbers $c_j \equiv \langle x_j|\Psi_0\rangle$ represent the state Ψ_0 on a grid of equally spaced coordinates $x_j = x_{min} + (j-1)\Delta$ with finite resolution $\Delta = (x_{max} - x_{min})/(n-1)$.

Note that the grid-based representation, introduced by Eq. (24), can be trivially generalized to a grid-based representation in the multidimensional space of parameters (*e.g.*, x_j, p_j, γ_j, ... etc.) when expanding the target state $\Psi_0(x)$ as a linear combination of basis functions $\langle x|x_j, p_j, \gamma_j\rangle$, with expansion coefficients as $c_j \equiv \langle x_j, p_j, \gamma_j|\Psi_0\rangle$.

13.1 Computational Problem 1

Write a computer program to represent the wave-packet, introduced by Eq. (22) on a grid of equally spaced coordinates $x_j = x_{min} + (j-1)\Delta$ with finite resolution $\Delta = (x_{max} - x_{min})/(n-1)$ and visualize the output. Choose $x_0 = 0$ and $p_0 = 0$, in the range x=(-20,20), with $\alpha = \omega m$, where $m = 1$ and $\omega = 1$.

Next, we consider grid-based representations in momentum space:

$$\Psi_0(p) = \langle p|\Psi_0\rangle. \tag{25}$$

Inserting the closure relation $\hat{1} = \int dx|x\rangle\langle x|$ in Eq. (25), we obtain that

$$\langle p|\Psi_0\rangle = \int dx\langle p|x\rangle\langle x|\Psi_0\rangle = (2\pi)^{-1/2}\int dx e^{-ipx}\langle x|\Psi_0\rangle. \tag{26}$$

is the Fourier transform of the initial state. The second equality in Eq. (26) was obtained by using:

$$\langle x|p\rangle = (2\pi)^{-1/2}e^{ipx}, \tag{27}$$

which is the eigenstate of the momentum operator $\hat{p} = -i\nabla$, with eigenvalue p, since $\hat{p}\langle x|p\rangle = p\langle x|p\rangle$.

The Fourier transform can be computationally implemented in $O(N\log(N))$ steps by using the Fast Fourier Transform (FFT) algorithm [see, Ch. 12 of Numerical Recipes by W.H. Press, B.P. Flannery, S.A. Teukolsky and W.T. Vetterling, Cambridge University Press, Cambridge, 1986 (f12-2.pdf)] when $\langle x|\Psi_0\rangle$ is represented on a grid with $N = 2^n$ points (where n is an integer). In contrast, the implementation of the Fourier transform by quadrature integration would require $O(N^2)$ steps.

13.2 Computational Problem 2

Write a computer program to represent the initial state, introduced by Eq. (22), in the momentum space by applying the FFT algorithm to the grid-based representation generated in Problem 1 and visualize the output. Represent the wave-packet amplitudes and phases in the range p=(-4,4) and compare your output with the corresponding values obtained from the analytic Fourier transform obtained by using:

$$\int dx\ \exp(-a_2x^2 + a_1x + a_0) = \sqrt{\pi/a_2}\ \exp(a_0 + a_1^2/(4a_2)).$$

Next, we consider the grid-based representation of operators (*e.g.*, $\hat{x}$, $\hat{p}$, $V(\hat{x})$, and $\hat{T} = \hat{p}^2/(2m)$) and learn how these operators act on states represented on grids in coordinate and momentum spaces. For simplicity, we assume that the potential is Harmonic:

$$V(\hat{x}) = \frac{1}{2}m\omega^2(\hat{x} - \bar{x})^2. \tag{28}$$

Consider first applying the potential energy operator to the initial state, as follows,

$$V(\hat{x})\Psi_0(x) = V(x)\Psi_0(x) \equiv \tilde{\Psi}_0(x). \tag{29}$$

Since $\tilde{\Psi}_0(x)$ is just another function, Eq. (29) indicates that $V(\hat{x})$ can be represented on the same grid of coordinates as before (*i.e.*, equally spaced coordinates $x_j = x_{min} + (j-1)\Delta$, with finite resolution $\Delta = (x_{max} - x_{min})/(n-1)$). Since for each x_j, $\tilde{\Psi}_0(x_j) = V(x_j)\Psi(x_j)$, the operator $V(\hat{x})$ can be represented just as an array of numbers $V(x_j)$ associated with the grid-points x_j, and its operation on a state is represented on such a grid as a simple multiplication.

13.3 Computational Problem 3

Write a computer program to compute the expectation values of the position $x(0) = \langle\Psi_0|\hat{x}|\Psi_0\rangle$ and the potential energy $V = \langle\Psi_0|V(\hat{x})|\Psi_0\rangle$, where $V(x)$ is defined according to Eq. (28) for the initial wave-packet, introduced by Eq. (22), with various possible values of x_0 and p_0, with $\alpha = \omega m$, where $m = 1$ and $\omega = 1$.

Now consider applying the momentum operator, $\hat{p} = -i\nabla$, to the initial state $\Psi_0(x)$ as follows,

$$G(x) = \langle x|\hat{p}|\Psi_0\rangle = -i\nabla\Psi_0(x). \tag{30}$$

One simple way of implementing this operation, when $\Psi_0(x)$ is represented on a grid of equally spaced points $x_j = x_{min} + (j-1)\Delta$, is by computing finite-increment derivatives as follows:

$$G(x_j) = -i\frac{\Psi_0(x_{j+1}) - \Psi_0(x_{j-1})}{2\Delta}. \tag{31}$$

However, for a more general operator (*e.g.*, $\hat{T} = \hat{p}^2/(2m)$) this finite increment derivative procedure becomes complicated. In order to avoid such procedures one can represent the initial state in momentum-space (by Fourier transform of the initial state); apply the operator by simple multiplication in momentum space and then transform the resulting product back to the coordinate representation (by inverse-Fourier transform). This method can be derived by inserting the closure relation $\hat{\mathbf{1}} = \int dp|p\rangle\langle p|$, in Eq. (30),

$$G(x) = \langle x|\hat{p}|\Psi_0\rangle = \int dp\langle x|\hat{p}|p\rangle\langle p|\Psi_0\rangle = (2\pi)^{-1/2}\int dp e^{ipx}p\langle p|\Psi_0\rangle, \tag{32}$$

since $\langle p|\Psi_0\rangle$ is defined according to Eq. (26) as the Fourier transform of the initial state. Note that the second equality of Eq. (32) is obtained by introducing the substitution

$$\langle x|p\rangle = (2\pi)^{-1/2}e^{ix\hat{p}}. \tag{33}$$

While Eq. (32) illustrates the method for the specific operator $\hat{p}$, one immediately sees that any operator which is a function of $\hat{p}$ (*e.g.*, $\hat{T} = \hat{p}^2/(2m)$) can be computed analogously according to the Fourier transform procedure.

13.4 Computational Problem 4

Write a computer program to compute the expectation values of the initial momentum $p(0) = \langle\Psi_0|\hat{p}|\Psi_0\rangle$ and the kinetic energy $T = \langle\Psi_0|\hat{p}^2/(2m)|\Psi_0\rangle$ by using the Fourier transform procedure, where Ψ_0 is the initial wave-packet introduced by Eq. (22), with $x_0 = 0$, $p_0 = 0$, and $\alpha = \omega m$, where $m = 1$ and $\omega = 1$. Compute the expectation value of the energy $E = \langle\Psi_0|\hat{H}|\Psi_0\rangle$, where $\hat{H} = \hat{p}^2/(2m) + V(\hat{x})$, with $V(x)$ defined according to Eq. (28) and compare your result with the zero-point energy $E_0 = \omega/2$.

14 SOFT Method

The Split-Operator Fourier Transform (SOFT) method is a numerical approach for solving the time-dependent Schrödinger equation by using grid-based representations of the time-evolving states and operators. It relies on the Fourier transform procedure to apply operators that are functions of $\hat{p}$ by simple multiplication of array elements. As an example, we will illustrate the SOFT algorithm as applied to the propagation of the harmonic oscillator, which can also be described analytically as follows:

$$\Psi_t(x) = \int dx' \langle x|e^{-i\hat{H}t}|x'\rangle\langle x'|\Psi_0\rangle, \tag{34}$$

where the Kernel $\langle x|e^{-i\hat{H}t}|x'\rangle$ is the quantum propagator

$$\langle x|e^{-i\hat{H}t}|x'\rangle = \sqrt{\frac{m\omega}{2\pi \text{sinh}(it\omega)}} \text{exp}\left(-\frac{m\omega}{2\text{sinh}(\omega it)}[(x^2+x'^2)\text{cosh}(\omega it) - 2xx']\right). \tag{35}$$

The essence of the method is to discretize the propagation time on a grid $t_k = (k-1)\tau$, with $k = 1, ..., n$ and time-resolution $\tau = t/(n-1)$, and obtain the wave-packet at the intermediate times t_k by recursively applying Eq. (34) as follows,

$$\Psi_{t_{k+1}}(x) = \int dx' \langle x|e^{-i\hat{H}\tau}|x'\rangle\langle x'|\Psi_{t_k}\rangle. \tag{36}$$

If τ is a sufficiently small time-increment (*i.e.*, n is large), the time-evolution operator can be approximated according to the Trotter expansion to second order accuracy,

$$e^{-i\hat{H}\tau} = e^{-iV(\hat{x})\tau/2} e^{-i\hat{p}^2\tau/(2m)} e^{-iV(\hat{x})\tau/2} + O(\tau^3), \tag{37}$$

which separates the propagator into a product of three operators, each of them depending either on $\hat{x}$, or $\hat{p}$.

14.1 Computational Problem 5

Expand the exponential operators in both sides of Eq. (37) and show that the Trotter expansion is accurate to second order in powers of τ.

Substituting Eq. (37) into Eq. (36) and inserting the closure relation $\hat{\mathbf{1}} = \int dp|p\rangle\langle p|$ gives,

$$\Psi_{t_{k+1}}(x) = \int dp \int dx' e^{-iV(\hat{x})\tau/2} \langle x|p\rangle e^{-ip^2\tau/(2m)} \langle p|x'\rangle e^{-iV(x')\tau/2} \Psi_{t_k}(x'). \tag{38}$$

By substituting $\langle p|x'\rangle$ and $\langle x|p\rangle$ according to Eqs. (27) and (33), respectively, we obtain:

$$\Psi_{t_{k+1}}(x) = e^{-iV(\hat{x})\tau/2} \frac{1}{\sqrt{2\pi}} \int dp e^{ixp} e^{-ip^2\tau/(2m)} \frac{1}{\sqrt{2\pi}} \int dx' e^{-ipx'} e^{-iV(x')\tau/2} \Psi_{t_k}(x'). \tag{39}$$

According to Eq. (39), then, the computational task necessary to propagate $\Psi_t(x)$ for a time-increment τ involves the following steps:

1. Represent $\Psi_{t_k}(x')$ and $e^{-iV(x')\tau/2}$ as arrays of numbers $\Psi_{t_k}(x_j)$ and $e^{-iV(x_j)\tau/2}$ associated with a grid of equally spaced coordinates $x_j = x_{min} + (j-1)\Delta$, with finite resolution $\Delta = (x_{max} - x_{min})/(n-1)$.

2. Apply the potential energy part of the Trotter expansion $e^{-iV(x')\tau/2}$ to $\Psi_{t_k}(x')$ by simple multiplication of array elements:
$$\tilde{\Psi}_{t_k}(x_j) = e^{-iV(x_j)\tau/2}\Psi_{t_k}(x_j).$$

3. Fourier transform $\tilde{\Psi}_{t_k}(x_j)$ to obtain $\tilde{\Psi}_{t_k}(p_j)$, and represent the kinetic energy part of the Trotter expansion $e^{-ip^2\tau/(2m)}$ as an array of numbers $e^{-ip_j^2\tau/(2m)}$ associated with a grid of equally spaced momenta $p_j = j/(x_{max} - x_{min})$.

4. Apply the kinetic energy part of the Trotter expansion $e^{-ip^2\tau/(2m)}$ to the Fourier transform $\tilde{\Psi}_{t_k}(p)$ by simple multiplication of array elements:
$$\widetilde{\Psi}_{t_k}(p_j) = e^{-ip_j^2\tau/(2m)}\tilde{\Psi}_{t_k}(p_j).$$

5. Inverse Fourier transform $\widetilde{\Psi}_{t_k}(p_j)$ to obtain $\widetilde{\Psi}_{t_k}(x_j)$ on the grid of equally spaced coordinates x_j.

6. Apply the potential energy part of the Trotter expansion $e^{-iV(x')\tau/2}$ to $\widetilde{\Psi}_{t_k}(x')$ by simple multiplication of array elements,
$$\Psi_{t_{k+1}}(x_j) = e^{-iV(x_j)\tau/2}\widetilde{\Psi}_{t_k}(x_j).$$

14.2 Imaginary time propagation

Note that with the variable substitution $\tau \to -it$, with real t, the time evolution operator becomes a decaying exponential $e^{-\hat{H}t/\hbar}$ that reduces the amplitude of the initial wavepacket $\Psi_0(x) = \sum_j c_j\phi_j(x)$, as follows:

$$\Psi_t(x) = e^{-i\hat{H}\tau/\hbar}\Psi_0(x) = \sum_j c_j e^{-E_j t}\phi_j(x), \tag{40}$$

where $\hat{H}\phi_j(x) = E_j\phi_j(x)$. Terms with higher E_j are reduced more than those with smaller E_j. After renormalizing the resulting wavefunction $\Psi_t(x)$ (by dividing it by the square root of its norm), we get a state enriched with low energy components. The imaginary time propagation and renormalization procedure can be repeated several times until the function stops changing since it composed solely by the ground state $\phi_0(x)$, after removal of all other components (of higher energies) at a faster rate.

Having found ϕ_0, we can proceed to find ϕ_1 as done for ϕ_0 but including orthogonalization relative to ϕ_0, $\Psi_t(x) \to \Psi_t(x) - \langle\phi_0|\Psi_t\rangle\phi_0(x)$, after each propagation step, right before renormalization. Higher energy states are found analogously, by orthogonalization of the propagated state relative to all previously found eigenstates.

14.3 Ehrenfest Dynamics

The goal of this section is to show that the expectation values $\langle\hat{x}\rangle = \langle\psi|\hat{x}|\psi\rangle$ and $\langle\hat{p}\rangle = \langle\psi|\hat{p}|\psi\rangle$ are conjugate variables in the sense that they evolve according to the classical equations of motion (*i.e.*, Hamilton's equaitons):

$$\begin{aligned}\frac{d}{dt}\langle\hat{x}\rangle &= \langle\frac{\partial\hat{H}}{\partial\hat{p}}\rangle \\ &= \frac{\langle\hat{p}\rangle}{m}, \\ \frac{d}{dt}\langle p\rangle &= -\langle\frac{\partial\hat{H}}{\partial\hat{x}}\rangle \\ &= -\langle V'\rangle,\end{aligned} \tag{41}$$

where $\hat{H} = \hat{p}^2/2m + V(\hat{x})$. This remarkable result, introduced by Eq. (41), is known as *Ehrenfest's theorem* and can be demonstrated, as follows.

First, we show that since ψ evolves according to the Schrödinger equation:

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi, \tag{42}$$

then

$$\langle\hat{p}\rangle = m\frac{d}{dt}\langle\hat{x}\rangle. \tag{43}$$

Using integration by parts, we obtain:

$$\begin{aligned}\langle\hat{p}\rangle &= -i\hbar\langle\psi|\frac{\partial}{\partial x}|\psi\rangle, \\ &= -\frac{i\hbar}{2}\langle\psi|\frac{\partial}{\partial x} + \frac{\partial}{\partial x}|\psi\rangle, \\ &= -\frac{i\hbar}{2}\int dx\left[\psi^*\frac{\partial\psi}{\partial x} + \psi^*\frac{\partial\psi}{\partial x}\right], \\ &= -\frac{i\hbar}{2}\int dx\left[\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right], \\ &= m\int j\,dx, \\ &= -m\int x\frac{\partial j}{\partial x}\,dx,\end{aligned} \tag{44}$$

where the current $j = -\frac{i\hbar}{2m}\left[\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right]$ satisfies the continuity equation,

$$\frac{d}{dt}\psi^*\psi + \frac{\partial j}{\partial x} = 0. \tag{45}$$

Therefore,

$$\begin{aligned}\langle\hat{p}\rangle &= m\int x\frac{d}{dt}\psi^*\psi\,dx,\\ &= m\frac{d}{dt}\int \psi^* x\psi\,dx,\\ &= m\frac{d}{dt}\langle\hat{x}\rangle.\end{aligned} \tag{46}$$

Next, we show that

$$\frac{d}{dt}\langle\hat{p}\rangle = -\langle V'\rangle, \tag{47}$$

by substituting Eq. (42) into Eq. (44) and integrating by parts, as follows:

$$\begin{aligned}\frac{d}{dt}\langle\hat{p}\rangle &= m\frac{d}{dt}\int_{-\infty}^{\infty} dx\; j,\\ &= -\frac{i\hbar}{2}\int_{-\infty}^{\infty} dx\left[\frac{d\psi^*}{dt}\frac{\partial\psi}{\partial x} + \psi^*\frac{\partial}{\partial x}\frac{d\psi}{dt} - \frac{d\psi}{dt}\frac{\partial\psi^*}{\partial x} - \psi\frac{\partial}{\partial x}\frac{d\psi^*}{dt}\right]\\ &= i\hbar\int_{-\infty}^{\infty} dx\left[\frac{d\psi}{dt}\frac{\partial\psi^*}{\partial x} + \frac{d\psi^*}{dt}\frac{\partial\psi}{\partial x}\right]\\ &= \int_{-\infty}^{\infty} dx\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}\frac{\partial\psi^*}{\partial x} + V\psi\frac{\partial\psi^*}{\partial x} + c.c.\right]\\ &= \int_{-\infty}^{\infty} dx\left[-\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left(\frac{\partial\psi}{\partial x}\frac{\partial\psi^*}{\partial x}\right) + V\left(\psi\frac{\partial\psi^*}{\partial x} + \psi^*\frac{\partial\psi}{\partial x}\right)\right],\\ &= \int_{-\infty}^{\infty} dx V\left(\psi\frac{\partial\psi^*}{\partial x} + \psi^*\frac{\partial\psi}{\partial x}\right),\end{aligned} \tag{48}$$

since $\frac{\partial\psi}{\partial x}\frac{\partial\psi^*}{\partial x} = 0$ when evaluated at $x = \pm\infty$. Therefore,

$$\begin{aligned}\frac{d}{dt}\langle\hat{p}\rangle &= \int_{-\infty}^{\infty} dx\frac{\partial\psi^*\psi}{\partial x}V,\\ &= -\int_{-\infty}^{\infty} dx\psi^*\frac{\partial V}{\partial x}\psi.\end{aligned} \tag{49}$$

14.4 Exercise: Real and Imaginary Time Evolution

1. Write a Matlab code to simulate the evolution of a wavepacket bouncing back and forth on a harmonic well, described by the Hamiltonian $H = p^2/(2*m) + V(x)$, with $V(x) = 0.5*x^2$ after initializing the state according to the ground state displaced from its equilibrium position, as follows: $\psi(x,0) = exp(-(x-1)^2/2)/\sqrt[4]{\pi}$.

2. Compute the expectation values of position and momentum as a function of time $x(t)$ and $p(t)$ and compare them to the corresponding classical values obtained by integrating Hamilton's equation with the Velocity-Verlet algorithm:

$$\begin{aligned} p_{j+1} &= p_j + (F(x_j) + F(x_{j+1}))\tau/2, \\ x_{j+1} &= x_j + p_j\tau/m + F(x_j)\tau^2/(2m), \end{aligned} \tag{50}$$

with $x_0 = 1$ and $p_0 = 0$ the initial position and momentum of the harmonic oscillator and x_j and p_j the position and momentum at time $t = j * \tau$, while $F(x_j) = -V'(x_j) = -x_j$.

3. Compute the expectation values of position and momentum as a function of time $x(t)$ and $p(t)$ and compare them to the Ehrenfest trajectory obtained by integrating Hamilton's equation, using mean force:

$$\begin{aligned} \langle p\rangle_{j+1} &= \langle p\rangle_j + (\langle F(x)\rangle_j + \langle F(x)\rangle_{j+1})\tau/2, \\ \langle x\rangle_{j+1} &= \langle x\rangle_j + \langle p\rangle_j\tau/m + \langle F(x)\rangle_j\tau^2/(2m), \end{aligned} \tag{51}$$

with $\langle x\rangle_0 = 1$ and $\langle p\rangle_0 = 0$ the initial position and momentum of the harmonic oscillator and $\langle x\rangle_j$ and $\langle p\rangle_j$ the mean position and momentum at time $t = j*\tau$, while $\langle F(x)\rangle_j = -\langle V'(x)\rangle_j = -\langle x\rangle_j$.

4. Find the ground state of the harmonic well by propagating the wavepacket in imaginary time (*i.e.*, using the propagation time increment $\tau = -it$, with real t) and renormalizing the wave function after each propagation step.

5. Find the first excited state of the harmonic well by propagating the wavepacket in imaginary time (*i.e.*, using the propagation time increment $\tau = -it$, with real t), projecting out the ground state component and renormalizing the wave function after each propagation step.

6. Find the first 9 excited states, iteratively, by imaginary time propagation as in item 4, projecting out lower energy states and renormalizing after each propagation step.

7. Change the potential to that of a Morse oscillator $V(x) = De(1 - exp(-a(x - x_e)))^2$, with $x_e = 0$, $D_e = 8$, and $a = \sqrt{k/(2D_e)}$, where $k = m\omega^2$. Recompute the wave-packet propagation with $x_0 = -0.5$ and $p_0 = 0$ for 100 steps with $\tau = 0.1$ a.u. Compare the expectation values $x(t)$ and $p(t)$ to the corresponding classical and Ehrenfest trajectories obtained according to the Velocity-Verlet algorithm.

Solution: The link (http://ursula.chem.yale.edu/∼batista/classes/vvv/HO570.tar) provides a Matlab implementation of the SOFT method as applied to the simulation of evolution of a wavepacket in a harmonic well in real time. In addition, the Matlab code implements the SOFT propagation method to find the lowest 10 eigenstates of the harmonic oscillator by 'evolution' in imaginary time.

14.5 Computational Problem 6

Write a computer program that propagates the initial state $\Psi_0(x)$ for a single time increment ($\tau = 0.1$ a.u.). Use $x_0 = -2.5$, $p_0 = 0$, and $\alpha = \omega m$, where $m = 1$ and $\omega = 1$. Implement the SOFT method for the Hamiltonian $\hat{H} = \hat{p}^2/(2m) + V(\hat{x})$, where $V(x)$ is defined according to Eq. (28). Compare the resulting propagated state with the analytic solution obtained by substituting Eq. (35) into Eq. (34).

14.6 Computational Problem 7

Loop the computer program developed in Problem 5 with $x_0 = -2.5$ and $p_0 = 0$ for 100 steps with $\tau = 0.1$ a.u. For each step compute the expectation values of coordinates $x(t)$ and momenta $p(t)$ as done in Problems 3 and 4, respectively. Compare your calculations with the analytic solutions obtained by substituting Eq. (35) into Eq. (34). Verify that these correspond to the classical trajectories $x(t) = \bar{x} + (x_0 - \bar{x})\cos(\omega t)$ and $p(t) = p_0 - (x_0 - \bar{x})\omega m \sin(\omega t)$, which can be computed according to the Velocity-Verlet algorithm:

$$\begin{aligned} p_{j+1} &= p_j + (F(x_j) + F(x_{j+1}))\tau/2 \\ x_{j+1} &= x_j + p_j\tau/m + F(x_j)\tau^2/(2m). \end{aligned} \tag{52}$$

14.7 Computational Problem 8

Change the potential to that of a Morse oscillator $V(\hat{x}) = De(1 - \exp(-a(\hat{x} - x_e)))^2$, with $x_e = 0$, $De = 8$, and $a = \sqrt{k/(2D_e)}$, where $k = m\omega^2$. Recompute the wave-packet propagation with $x_0 = -0.5$ and $p_0 = 0$ for 100 steps with $\tau = 0.1$ a.u., and compare the expectation values $x(t)$ and $p(t)$ with the corresponding classical trajectories obtained by recursively applying the Velocity-Verlet algorithm.

14.8 Computational Problem 9

Simulate the propagation of a wave-packet with $x_0 = -5.5$ and initial momentum $p_0 = 2$ colliding with a barrier potential $V(x) = 3$, if abs$(x) < 0.5$, and $V(x) = 0$, otherwise. Hint: In order to avoid artificial recurrences you might need to add an absorbing imaginary potential $V_a(x) = i(\text{abs}(x) - 10)^4$, if abs$(x) > 10$, and $V_a(x) = 0$, otherwise.

15 Time Independent Perturbation Theory

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

$$\hat{H}\phi_n(x) = E_n\phi_n(x), \tag{53}$$

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

$$(\hat{H} + \lambda\hat{\omega})\tilde{\Phi}_n(\lambda, x) = \tilde{E}_n(\lambda)\tilde{\Phi}_n(\lambda, x), \tag{54}$$

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,

$$C_{ln}(\lambda)E_l + \lambda\sum_j C_{jn}(\lambda) < \phi_l|\hat{\omega}|\phi_j >= \tilde{E}_n(\lambda)C_{ln}(\lambda). \tag{55}$$

Expanding C_{kj} and $\tilde{E}_n$ in powers of λ we obtain,
$C_{kj}(\lambda) = C_{kj}^{(0)} + C_{kj}^{(1)}\lambda + C_{kj}^{(2)}\lambda^2 + ...,$
and
$\tilde{E}_n(\lambda) = E_n^{(0)} + E_n^{(1)}\lambda + E_n^{(2)}\lambda^2 + ...$
Substituting these expansions into Eq. (55) we obtain,
$(C_{ln}^{(0)}E_l - E_n^{(0)}C_{ln}^{(0)}) + \lambda(C_{ln}^{(1)}E_l + \sum_j C_{jn}^{(0)} < \phi_l|\hat{\omega}|\phi_j > -E_n^{(0)}C_{ln}^{(1)} - E_n^{(1)}C_{ln}^{(0)}) +$
$\times\lambda^2(C_{ln}^{(2)}E_l + \sum_j C_{jn}^{(1)} < \phi_l|\hat{\omega}|\phi_j > -E_n^{(2)}C_{ln}^{(0)} - E_n^{(0)}C_{ln}^{(2)} - E_n^{(1)}C_{ln}^{(1)}) + ... = 0.$
This equation must be valid for any λ. Therefore, each of the terms in between parenthesis must be equal to zero.

$$\text{Zeroth order in } \lambda \begin{cases} C_{ln}^{(0)}(E_l - E_n^{(0)}) = 0, \\ \text{if } l \neq n, \text{ then } C_{ln}^{(0)} = 0, \\ \text{if } l = n, \text{ then } C_{nn}^{(0)} = 1, \text{ and } E_l = E_n^{(0)}. \end{cases}$$

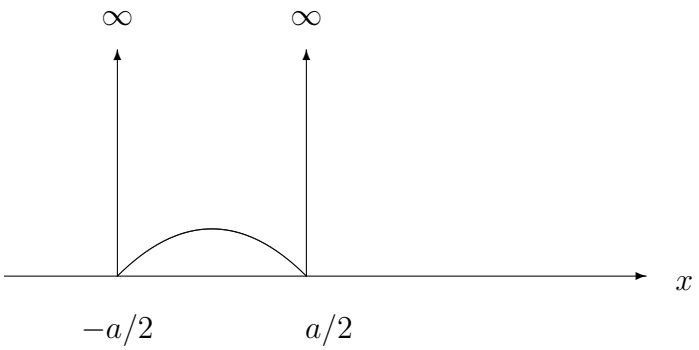
$$\text{First order in } \lambda \begin{cases} C_{ln}^{(1)}(E_l - E_n^{(0)}) = E_n^{(1)}C_{ln}^{(0)} - \sum_j C_{jn}^{(0)} < \phi_l|\hat{\omega}|\phi_j >, \\ \text{if } l \neq n, \text{ then } C_{ln}^{(1)}(E_l - E_n^{(0)}) = -C_{nn}^{(0)} < \phi_l|\hat{\omega}|\phi_n >, \\ \text{if } l = n, \text{ then } E_n^{(1)}C_{ln}^{(0)} = C_{nn}^{(0)} < \phi_n|\hat{\omega}|\phi_n > . \end{cases}$$

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.

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

15.1 Exercise 9: How accurate is first order time-independent perturbation theory?

1. Calculate the energies predicted by first order perturbation theory for the first 5 states of the particle in the box described by the 'bottle bottom' potential, $W(x) = \lambda\sin(\frac{\pi}{a}(\frac{a}{2} - x))$, with $\lambda = 1$:



2. Compare the energies to the numerical results obtained by diagonalization of the corresponding Fourier grid Hamiltonian.
3. Compare the % error for each eigenvalue to the corresponding results when $\lambda = 2$.

The link (http://ursula.chem.yale.edu/∼batista/classes/vvv/pbottle.m) , provides a Matlab solution to the 'particle in the bottle' computational assignment.

16 Time Dependent Perturbation Theory

Given an arbitary 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 $\hat{H}\hat{\Phi}_j = E_j\Phi_j$ and $i\hbar\frac{\partial\tilde{\psi}}{\partial t} = \hat{H}\tilde{\psi}$, let us obtain the solution of the time dependent Schrödinger equation:

$$i\hbar\frac{\partial\psi}{\partial t} = [\hat{H} + \lambda\hat{\omega}(t)]\psi, \tag{56}$$

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

$$\psi_\lambda(x,t) = \sum_j \sum_{l=0}^{\infty} C_{jl}(t)\lambda^l \Phi_j(x) e^{-\frac{i}{\hbar}E_j t}. \tag{57}$$

Substituting Eq. (57) into Eq. (56) we obtain,

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

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

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

Since,

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

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

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

$$i\hbar[\dot{C}_{k_1}(t)e^{-\frac{i}{\hbar}E_k t} + C_{k_1}(t)(-\frac{i}{\hbar}E_k)e^{-\frac{i}{\hbar}E_k t}] = \sum_j C_{j_1}(t)\delta_{kj}E_j e^{-\frac{i}{\hbar}E_j t} + C_{j_0}(t) < \Phi_k|\hat{\omega}|\Phi_j > e^{-\frac{i}{\hbar}E_j t},$$

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

Therefore,

$$\dot{C}_{k_1}(t) = -\frac{i}{\hbar}\sum_j C_{j_0}(0) < \Phi_k|e^{\frac{i}{\hbar}E_k t}\hat{\omega}e^{-\frac{i}{\hbar}E_j t}|\Phi_j >= -\frac{i}{\hbar}\sum_j C_{j_0}(0) < \Phi_k|e^{\frac{i}{\hbar}\hat{H}t}\hat{\omega}e^{-\frac{i}{\hbar}\hat{H}t}|\Phi_j >, \tag{58}$$

Eq. (58) was obtained by making the substitution $e^{-\frac{i}{\hbar}\hat{H}t}|\Phi_j >= e^{-\frac{i}{\hbar}E_j t}|\Phi_j >$, which is justified in the note that follows this derivation. Integrating Eq. (58) we obtain,

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

which can also be written as follows:

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

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

Note: The substitution made in Eq. (58) can be justified as follows. The exponential function is defined in powers series as follows,

$$e^A = \sum_{n=0}^{\infty}\frac{A^n}{n!} = 1 + A + \frac{1}{2!}AA + ..., \qquad \textbf{R4(169)}$$

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

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

Furthermore, since

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

and,

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

we obtain,

$$e^{-\frac{i}{\hbar}\hat{H}t}|\Phi_j>=[1+(-\frac{i}{\hbar}E_jt)+\frac{1}{2!}(-\frac{i}{\hbar}t)^2E_j^2+...]|\Phi_j>=e^{-\frac{i}{\hbar}E_jt}|\Phi_j>,$$

which is the substitution implemented in Eq. (58).

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

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

$$\dot{C}_{k_2}(t)=-\frac{i}{\hbar}\sum_j<\Phi_k|e^{\frac{i}{\hbar}\hat{H}t}\hat{\omega}e^{-\frac{i}{\hbar}\hat{H}t}|\Phi_j>C_{j_1}(t),$$

$$C_{k_2}(t)=\left(-\frac{i}{\hbar}\right)\int_{-\infty}^{t}dt'\sum_j<\Phi_k|e^{\frac{i}{\hbar}\hat{H}t'}\hat{\omega}e^{-\frac{i}{\hbar}\hat{H}t'}|\Phi_j>C_{j_1}(t'),$$

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

Since $1=\sum_j|\Phi_j><\Phi_j|$,

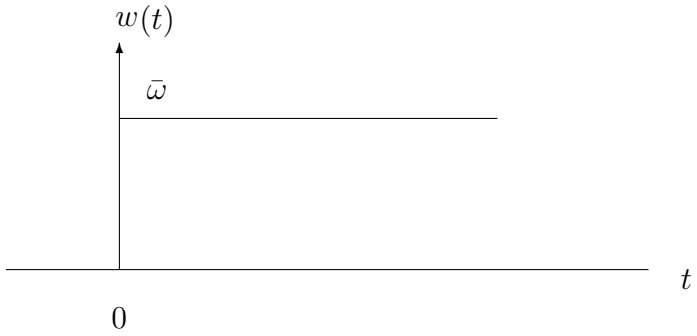
$$C_{k_2}(t)=\left(-\frac{i}{\hbar}\right)^2\int_{-\infty}^{t}dt'\int_{-\infty}^{t'}dt''<\Phi_k|e^{\frac{i}{\hbar}\hat{H}t'}\hat{\omega}e^{-\frac{i}{\hbar}\hat{H}(t'-t'')}\hat{\omega}e^{-\frac{i}{\hbar}\hat{H}t''}|\tilde{\psi}_0>.$$

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,

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

therefore,

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

Assuming that initially: $C_j = \delta_{lj}, \qquad \Rightarrow \qquad C_{j0} = \delta_{lj}$. Therefore,

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

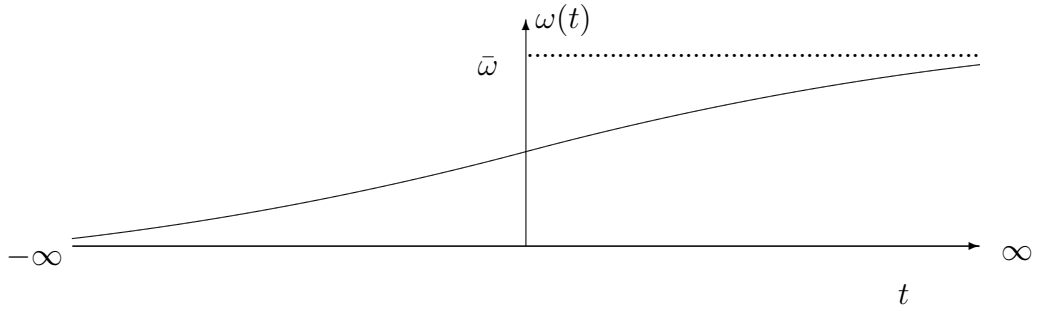
when $k \neq l$. Note that $C_{l_1}(t)$ must be obtained from the normalization of the wave function expanded to first order in λ.

16.1 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 ($\frac{d\omega_t}{dt} << \epsilon$, with ϵ arbitrarily small):**R2(448)**



$$C_{k_1}(t) = (-\frac{i}{\hbar}) \int_{-\infty}^{t} dt' < \Phi_k|\omega(t')|\Phi_l > e^{-\frac{i}{\hbar}(E_l - E_k)t'}.$$

Integrating by parts we obtain,

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

and, since $< \Phi_k|w(-\infty)|\Phi_l >= 0$,

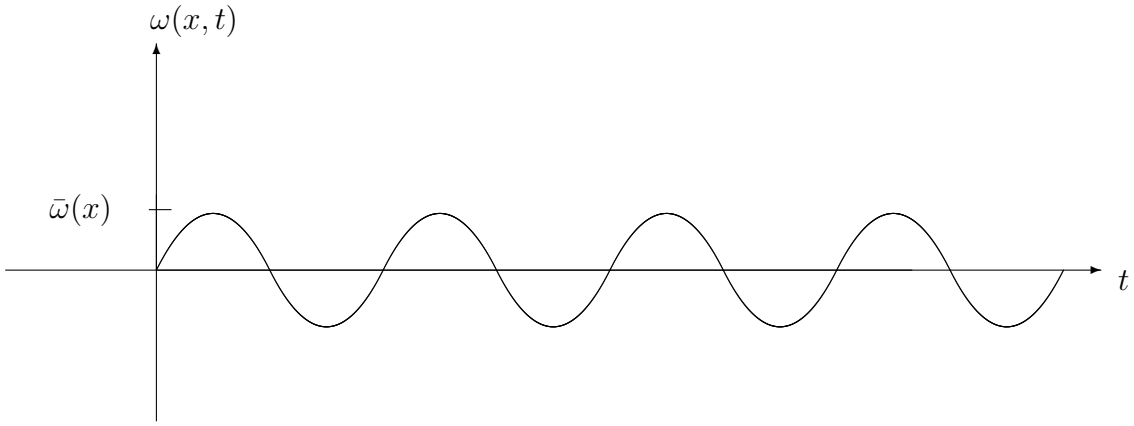
$$C_{k_1}(t) = \frac{< \Phi_k|\omega(t)|\Phi_l >}{(E_l - E_k)} e^{-\frac{i}{\hbar}(E_l - E_k)t},$$

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.

16.2 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,

$$C_{k_1}(t) = -\frac{i}{\hbar}\int_0^t dt' < \Phi_k|e^{\frac{i}{\hbar}\hat{H}t'}\hat{\omega}(t')e^{-\frac{i}{\hbar}\hat{H}t'}|\tilde{\psi}_0 >, \tag{59}$$

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

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

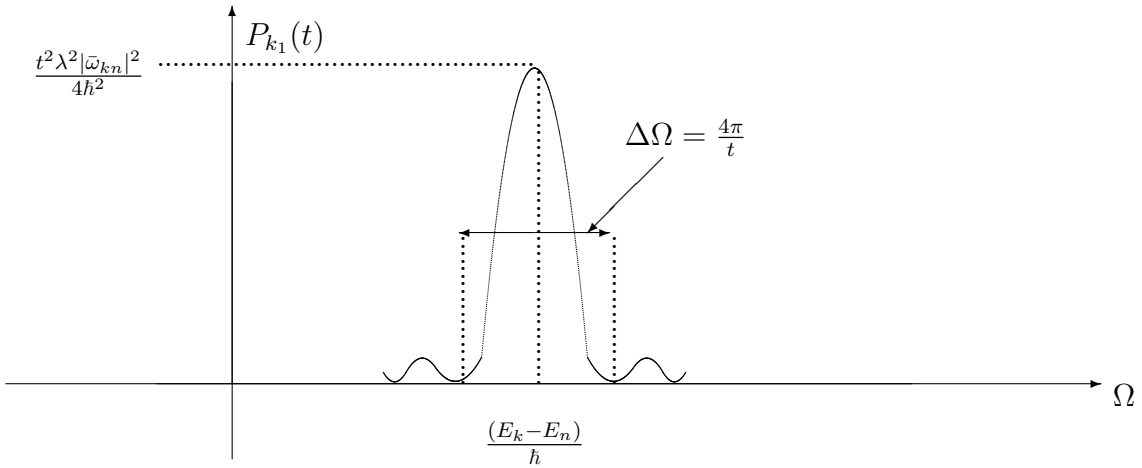
and therefore,

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

Without lost of generality, let us assume that $C_j = \delta_{nj}$ (i.e., initially only state n is occupied). For $k \geq n$ we obtain,

$$|C_{k_1}(t)|^2 = \frac{|\bar{\omega}_{kn}|^2}{4\hbar^2}\left|\frac{1-e^{i[\frac{(E_k-E_n)}{\hbar}+\Omega]t}}{\frac{(E_k-E_n)}{\hbar}+\Omega} - \frac{1-e^{i[\frac{(E_k-E_n)}{\hbar}-\Omega]t}}{\frac{(E_k-E_n)}{\hbar}-\Omega}\right|^2.$$

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 $P_{k1} << 1$ indicates that the system has been slightly perturbed. Such condition is satisfied only when $t << \frac{2\hbar}{|\bar{\omega}_{kn}|\lambda}$. Therefore, the theory is useful *only* at sufficiently short times.

17 Golden Rule

The goal of this section is to introduce the so-called *Fermi Golden Rule* expression, given by first-order time dependent perturbation theory.

We consider a system initially prepared in state $|i\rangle$. At time $t = 0$, we turn on the perturbation $W(t)$ and we analyze the decay to the final state $|f\rangle$, as described by first order time-dependent perturbation theory:

$$c_f(t) = -\frac{i}{\hbar}\int_0^t dt' \langle f|\hat{W}(t')|i\rangle e^{\frac{i}{\hbar}(E_f - E_i)t'}, \tag{60}$$

Therefore, the probability of observing the system in the final state is

$$P_{fi}(t) = \frac{1}{\hbar^2}\int_0^t dt'' \int_0^t dt' \langle i|\hat{W}^*(t'')|f\rangle\langle f|\hat{W}(t')|i\rangle e^{\frac{i}{\hbar}(E_f - E_i)(t'-t'')}, \tag{61}$$

17.1 Monochromatic Plane Wave

Assuming that the perturbation involves a single frequency component, $\hat{W}(t') = \hat{A}e^{-iwt'}$, we obtain:

$$\begin{aligned} c_f(t) &= \langle f|\hat{A}|i\rangle \frac{[1 - e^{i(w_{fi} - w)t}]}{\hbar(w_{fi} - \omega)}, \\ &= -\frac{i}{\hbar} t \langle f|\hat{A}|i\rangle e^{i(w_{fi} - w)t/2} \frac{\sin[(w_{fi} - w)t/2]}{(w_{fi} - \omega)t/2}. \end{aligned} \tag{62}$$

Therefore, the probability of observing the system in the final state is

$$P_{fi}(t) = \frac{t^2}{\hbar^2}|\langle f|\hat{A}|i\rangle|^2 \frac{\sin^2[(w_{fi} - w)t/2]}{[(w_{fi} - \omega)t/2]^2}. \tag{63}$$

To compute the survival probability that the system remains in the initial state, we must add up the probability over all possible final states,

$$\begin{aligned} P(t) &= 1 - \frac{t^2}{\hbar^2} \sum_f |\langle f|\hat{A}|i\rangle|^2 \frac{\sin^2[(w_{fi}-w)t/2]}{[(w_{fi}-\omega)t/2]^2} \\ &= 1 - \frac{t^2}{\hbar^2} \int_{-\infty}^{\infty} dE_f \rho(E_f) |\langle f|\hat{A}|i\rangle|^2 \frac{\sin^2[(w_{fi}-w)t/2]}{[(w_{fi}-\omega)t/2]^2} \end{aligned} \tag{64}$$

If the very short time limit, $P(t) = exp(-\alpha t^2) \approx 1 - \alpha t^2 + \cdots$, where

$$\begin{aligned} \alpha &= \lim_{t\to 0} \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dE_f |\langle f|\hat{A}|i\rangle|^2 \rho(E_f) \frac{\sin^2[(E_f - E_i - \hbar w)t/(2\hbar)]}{[(E_f - E_i - \hbar w)t/(2\hbar)]^2}, \\ &= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dE_f |\langle f|\hat{A}|i\rangle|^2 \rho(E_f), \end{aligned} \tag{65}$$

In the longer time limit, the kernel of Eq. (64) is approximated as the delta function to obtain:

$$\begin{aligned} P(t) &= 1 - \frac{t}{\hbar^2} \int_{-\infty}^{\infty} d(tE_f) \rho(E_f) |\langle f|\hat{A}|i\rangle|^2 \pi \delta((E_f t - (E_i + \hbar w)t)/(2\hbar)) \\ &= 1 - t\frac{2\pi}{\hbar} \int_{-\infty}^{\infty} d\xi \rho(\xi 2\hbar/t) |\langle f|\hat{A}|i\rangle|^2 \delta(\xi - (E_i + \hbar w)t/(2\hbar)) \\ &= 1 - t\frac{2\pi}{\hbar} \rho(E_i + \hbar w) |\langle E_i + \hbar w|\hat{A}|i\rangle|^2 \end{aligned} \tag{66}$$

so $P(t) = exp(-\Gamma t) \approx 1 - \Gamma t + \cdots$, where

$$\begin{aligned} \Gamma &= \frac{2\pi}{\hbar} \rho(E_i + \hbar w) |\langle E_i + \hbar w|\hat{A}|i\rangle|^2, \\ &= \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} dE_f \rho(E_f) |\langle f|\hat{A}|i\rangle|^2 \delta(E_f - (E_i + \hbar w)), \end{aligned} \tag{67}$$

or as a discrete sum over states,

$$\Gamma = \frac{2\pi}{\hbar} \sum_f |\langle f|\hat{A}|i\rangle|^2 \delta(E_f - E_i - \hbar w), \tag{68}$$

which is known as Fermi's Golden rule.

17.2 Vibrational Cooling

In the subsection, we illustrate the Golden Rule as applied to the description of vibrational cooling of a harmonic diatomic molecule coupled to a metal surface as implemented by Head-Gordon and Tully [*J. Chem. Phys.* (1992) **96**:3939-3949] .

For a molecule interacting with a surface, the general form of the coupling matrix element A_{fi} follows from the Born-Oppenheimer approximation in which the nuclear kinetic energy term is neglected when obtaining the electronic wave functions. The states are Born-Oppenheimer products of nuclear (vibrational) and electronic wave functions which we write, as follows:

$$\begin{aligned} |i\rangle &= |\nu_i\rangle|e_i\rangle, \\ |f\rangle &= |\nu_f\rangle|e_f\rangle, \end{aligned} \tag{69}$$

Therefore, the coupling between the two states is the matrix element of the nuclear kinetic-energy operator (for simplicity, we consider only a single normal mode x, which will be the high-frequency adsorbate vibration):

$$\begin{aligned} \langle f|\hat{A}|i\rangle &= -\frac{\hbar^2}{2m}\langle \nu_f e_f|\frac{\partial^2}{\partial x^2}|\nu_i e_i\rangle \\ &= -\frac{\hbar^2}{2m}\left[\langle\nu_f|\nu_i\rangle\langle e_f|\frac{\partial^2}{\partial x^2}|e_i\rangle + 2\langle \nu_f e_f|\frac{\partial}{\partial x}|e_i\rangle\frac{\partial}{\partial x}|\nu_i\rangle\right] \end{aligned} \tag{70}$$

where m is the reduced mass of the vibrational mode x.

To obtain a tractable expression, the nuclear and electronic coordinates in the matrix element must be separated. Following Brivio and Grimley (G. P. Brivio and T. B. Grimley, J. Phys. C 10, 2351 (1977); G. P. Brivio and T. B. Grimley, Surf. Sci. 89, 226 (1979)), this can be done by observing that since the amplitude of vibration is small (about 1/100 of the bondlength for diatomics in low vibrational states), it is reasonable to expand the electronic matrix elements in powers of the displacement x, keeping only the leading term. If we also assume that the electronic states $|e_i\rangle$ and $|e_f\rangle$ represent parallel potential-energy surfaces then $|\nu\rangle$ and $|\nu'\rangle$ will be orthogonal members of the same complete set, and the first term of Eq. (70) vanishes, leaving

$$\langle f|\hat{A}|i\rangle = -\frac{\hbar^2}{m}\left[\langle\nu_f|\frac{\partial}{\partial x}|\nu_i\rangle\langle e_f|\frac{\partial}{\partial x}|e_i\rangle\right] \tag{71}$$

To compute $\langle\nu_f|\frac{\partial}{\partial x}|\nu_i\rangle$, we assume that the vibrational states can be approximated as harmonic oscillator wave functionsm with frequency w, for which:

$$\begin{aligned} \hat{a}|\nu\rangle &= \sqrt{\nu}|\nu-1\rangle, \\ \hat{N}|\nu\rangle &= \nu|\nu\rangle = \hat{a}^\dagger\hat{a}|\nu\rangle = \sqrt{\nu}\hat{a}^\dagger|\nu-1\rangle, \end{aligned} \tag{72}$$

so $\hat{a}^\dagger|\nu\rangle = \sqrt{\nu+1}|\nu+1\rangle$, with $\hat{a} = \frac{1}{\sqrt{2}}(\tilde{x}+i\tilde{p})$, $\hat{a}^\dagger = \frac{1}{\sqrt{2}}(\tilde{x}-i\tilde{p})$. Here, $\tilde{x} = \hat{x}\sqrt{\frac{mw}{\hbar}}$ and $\tilde{p} = \hat{p}\sqrt{\frac{1}{\hbar mw}}$, with $\hat{p} = -i\hbar\frac{\partial}{\partial x}$. Therefore, $\hat{a}-\hat{a}^\dagger = i\sqrt{\frac{2}{\hbar mw}}\hat{p} = \sqrt{\frac{2\hbar}{mw}}\frac{\partial}{\partial x}$ which gives,

$$\begin{aligned} \langle\nu_f|\frac{\partial}{\partial x}|\nu_i\rangle &= \sqrt{\frac{mw}{2\hbar}}\left[\langle\nu_f|\hat{a}|\nu_i\rangle - \langle\nu_f|\hat{a}^\dagger|\nu_i\rangle\right], \\ &= \sqrt{\frac{mw}{2\hbar}}\left[\sqrt{\nu_i}\delta_{\nu_f,\nu_i-1} - \sqrt{\nu_i+1}\delta_{\nu_f,\nu_i+1}\right] \end{aligned} \tag{73}$$

Substituting Eq. (73) into Eq. (71), with $\nu_f = \nu_i - 1$, we obtain:

$$\langle f|\hat{A}|i\rangle = -\hbar\sqrt{\frac{\hbar w\nu_i}{2m}}\langle e_f|\frac{\partial}{\partial x}|e_i\rangle. \tag{74}$$

and

$$|\langle f|\hat{A}|i\rangle|^2 = \hbar^2\frac{\hbar w\nu_i}{2m}|\langle e_f|\frac{\partial}{\partial x}|e_i\rangle|^2. \tag{75}$$

Substituting Eq. (75) into Eq. (68), we obtain:

$$\Gamma = \frac{\hbar}{m}\sum_f \hbar w\nu_i|\langle e_f|\frac{\partial}{\partial x}|e_i\rangle|^2\delta(e_f - e_i - \hbar w), \tag{76}$$

Integrating over the number of electrons that could be promoted to an unoccupied state by absorbing a quantum of energy $\hbar w$, we obtain the total vibrational linewidth:

$$\begin{aligned}\Gamma &= 2\frac{\hbar}{m}\int de_i \frac{\rho(e_i)}{e^{\beta(e_i-\mu_F)}+1}\sum_f \hbar w\nu_i|\langle e_f|\frac{\partial}{\partial x}|e_i\rangle|^2\delta(e_f - e_i - \hbar w),\\ &= 2\frac{\hbar}{m}\int de_i\int de_f \frac{\rho(e_i)}{e^{\beta(e_i-\mu_F)}+1}\frac{\rho(e_f)}{e^{-\beta(e_f-\mu_F)}+1}\hbar w\nu_i|\langle e_f|\frac{\partial}{\partial x}|e_i\rangle|^2\delta(e_f - e_i - \hbar w),\end{aligned} \tag{77}$$

where μ_F is the Fermi energy. In the low-temperature limit ($\beta \to \infty$), for $\nu_i = 1$, we obtain:

$$\Gamma = 2\frac{\hbar}{m}\sum_{i<F}\sum_{f>F}\hbar w|\langle e_f|\frac{\partial}{\partial x}|e_i\rangle|^2\delta(e_f - e_i - \hbar w) \tag{78}$$

Reinserting the kernel of Eq. (65) and introducing the change of variables $\Delta = e_f - e_i$, we can rewrite Eq. (77), as follows:

$$\begin{aligned}\Gamma &= 2\frac{\hbar}{m}\int de_i \frac{\rho(e_i)}{e^{\beta(e_i-\mu_F)}+1}\sum_f \hbar w\nu_i|\langle e_f|\frac{\partial}{\partial x}|e_i\rangle|^2\delta(e_f - e_i - \hbar w),\\ &= 2\frac{\hbar}{m}\sum_\Delta\sum_i \frac{\rho(e_i)}{e^{\beta(e_i-\mu_F)}+1}\frac{\rho(e_i+\Delta)}{e^{-\beta(e_i+\Delta-\mu_F)}+1}\hbar w\nu_i|\langle e_i+\Delta|\frac{\partial}{\partial x}|e_i\rangle|^2\frac{\sin^2[(\Delta-\hbar w)t/(2\hbar)]}{[(\Delta-\hbar w)t/(2\hbar)]^2},\\ &= \sum_\Delta f(\Delta)\frac{\sin^2[(\Delta-\hbar w)t/(2\hbar)]}{[(\Delta-\hbar w)t/(2\hbar)]^2},\end{aligned} \tag{79}$$

where

$$f(\Delta) = \sum_i \frac{\rho(e_i)}{e^{\beta(e_i-\mu_F)}+1}\frac{\rho(e_i+\Delta)}{e^{-\beta(e_i+\Delta-\mu_F)}+1}\hbar w\nu_i|\langle e_i+\Delta|\frac{\partial}{\partial x}|e_i\rangle|^2, \tag{80}$$

and t is a time sufficiently long so that the decay is no longer Gaussian but rather exponential so that Γ is time independent.

17.3 Electron Transfer

The rate of electron transfer from the initial state $|i\rangle = |\nu_i\rangle|e_i\rangle$ to the final state $|f\rangle = |\nu_f\rangle|e_f\rangle$ of weakly coupled redox species can also be described according to the Golden rule expression derived from first order perturbation theory:

$$\begin{aligned}\Gamma_i &\approx \frac{2\pi}{\hbar}\sum_f |\langle f|\hat{A}|i\rangle|^2\delta(E_f - \hbar(w_i + w)),\\ &\approx \frac{2\pi}{\hbar}|H_{if}|^2\sum_f |\langle \nu_f|\nu_i\rangle|^2\delta(E_f - E_i - \Delta E),\end{aligned} \tag{81}$$

where $H_{if} = \langle e_f|\hat{A}|e_i\rangle$ is the coupling between electronic states, assumed to be independent of vibrational coordinates, and $\Delta E = \hbar\omega$ is the change in vibrational energy.

For the harmonic potentials shown in Fig. (17.3), it can be shown that

$$\sum_f |\langle \nu_f|\nu_i\rangle|^2\delta(E_f - E_i - \Delta E) \approx \frac{1}{\hbar\Omega\pi x_{if}k^*}, \tag{82}$$

when $E_i, E_f > E^*$, with $k^* = \sqrt{2m(E_i - E^*)}/\hbar$ and $x_{if} = \sqrt{2E_\lambda/(m\Omega^2)}$, giving

$$\begin{aligned}\Gamma_i &\approx 2|H_{if}|^2\frac{1}{\sqrt{2\hbar E_\lambda/m}\sqrt{2m(E_i - E^*)}}\\ &\approx |H_{if}|^2\frac{1}{\hbar\sqrt{E_\lambda}\sqrt{(E_i - E^*)}}\end{aligned} \tag{83}$$

Computing the thermal average over all initial states, we obtain the overall rate:

$$\begin{aligned}\Gamma &\approx |H_{if}|^2\frac{1}{\hbar\sqrt{E_\lambda}}\frac{\int dE_i exp(-\beta E_i)\frac{1}{\sqrt{(E_i - E^*)}}}{\int dE_i exp(-\beta E_i)}\\ &\approx |H_{if}|^2\frac{1}{\hbar\sqrt{E_\lambda}}exp(-\beta E^*)\frac{\int dE exp(-\beta E)\frac{1}{\sqrt{E}}}{\int dE exp(-\beta E)}\\ &\approx |H_{if}|^2\frac{1}{\hbar\sqrt{E_\lambda}}exp(-\beta E^*)\frac{\int_0^\infty dp 2p exp(-\beta p^2)\frac{1}{p}}{\int dE exp(-\beta E)}\\ &\approx |H_{if}|^2\frac{1}{\hbar\sqrt{E_\lambda}}exp(-\beta E^*)\frac{\int_0^\infty dp exp(-\beta p^2)}{\int dE exp(-\beta E)}\\ &\approx |H_{if}|^2\frac{1}{\hbar\sqrt{E_\lambda}}exp(-\beta E^*)\frac{\sqrt{\pi/\beta}}{\beta^{-1}}\\ &\approx |H_{if}|^2\frac{1}{\hbar\sqrt{E_\lambda}}exp(-\beta E^*)\sqrt{\pi\beta}\\ &\approx |H_{if}|^2\frac{\sqrt{2\pi\beta/m}}{\hbar\Omega x_{if}}exp(-\beta E^*)\end{aligned} \tag{84}$$

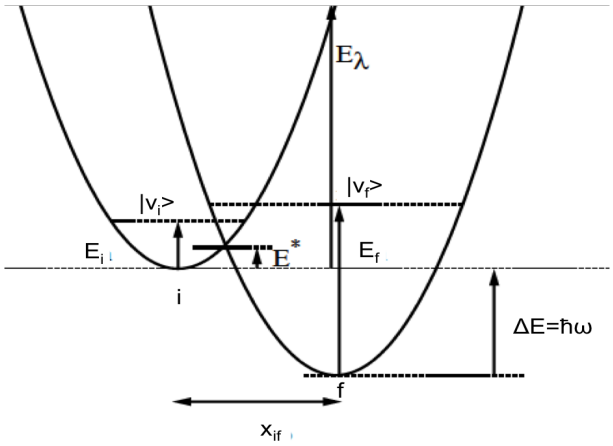


Figure 17.3 shows a schematic description of the energy diagram, assuming that the potential energy surfaces along the vibronic coordinates are parabolas displaced in $x_{fi} = x_f - x_i$ with frequency Ω, we have $V_i = 1/2m\Omega^2(x - x_i)^2$ and $V_f = 1/2m\Omega^2(x - x_f)^2 - \Delta E$, which cross at x^* with energy

$$E^* = (E_\lambda - \Delta E)^2/(4E_\lambda). \tag{85}$$

To derive Eq. (85), we observe that $E^* = 1/2m\Omega^2(x^* - x_i)^2 = 1/2m\Omega^2(x^* - x_i - x_{fi})^2 - \Delta E$. Therefore, $E^* = 1/2m\Omega^2(x^* - x_i)^2 + 1/2m\Omega^2 x_{fi}^2 - m\Omega^2(x^* - x_i)x_{fi} - \Delta E$ which gives $E^* = E^* + E_\lambda - m\Omega^2(x^* - x_i)x_{fi} - \Delta E$. Simplifying, we obtain: $E_\lambda = m\Omega^2(x^* - x_i)x_{fi} + \Delta E = m\Omega^2\sqrt{2E^*/(m\Omega^2)}\sqrt{2E_\lambda/(m\Omega^2)} + \Delta E$.

18 Problem Set

18.1 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 $Q_i, \mathbf{r}_i$, and the radiation frequency ω and amplitude ϵ_0.
Solution: The dipole moment is defined as the sum of the product of charges and their corresponding coordinates, as follows: $\mu = \sum_j Q_j \mathbf{r}_j$. Thus, the perturbation under the dipolar approximation is $\hat{W}(t) = -\mu \cdot \mathcal{E}(t)$, with the electric field defined, as follows: $\mathcal{E}(t) = \epsilon_0 e^{i\omega t} + c.c.$ Therefore, $\hat{W}(t) = -\sum_j Q_j \mathbf{r}_j \cdot \epsilon_0 e^{i\omega t} + c.c.$
(B) Expand the time dependent wave function ψ of the charge distribution in terms of the eigenfunctions ϕ_k of the unperturbed charge distribution.
Solution: $\psi(\mathbf{r}, t) = \sum_k c_k(t) e^{-\frac{i}{\hbar}E_k t}\phi_k(\mathbf{r})$, with $c_k(0) = \delta_{jk}$.
(C) Find the expansion coefficients, according to first order time dependent perturbation theory.
Solution: $c_k(t) = -\left(\frac{i}{\hbar}\right)\int_0^t dt' \langle\phi_k|e^{\frac{i}{\hbar}E_k t'}\hat{W}(t')e^{-\frac{i}{\hbar}E_j t'}|\phi_j\rangle = \left(\frac{i}{\hbar}\right)\langle\phi_k|\mu\cdot\epsilon|\phi_j\rangle \int_0^t dt' e^{-\frac{i}{\hbar}(E_{jk}-\hbar\omega)t'} + e^{-\frac{i}{\hbar}(E_{jk}+\hbar\omega)t'}$, with $E_{jk} = E_j - E_k$. So, $c_k(t) = \langle\phi_k|\mu\cdot\epsilon|\phi_j\rangle \left(\left[\frac{e^{-\frac{i}{\hbar}(E_{jk}-\hbar\omega)t}-1}{(-E_{jk}+\hbar\omega)}\right] - \left[\frac{e^{-\frac{i}{\hbar}(E_{jk}+\hbar\omega)t}-1}{(E_{jk}+\hbar\omega)}\right]\right)$.
(D) What physical information is given by the square of the expansion coefficients?
Solution: The square of the expansion coefficient $c_k(t)$ gives the probability of observing the system in state k at time t.
(E) What frequency would be optimum to populate state k? Assume $E_k \geq E_j$.
Solution: The optimum frequency is $\omega = \frac{E_k - E_j}{\hbar}$ since it maximizes $c_k(t)$ by bringing in resonance the second square bracket in the expression of $c_k(t)$.
(F) Which other state could be populated with radiation of the optimum frequency found in term (E)?
Solution: The other state that could be populated by a perturbation with frequency ω is a state k with $E_k < E_j$ such that $E_{jk} = \hbar\omega$ since it would blow up the first square bracket in the expression of $c_k(t)$.
(G) When would the transition $j \to k$ be forbidden?
Solution: A transition would be forbidden when $\langle\phi_k|\mu\cdot\epsilon|\phi_j\rangle = 0$ since $c_k(t) = 0$ for all values of ω.

18.2 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 $t >> \tau$?
Solution: We represent the time dependent wavefunction as a linear combination of eigenfunction ϕ_j of the particle in the box Hamiltonian: $\psi(x,t) = \sum_j c_j(t) e^{-\frac{i}{\hbar}E_j t}\phi_j(x)$, with $c_j(0) = \delta_{j1}$ and $c_k(t) = -\left(\frac{i}{\hbar}\right)\int_{-\infty}^{t} dt' \langle\phi_k| e^{\frac{i}{\hbar}E_k t'} a x e^{-t'^2/\tau} e^{-\frac{i}{\hbar}E_j t'}|\phi_1\rangle$. Therefore, the probability that the particle ends up in the first excited state after a long time $t << \tau$ is $P_{21} = |\lim_{t\to\infty} c_2(t)|^2$, with $\lim_{t\to\infty} c_2(t) = -\left(\frac{i}{\hbar}\right)\langle\phi_2|ax|\phi_1\rangle \int_{-\infty}^{\infty} dt' e^{-t'^2/\tau} e^{-\frac{i}{\hbar}E_{jk}t'} = -\left(\frac{i}{\hbar}\right)\langle\phi_2|ax|\phi_1\rangle\sqrt{\pi\tau}e^{-\frac{E_{jk}^2}{4\hbar^2}\tau}$.
(B) How does that probability depend on τ?

Solution: The probability depends on τ, as follows: $P_{21} = \left(\frac{1}{\hbar^2}\right)|\langle\phi_2|ax|\phi_1\rangle|^2 \pi\tau e^{-\frac{E_{jk}^2}{2\hbar^2}\tau}$.

18.3 Exercise 13

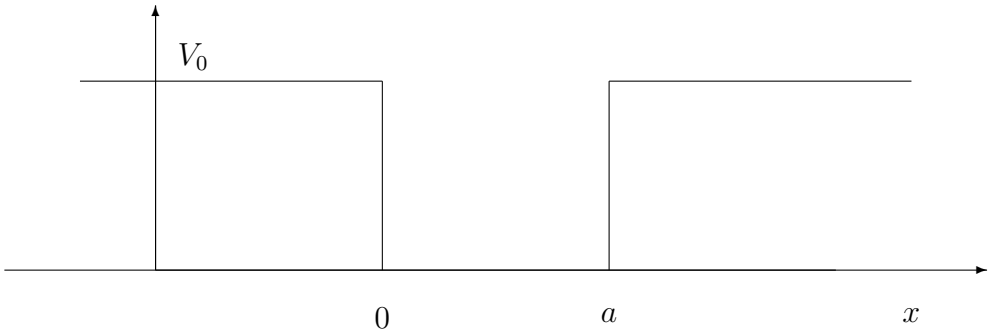


Figure 1

(a) Compute the minimum energy stationary state for a particle in the square well (See Fig.1) by solving the time independent Schrödinger equation.
Solution: A solution can be obtained analytically by solving the problem piecewise (for the regions with $x < 0$, $0 < x < a$, and $x > a$), and enforcing continuity at the boundaries of each piece as described by Vern Lindberg.
(b) What would be the minimum energy absorbed by a particle in the potential well of Fig.1?
Solution: Having found the eigenvalues E_j in (a), the minimum energy absorbed by the particle would be $E = E_2 - E_1$ where E_1 is the ground energy and E_2 is the first excited state.
(c) What would be the minimum energy of the particle in the potential well of Fig.1?
Solution: The minimum energy of the particle would be E_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.
Solution: Having found the eigenvalues E_j and eigenfunctions ϕ_j for the unperturbed potential in (a), the minimum energy minimum energy absorbed by a particle in the potential well shown in Fig. 2 would be $E = E_2 - E_1 + E_2^{(1)} - E_1^{(1)}$, where $E_j^{(1)} = \langle\phi_j|V|\phi_j\rangle$, with $V(x) = \lambda$ for $0.5 < x < 1$ and $V(x) = 0$ otherwise.

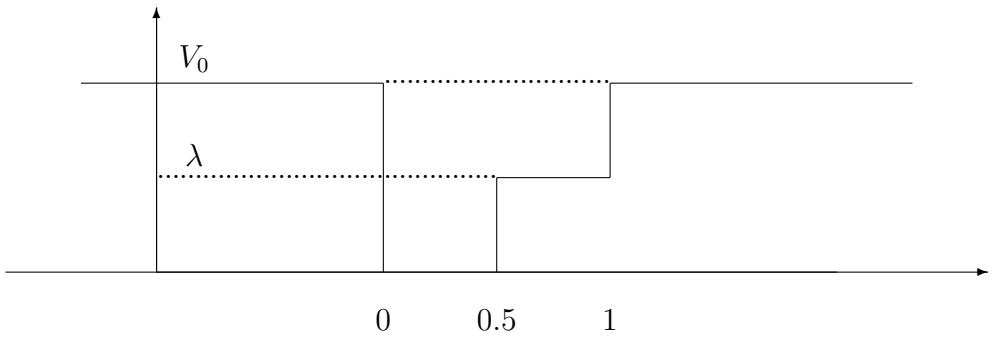


Figure 2

18.4 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.

18.5 Time Evolution Operator

18.5.1 Evolution in the basis of eigenstates:

Show that

$$e^{-\frac{i}{\hbar}\hat{H}t}|\psi_j\rangle = e^{-\frac{i}{\hbar}\hat{E}_j t}|\psi_j\rangle \tag{86}$$

when $|\psi_j\rangle$ is an eigenstate of $\hat{H}$ with eigenvalue E_j.

18.5.2 Trotter expansion of the time evolution operator:

Show that

$$e^{-i\hat{H}\tau} = e^{-iV(\hat{x})\tau/2}e^{-i\hat{p}^2\tau/(2m)}e^{-iV(\hat{x})\tau/2} + O(\tau^3). \tag{87}$$

Hint: Expand the exponential operators in both sides of Eq. (87) and show that the Trotter expansion is accurate to second order in powers of τ.

18.5.3 Numerical Comparison:

Consider a particle of unit mass (m=1) in a box of unit length (L=1), initially prepared in the superposition state

$$\psi(x,0) = \frac{1}{\sqrt{2}}(\phi_1(x) - \phi_2(x))$$

where $\phi_1(x)$ and $\phi_2(x)$ are the eigenstates with eigenvalues E_1 and E_2 obtained by solving the time-independent Schrödinger equation

$$\hat{H}\phi_j(x) = E_j\phi)j(x)$$

Compute the time evolved wavefunction at time $t = 10\tau$ (with $\tau = 1$) by analytically applying the time evolution operator $e^{-i\hat{H}t}$ to $\psi(x, 0)$ term by term. Compare $\psi(x, t)$ to the resulting wavefunction obtained by numerically applying the Trotter expansion of $e^{-i\hat{H}\tau}$ 10 times to the initial superposition state.

19 Adiabatic Approximation

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

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi, \tag{88}$$

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. (88). In fact, it satisfies Eq. (88) *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. (88) we obtain,

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

where,

$$\dot{C}_k = -\sum_n C_n < \Phi_k|\dot{\Phi}_n > e^{-\frac{i}{\hbar}\int_0^t dt'(E_n(t')-E_k(t'))}. \tag{89}$$

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,

$$< \Phi_k|\frac{\partial H}{\partial t}|\Phi_n > + < \Phi_k|H|\dot{\Phi}_n >= \frac{\partial E_k}{\partial t}\delta_{kn} + E_n < \Phi_k|\dot{\Phi}_n >,$$

$$\text{since } < \Phi_k|H|\dot{\Phi}_n > = < \dot{\Phi}_n|H|\Phi_k >^* .$$

Furthermore, if $k \neq n$ then,

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

Substituting this expression into Eq. (89) we obtain,

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

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

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

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

$$C_k \approx \frac{< \Phi_k|\frac{\partial H}{\partial t}|\Phi_j >}{\frac{i}{\hbar}(E_j - E_k)^2}[e^{-\frac{i}{\hbar}(E_j - E_k)t} - e^{-\frac{i}{\hbar}(E_j - E_k)t_0}],$$

$$\text{since} \qquad |e^{-\frac{i}{\hbar}(E_j - E_k)t} - e^{-\frac{i}{\hbar}(E_j - E_k)t_0}| \qquad \leq \qquad 2.$$

Therefore,

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

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

$$\left| < \Phi_k|\frac{\partial H}{\partial t}|\Phi_j > \right| << \frac{(E_j - E_k)^2}{\hbar}, \tag{90}$$

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. (90) 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,

$$\tfrac{\tau}{2\pi}| < \Phi_k|\tfrac{\partial H}{\partial t}|\Phi_j > | << (E_j - E_k).$$

20 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 $|\phi_1>$ and $|\phi_2>$, 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,

$$\hat{H}_0|\phi_1>= E_1|\phi_1>,$$
$$\hat{H}_0|\phi_2>= E_2|\phi_2> .$$

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 $|\phi_1>$ and $|\phi_2>$ are no longer eigenstates of the system.

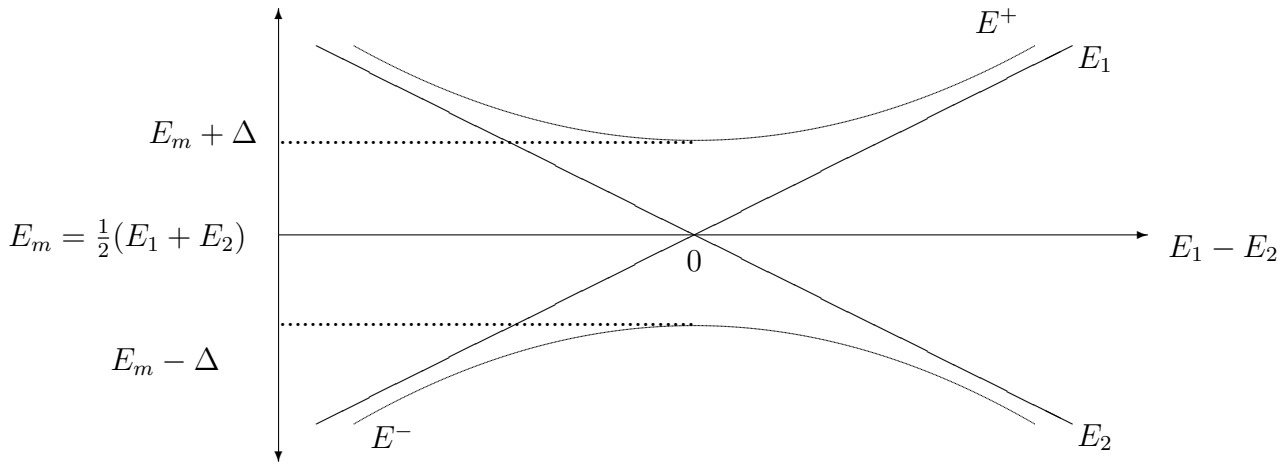
The goal of this section is to compute the eigenstates of the system in the presence of the perturbation W. The eigenvalue problem,

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} C_l^{(1)} \\ C_l^{(2)} \end{pmatrix} = \begin{pmatrix} E_l & 0 \\ 0 & E_l \end{pmatrix} \begin{pmatrix} C_l^{(1)} \\ C_l^{(2)} \end{pmatrix},$$

is solved by finding the roots of the characteristic equation, $(H_{11} - E_l)(H_{22} - E_l) - H_{12}H_{21} = 0$. The values of E_l that satisfy such equation are,

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

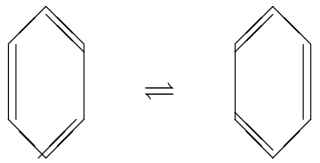
These eigenvalues $E_l^{\pm}$ can be represented as a function of the energy difference $(E_1 - E_2)$, according to the following diagram:



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 $|\psi_{\pm}>= C_{\pm}^{(1)}|\phi_1\rangle + C_{\pm}^{(2)}|\phi_2\rangle$ by solving for $C_{\pm}^{(1)}$ and $C_{\pm}^{(2)}$

from the following equations:
$C_{\pm}^{(1)}(H_{11} - E_{\pm}) + C_{\pm}^{(2)} H_{12} = 0$,
$\sum_{j=1}^{2} C_{\pm}^{(j)*} C_{\pm}^{(j)} = 1$.
We see that in the presence of the perturbation the minimum energy state $|\psi_- >$ is always more stable than the minimum energy state of the unperturbed system.

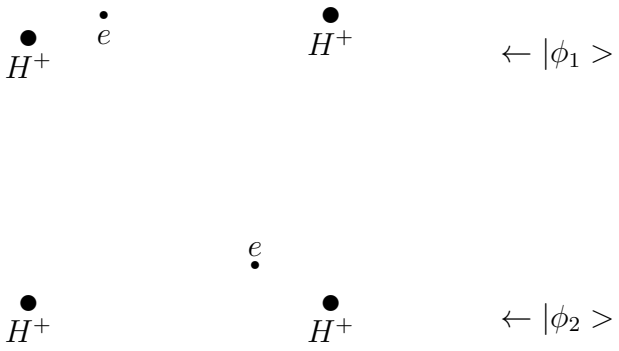
Example 1. Resonance Structure



ϕ_1 ϕ_2 $E_1 = E_2 = E_m$

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 $< \phi_1 | H | \phi_2 > \neq 0$.

Time Evolution

Consider a two level system described by the Hamiltonian $H = H_0 + W$, with $H_0 \mid \phi_1 >= E_1 \mid \phi_1 >$. Assume that the system is initially prepared in state $\mid \psi(0) >= \mid \phi_1 >$. Due to the presence of the perturbation W, state $\mid \phi_1 >$ is not a stationary state. Therefore, the initial state evolves in

time according to the time-dependent Schrödinger Equation,

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

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

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

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

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

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 $|\psi(t)>$ can be written in terms of $|\psi_\pm>$ as follows,

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

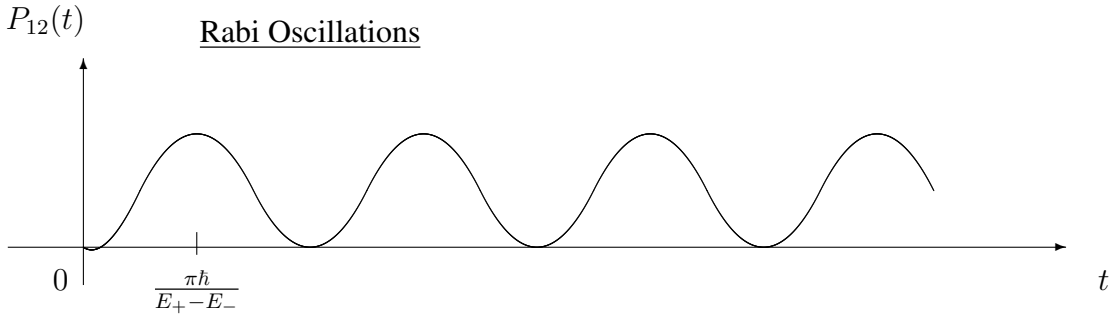
The probability amplitude of finding the system in state $|\phi_2>$ at time t is,

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

which can also be written as follows,

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

where $C_{2\pm} = <\phi_2 \mid \Psi_\pm>$. 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 $|\phi_1>$ and $|\phi_2>$, 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.

21 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)** click

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

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:

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

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

21.1 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 $\hat{H}|\Phi_\nu >= E_\nu|\Phi_\nu >$, then $\hat{N}|\Phi_\nu >= \nu|\Phi_\nu >$, with $\nu = \frac{E_\nu}{\hbar\omega} - \frac{1}{2}$.

Solution: If $\hat{H}|\Phi_\nu >= E_\nu|\Phi_\nu >$, then $(\hat{N}\hbar\omega + \frac{\hbar\omega}{2})|\Phi_\nu >= E_\nu|\Phi_\nu >$ since $\hat{H} = (\hat{N} + 1/2)\hbar\omega$. Therefore, $\hat{N}\hbar\omega|\Phi_\nu >= (E_\nu - \frac{\hbar\omega}{2})|\Phi_\nu >$, and $\hat{N}|\Phi_\nu >= (\frac{E_\nu}{\hbar\omega} - \frac{1}{2})|\Phi_\nu >$.

Theorem I

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

Proof:

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

$< \Phi_\nu|\hat{a}^+\hat{a}|\Phi_\nu > \geq 0$,

$\nu < \Phi_\nu|\Phi_\nu > \geq 0$.

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

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

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

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

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

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

where $A = \sqrt[4]{\frac{m\omega}{\pi\hbar}}$. 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 $\hat{a}|\Phi_\nu >$ is an eigenstate of $\hat{N}$ with eigenvalue equal to (ν -1).

Proof:

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

$$\hat{N}\hat{a}|\Phi_\nu >= (\nu - 1)\hat{a}|\Phi_\nu > . \tag{91}$$

We first observe that,

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

Therefore,

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

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

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

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

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

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

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

and, therefore,

$\hat{N}\hat{a}|\Phi_\nu > -\hat{a}\nu|\Phi_\nu >= -\hat{a}|\Phi_\nu >$, 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,

$$\hat{N}\hat{a}^p|\Phi_\nu >= (\nu - p)\hat{a}^p|\Phi_\nu > . \tag{92}$$

In order to prove Eq. (92) we apply $\hat{a}$ to both sides of Eq. (91):

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

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

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

and

$$\hat{N}\hat{a}^2|\Phi_\nu >= (\nu - 2)\hat{a}^2|\Phi_\nu > . \tag{93}$$

Applying $\hat{a}$ to Eq. (93) we obtain,

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

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

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

Repeating this procedure p times we obtain Eq. (92).

Having proved Eq. (92) we now realize that if $\nu = n$, with n an integer number,

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

when $p > n$. This is because state $\hat{a}^n|\Phi_n >$ is the eigenstate of $\hat{N}$ with eigenvalue equal to zero, i.e., $\hat{a}^n|\Phi_n >= |\Phi_0 >$. Therefore $\hat{a}|\Phi_0 >= \hat{a}^p|\Phi_n >= 0$, when $p > n$. Note that Eq. (93) would contradict Theorem I if ν was not an integer, because starting with a nonzero function $|\Phi_\nu >$ it would be possible to obtain a function $\hat{a}^p|\Phi_\nu >$ different from zero with a negative eigenvalue.

Eigenfunctions of $\hat{N}$

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

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

and

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

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

$$\hat{a}|\Phi_{\nu+1} >= C_{\nu+1}|\Phi_\nu > \tag{94}$$

Applying $\hat{a}^+$ to Eq. (94) we obtain,

$$\hat{N}|\Phi_{\nu+1} >= C_{\nu+1}\hat{a}^+|\Phi_\nu >,$$

$$|\Phi_{\nu+1} >= \frac{C_{\nu+1}}{(\nu+1)}\hat{a}^+|\Phi_\nu >,$$

$$< \Phi_{\nu+1}|\Phi_{\nu+1} >= 1 = \frac{C_{\nu+1}^2}{(\nu+1)^2} < \Phi_\nu|\hat{N} + 1|\Phi_\nu >,$$

$$C_{\nu+1} = \sqrt{\nu+1}.$$

Therefore,

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

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

$$|\Phi_\nu >= \frac{1}{\sqrt{\nu!}}2^{-\nu/2}\left(\hat{x}\sqrt{\frac{m\omega}{\hbar}} - i\frac{\hat{p}}{\sqrt{\hbar\omega m}}\right)^\nu |\Phi_0 >,$$

$$\Phi_\nu(x) = \frac{1}{\sqrt{\nu!}} 2^{-\nu/2} \left(x\sqrt{\frac{m\omega}{\hbar}} - \frac{\hbar}{\sqrt{\hbar\omega m}} \frac{\partial}{\partial x} \right)^\nu \Phi_0(x).$$

For example,

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

$$\Phi_1(x) = \sqrt{\frac{m\omega}{2\hbar}} \underbrace{2x} \sqrt[4]{\frac{m\omega}{\pi\hbar}} e^{-\frac{m\omega}{2\hbar}x^2}.$$

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,

$$\bar{A}_t = < \psi_t | \hat{A} | \psi_t >,$$

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

$$\langle x|\psi_t\rangle = \sum_n C_n e^{-\frac{i}{\hbar}E_n t} \langle x|\Phi_n\rangle, \tag{95}$$

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

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

21.2 Exercise: Analytical versus SOFT Propagation

1. Write a code to simulate the SOFT propagation of a wavepacket bouncing back and forth on a harmonic well, as described by the Hamiltonian $H = p^2/(2 * m) + V(x)$, with $m = 1$ and $V(x) = 0.5 * x^2$ after initializing the state according to the ground state displaced from its equilibrium position, as follows: $\psi(x, 0) = exp(-(x - 1)^2/2)/\sqrt[4]{\pi}$.
2. Compute the first 5 eigenvalues E_n and eigenstates Φ_n with n =1–5 of the harmonic oscillator by using imaginary time propagation.
3. Compare the quantum dynamics simulation based on the SOFT method to the corresponding simulation based on the superposition of the first 5 eigenstates (Eq. (95) on p. 59 of the lecture notes). Note that both methods agree with each other, although the SOFT method by-passes the need of computing the eigenvalues and eigenfunctions of the Hamiltonian.

Solution: The link (http://ursula.chem.yale.edu/∼batista/classes/vvv/HO570.tar) provides a Matlab implementation of the SOFT method to the simulation of evolution of a wavepacket in a harmonic

well in real time, as solved for Exercise 5. In addition, the Matlab code implements the SOFT propagation method to find the lowest 5 eigenstates of the harmonic oscillator by 'evolution' in imaginary time.

22 Problem Set

22.1 Exercise 16

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

Solution: Solving for x from $\hat{a} = \frac{1}{\sqrt{2}}(\tilde{x} + i\tilde{p})$ and $\hat{a}^\dagger = \frac{1}{\sqrt{2}}(\tilde{x} - i\tilde{p})$, with $\tilde{x} = \hat{x}\sqrt{\frac{m\omega}{\hbar}}$ and $\tilde{p} = \hat{p}\sqrt{\frac{1}{\hbar m\omega}}$, we obtain: $\hat{a} + \hat{a}^\dagger = \frac{2}{\sqrt{2}}\hat{x}\sqrt{\frac{m\omega}{\hbar}}$, or $x = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}^\dagger + \hat{a})$. Therefore, $\langle\Phi_{n'}|x|\Phi_n\rangle = \sqrt{\frac{\hbar}{2m\omega}}(\langle\Phi_{n'}|\hat{a}^\dagger|\Phi_n\rangle + \langle\Phi_{n'}|\hat{a}|\Phi_n\rangle)$. Considering that $\hat{a}|\Phi_n\rangle = \sqrt{n}|\Phi_{n-1}\rangle$, and therefore $\hat{a}^\dagger|\Phi_n\rangle = \sqrt{n+1}|\Phi_{n+1}\rangle$, we obtain $\sqrt{\frac{\hbar}{2m\omega}}(\langle\Phi_{n'}|\hat{a}^\dagger|\Phi_n\rangle + \langle\Phi_{n'}|\hat{a}|\Phi_n\rangle) = \sqrt{\frac{\hbar}{2m\omega}}(\sqrt{n+1}\delta_{n',n+1} + \sqrt{n}\delta_{n',n-1})$.

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

Solution: Analogously to (A), we solve for $\hat{p}$ from $\hat{a} = \frac{1}{\sqrt{2}}(\tilde{x} + i\tilde{p})$ and $\hat{a}^\dagger = \frac{1}{\sqrt{2}}(\tilde{x} - i\tilde{p})$, with $\tilde{x} = \hat{x}\sqrt{\frac{m\omega}{\hbar}}$ and $\tilde{p} = \hat{p}\sqrt{\frac{1}{\hbar m\omega}}$, to obtain: $\hat{a} - \hat{a}^\dagger = \frac{2i}{\sqrt{2}}\hat{p}\sqrt{\frac{1}{\hbar m\omega}}$, or $\hat{p} = -i\sqrt{\frac{\hbar m\omega}{2}}(\hat{a} - \hat{a}^\dagger)$. Therefore, $\langle\Phi_{n'}|\hat{p}|\Phi_n\rangle = -i\sqrt{\frac{\hbar m\omega}{2}}(\langle\Phi_{n'}|\hat{a}|\Phi_n\rangle - \langle\Phi_{n'}|\hat{a}^\dagger|\Phi_n\rangle)$. Considering that $\hat{a}|\Phi_n\rangle = \sqrt{n}|\Phi_{n-1}\rangle$, and therefore $\hat{a}^\dagger|\Phi_n\rangle = \sqrt{n+1}|\Phi_{n+1}\rangle$, we obtain $i\sqrt{\frac{\hbar m\omega}{2}}(\langle\Phi_{n'}|\hat{a}|\Phi_n\rangle - \langle\Phi_{n'}|\hat{a}^\dagger|\Phi_n\rangle) = i\sqrt{\frac{\hbar m\omega}{2}}(\sqrt{n}\delta_{n',n-1} - \sqrt{n+1}\delta_{n',n+1})$.

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

Solution: $\hat{a}|\Phi_\nu\rangle = C_\nu|\Phi_{\nu-1}\rangle$. Squaring, we obtain: $\langle\Phi_\nu|\hat{a}^\dagger\hat{a}|\Phi_\nu\rangle = C_\nu^2 = \nu$. Therefore, $C_\nu = \sqrt{\nu}$. In addition, $\hat{a}^\dagger\hat{a}|\Phi_{\nu+1}\rangle = (\nu+1)|\Phi_{\nu+1}\rangle$, or according to the result $\hat{a}\Phi_{\nu+1} = \sqrt{\nu+1}\Phi_\nu$, we obtain $\hat{a}^\dagger\sqrt{\nu+1}|\Phi_\nu\rangle = (\nu+1)|\Phi_{\nu+1}\rangle$. Therefore, $\hat{a}^\dagger|\Phi_\nu\rangle = \sqrt{\nu+1}|\Phi_{\nu+1}\rangle$.

(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.

Solution: The minimum vibrational energy is $E_0 = \frac{\hbar\omega}{2}$. Considering that $k = m_{CD}\omega_{CD}^2 = m_{CH}\omega_{CH}^2$, we obtain $\frac{\omega_{CD}}{\omega_{CH}} = \sqrt{\frac{m_{CH}}{m_{CD}}}$, or $\frac{E_{CD}}{E_{CH}} = \sqrt{\frac{m_{CH}}{m_{CD}}}$, where $\frac{1}{m_{CD}} = \frac{1}{m_C} + \frac{1}{m_D}$, or $m_{CD} = \frac{m_C m_D}{m_C+m_D}$ and $\frac{m_{CH}}{m_{CD}} = \frac{m_C m_H(m_C+m_D)}{m_C m_D(m_C+m_H)} = \frac{(m_C+2m_H)}{2(m_C+m_H)} = \frac{14}{26}$. Therefore, $\frac{E_{CD}}{E_{CH}} = \sqrt{\frac{7}{13}} \approx \sqrt{\frac{1}{2}}$.

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

Solution: Expanding the Morse potential to second order around $R = R_{eq}$, we obtain:

$$V(R) = D_e(1 - \exp(-a(R - R_{eq})))^2 \approx V(R_{eq}) + V'(R_eq)(R - R_{eq}) + \frac{1}{2}V''(R_eq)(R - R_{eq})^2,$$

where $V(R_{eq}) = 0$, $V'(R_{eq}) = D_e 2(1 - exp(-a(R_{eq} - R_{eq})))aexp(-a(R_{eq} - R_{eq})) = 0$, and $V''(R_{eq}) = D_e 2a^2$. Therefore, near the equilibrium postion,

$$V(R) = D_e a^2 (R - R_{eq})^2 = \frac{1}{2} m\omega^2 (R - R_{eq})^2,$$

with $\omega = \sqrt{\frac{2D_e a^2}{m}}$. So, the first excited state has energy $E_1 = \hbar\sqrt{\frac{2D_e a^2}{m}}(\frac{1}{2} + 1)$.

22.2 Exercise 17

Prove that $< \Phi_k|\frac{\partial \hat{H}}{\partial t}|\Phi_n >= (E_n - E_k) < \Phi_k|\frac{\partial}{\partial t}|\Phi_n >$, when $n \neq k$ and $< \Phi_k|\Phi_n >= \delta_{kn}$, with

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

Solution: Starting with $\hat{H}(t)\Phi_j(x,t) = E_j(t)\Phi_j(x,t)$, we compute the derivative with respect to time of both sides of that equation to obtain: $\frac{\partial \hat{H}}{\partial t}|\Phi_j\rangle + \hat{H}|\frac{\partial \Phi_j(x,t)}{\partial t}\rangle = \frac{\partial E_j(t)}{\partial t}|\Phi_j(t)\rangle + E_j(t)|\frac{\partial \Phi_j(t)}{\partial t}\rangle$. Therefore, $\langle\Phi_k|\frac{\partial \hat{H}}{\partial t}|\Phi_j\rangle + \langle\Phi_k|\hat{H}|\frac{\partial \Phi_j(x,t)}{\partial t}\rangle = \frac{\partial E_j(t)}{\partial t}\langle\Phi_k|\Phi_j(t)\rangle + E_j(t)\langle\Phi_k|\frac{\partial \Phi_j(t)}{\partial t}\rangle$, which gives $\langle\Phi_k|\frac{\partial \hat{H}}{\partial t}|\Phi_j\rangle + E_k\langle\Phi_k|\frac{\partial \Phi_j(x,t)}{\partial t}\rangle = E_j(t)\langle\Phi_k|\frac{\partial \Phi_j(t)}{\partial t}\rangle$, when $k \neq j$.

22.3 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 $\psi = R(x)e^{-\frac{i}{\hbar}Et}$.
Solution: According to the continuity equation, $\nabla \cdot j = -\frac{\partial \rho}{\partial t}$, with $\rho = \psi^*\psi$. Since, $\psi = R(x)e^{-\frac{i}{\hbar}Et}$ then $\rho = |R(x)|^2$ and $\frac{\partial \rho}{\partial t} = 0$. Thus, $\nabla \cdot j = 0$.

22.4 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

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

Compute the probability of finding the system in state Φ_2 at time t after suddenly changing the frequency of the oscillator to ω'.
Solution: The time dependent perturbation is $W(t) = \frac{1}{2}m(\omega'^2 - \omega^2)x^2$, when $t > 0$ and $W(t) = 0$, otherwise. Therefore, $c_2(t) = -\frac{i}{\hbar}\int_0^t dt' \langle\phi_2|e^{\frac{i}{\hbar}E_2 t'}\frac{1}{2}m(\omega'^2 - \omega^2)x^2 e^{-\frac{i}{\hbar}E_0 t'}|\phi_0\rangle = -\frac{i}{\hbar}\langle\phi_2|\frac{1}{2}m(\omega'^2 - \omega^2)x^2|\phi_0\rangle \int_0^t dt' e^{\frac{i}{\hbar}(E_2 - E_0)t'} = -\frac{m}{2}(\omega'^2 - \omega^2)\langle\phi_2|x^2|\phi_0\rangle\frac{(e^{\frac{i}{\hbar}E_{20}t} - 1)}{E_{20}}$, or

$$c_2(t) = -\frac{m}{2}(\omega'^2 - \omega^2)\langle\phi_2|x^2|\phi_0\rangle e^{\frac{i}{\hbar}E_{20}\frac{t}{2}}\frac{t}{2\hbar}\frac{(e^{\frac{i}{\hbar}E_{20}\frac{t}{2}} - e^{-\frac{i}{\hbar}E_{20}\frac{t}{2}})}{E_{20}\frac{t}{2\hbar}}.$$

Thus, the probability of finding the system in state Φ_2 at time t is

$$P_2(t) = c_2(t)^* c_2(t) = \frac{m^2}{4}(\omega'^2 - \omega^2)^2 |\langle\phi_2|x^2|\phi_0\rangle|^2 \hbar^{-2} t^2 sin^2(E_{20}t/(2\hbar)).$$

22.5 Exercise 20: Morse Oscillator

Show that the radial component of the two dimensional harmonic oscillator:

$$\begin{aligned} \hat{H}_h &= \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{1}{2}m\omega^2(x^2+y^2), \\ &= \frac{\hbar\omega}{2}\left(\tilde{p}_x^2 + \tilde{p}_y^2 + \tilde{x}^2 + \tilde{y}^2\right), \end{aligned} \tag{96}$$

can be mapped into the Morse oscillator,

$$\hat{H}_m = \frac{p_\rho^2}{2m} + D(e^{-2a\rho} - 2e^{-a\rho}), \tag{97}$$

as discussed by Berrondo, 1987 and Copper, 1993 , with $a\rho = \ln(\frac{2K}{r^2})$, $D = \frac{K^2}{2m}\hbar^2 a^2$, and $r = \sqrt{\tilde{x}^2 + \tilde{y}^2}$, where $\tilde{x} = \hat{x}\sqrt{\frac{m\omega}{\hbar}}$, $\tilde{y} = \hat{y}\sqrt{\frac{m\omega}{\hbar}}$, and $\tilde{p}_x = \hat{p}_x \frac{1}{\sqrt{m\omega\hbar}} = -i\sqrt{\frac{\hbar}{m\omega}}\frac{\partial}{\partial x} = -i\frac{\partial}{\partial\tilde{x}}$.
Solution: Introducing the polar coordinates, $\tilde{x} = rcos(\theta)$ and $\tilde{y} = rsin(\theta)$ and considering that

$$\begin{aligned} \tilde{p}_x &= -i\frac{\partial}{\partial\tilde{x}} = -i\frac{\partial\theta}{\partial\tilde{x}}\frac{\partial}{\partial\theta} - i\frac{\partial r}{\partial\tilde{x}}\frac{\partial}{\partial r}, \\ \tilde{p}_y &= -i\frac{d}{d\tilde{y}} = -i\frac{\partial\theta}{\partial\tilde{y}}\frac{\partial}{\partial\theta} - i\frac{\partial r}{\partial\tilde{y}}\frac{\partial}{\partial r}, \end{aligned} \tag{98}$$

so $r = (\tilde{x}^2 + \tilde{y}^2)^{1/2}$ and $\frac{\partial r}{\partial\tilde{x}} = \frac{\tilde{x}}{(\tilde{x}^2+\tilde{y}^2)^{1/2}} = \frac{\tilde{x}}{r} = cos(\theta)$, $\frac{\partial r}{\partial\tilde{y}} = \frac{\tilde{y}}{r} = sin(\theta)$, and $tan(\theta) = \frac{\tilde{y}}{\tilde{x}}$, so $\frac{1}{cos^2(\theta)}\frac{\partial\theta}{\partial\tilde{y}} = \frac{1}{\tilde{x}}$, or $\frac{\partial\theta}{\partial\tilde{y}} = \frac{cos(\theta)}{r}$ and $\frac{1}{cos^2(\theta)}\frac{\partial\theta}{\partial\tilde{x}} = -\frac{\tilde{y}}{\tilde{x}^2}$ or $\frac{\partial\theta}{\partial\tilde{x}} = -\frac{sin(\theta)}{r}$. Therefore,

$$\begin{aligned} \tilde{p}_x &= -i\frac{\partial}{\partial\tilde{x}} = i\frac{sin(\theta)}{r}\frac{\partial}{\partial\theta} - icos(\theta)\frac{\partial}{\partial r}, \\ \tilde{p}_y &= -i\frac{d}{d\tilde{y}} = -i\frac{cos(\theta)}{r}\frac{\partial}{\partial\theta} - isin(\theta)\frac{\partial}{\partial r}, \end{aligned} \tag{99}$$

and

$$\begin{aligned} \tilde{p}_x^2 &= -\frac{sin^2(\theta)}{r^2}\frac{\partial^2}{\partial\theta^2} - \frac{sin(\theta)cos(\theta)}{r^2}\frac{\partial}{\partial\theta} - cos^2(\theta)\frac{\partial^2}{\partial r^2} - \frac{sin(\theta)cos(\theta)}{r^2}\frac{\partial}{\partial\theta} - \frac{sin^2(\theta)}{r}\frac{\partial}{\partial r} \\ &\quad + 2\frac{sin(\theta)cos(\theta)}{r}\frac{\partial^2}{\partial\theta\partial r} \\ \tilde{p}_y^2 &= -\frac{cos^2(\theta)}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{sin(\theta)cos(\theta)}{r^2}\frac{\partial}{\partial\theta} - \frac{cos^2(\theta)}{r}\frac{\partial}{\partial r} - 2\frac{cos(\theta)sin(\theta)}{r}\frac{\partial^2}{\partial\theta\partial r} \\ &\quad - sin^2(\theta)\frac{\partial^2}{\partial r^2} + \frac{sin(\theta)cos(\theta)}{r^2}\frac{\partial}{\partial\theta}. \end{aligned} \tag{100}$$

Therefore,

$$\tilde{p}_x^2 + \tilde{p}_y^2 = -\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} - \frac{\partial^2}{\partial r^2} - \frac{1}{r}\frac{\partial}{\partial r}, \tag{101}$$

giving the Hamiltonian,

$$\hat{H}_h = \frac{\hbar\omega}{2}\left(-\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} - \frac{\partial^2}{\partial r^2} - \frac{1}{r}\frac{\partial}{\partial r} + r^2\right), \tag{102}$$

and eigenvalue equation

$$\begin{aligned}\hat{H}_h\Phi(\theta)\Psi(r) &= \frac{\hbar\omega}{2}\left(-\frac{\Psi}{r^2}\frac{\partial^2\Phi}{\partial\theta^2} - \Phi\frac{\partial^2\Psi}{\partial r^2} - \frac{\Phi}{r}\frac{\partial\Psi}{\partial r} + r^2\Phi(\theta)\Psi(r)\right), \\ E &= \frac{\hbar\omega}{2}\left(-\frac{1}{\Phi r^2}\frac{\partial^2\Phi}{\partial\theta^2} - \frac{1}{\Psi}\frac{\partial^2\Psi}{\partial r^2} - \frac{1}{\Psi r}\frac{\partial\Psi}{\partial r} + r^2\right).\end{aligned} \tag{103}$$

Therefore,

$$-\frac{\partial^2\Phi}{\partial\theta^2} = l^2\Phi, \tag{104}$$

with $\Phi(\theta) = e^{\pm il\theta}/\sqrt{2\pi}$ and

$$-\frac{\partial^2\Psi}{\partial r^2} - \frac{1}{r}\frac{\partial\Psi}{\partial r} + \left(r^2 + \frac{l^2}{r^2}\right)\Psi = (N+1)\Psi, \tag{105}$$

where N is defined, as follows: $E = \frac{\hbar\omega}{2}(N+1)$.

Equation (105) is the eigenvalue equation for the radial part of the 2-dimensional harmonic oscillator that can be rewritten as the eigenvalue equation for the Morse potential by introducing the change of variables: $r^2 = 2Ke^{-R}$, or $ln(r) = -\frac{R}{2} + \frac{1}{2}ln(2K)$, or $R = -2ln(r) + ln(2K)$, so:

$$\begin{aligned}\frac{\partial}{\partial r} &= \frac{\partial R}{\partial r}\frac{\partial}{\partial R}, \\ &= -\frac{2}{r}\frac{\partial}{\partial R} = -\frac{2}{\sqrt{2K}}e^{R/2}\frac{\partial}{\partial R}, \\ \frac{1}{r}\frac{\partial}{\partial r} &= -\frac{2}{(2K)}e^{R}\frac{\partial}{\partial R}, \\ \frac{\partial^2}{\partial r^2} &= \frac{4}{(2K)}e^{R}\frac{\partial^2}{\partial R^2} + \frac{2}{(2K)}e^{R}\frac{\partial}{\partial R}\end{aligned} \tag{106}$$

Therefore,

$$\begin{aligned} -\frac{2}{K}e^{R}\frac{\partial^2\Psi}{\partial R^2}+\left(2Ke^{-R}+\frac{l^2}{2Ke^{-R}}\right)\Psi &= (N+1)\Psi, \\ -\frac{\partial^2\Psi}{\partial R^2}+\left(K^2e^{-2R}+\frac{l^2}{4}\right)\Psi &= (N+1)\frac{K}{2}e^{-R}\Psi, \\ -\frac{\partial^2\Psi}{\partial R^2}+K^2\left(e^{-2R}-\frac{(N+1)}{2K}e^{-R}\right)\Psi &= -\frac{l^2}{4}\Psi, \\ -\frac{\partial^2\Psi}{\partial R^2}+K^2\left(e^{-2R}-2e^{-R}\right)\Psi &= \epsilon\Psi, \end{aligned} \tag{107}$$

where $\epsilon \equiv -l^2/4$ and $K \equiv (N+1)/4$. Completing squares, we obtain:

$$\begin{aligned} -\frac{\partial^2\Psi}{\partial R^2}+K^2\left(e^{-R}-1\right)^2\Psi &= (\epsilon+K^2)\Psi, \\ -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial R^2}+\frac{D}{a^2}\left(e^{-2R}-2e^{-R}\right)\Psi &= \frac{E}{a^2}\Psi, \end{aligned} \tag{108}$$

where $D/a^2 \equiv K^2\hbar^2/(2m)$, $E/a^2 \equiv (\epsilon+K^2)\hbar^2/(2m)$. Therefore,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial\rho^2}+D\left(e^{-2a\rho}-2e^{-a\rho}\right)\Psi = E\Psi, \tag{109}$$

where $R = a\rho$.

23 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:

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

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

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

These components satisfy the following *commutation relations*

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

23.1 Exercise 21

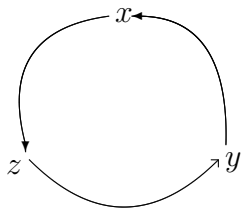
Show that,

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

Hint: Show that, $i\hbar L_x = [L_y, L_z]$.
Solution:

$$\begin{aligned}
L \times L &= \hat{i}L_yL_z - LzL_y - \hat{j}L_xL_z - LzL_x + \hat{k}L_xL_y - LyL_x, \\
&= \hat{i}i\hbar L_x - \hat{j}(-i\hbar)L_y + \hat{k}i\hbar L_z, \\
&= i\hbar(\hat{i}L_x + \hat{j}L_y + \hat{k}L_z), \\
&= i\hbar L.
\end{aligned}$$

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:



$$\Longrightarrow \quad [L_y, L_z] = i\hbar L_x, \qquad [L_z, L_x] = i\hbar L_y.$$

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,

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

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

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,

$$L^2 Y = aY, \tag{110}$$

and

$$L_z Y = bY, \tag{111}$$

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. (111) with L_+ and we obtain,
$L_+ L_z Y = bL_+ Y$.
Then, we substitute $L_+ L_z$ by $[L_+, L_z] + L_z L_+$, 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
$L_+ L_z - L_z L_+ = -i\hbar(L_y - iL_x) = -\hbar L_+$.
Consequently,
$(-\hbar L_+ + L_z L_+)Y = bL_+ Y$,
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:

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

23.2 Exercise 22

Show that:

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

Solution:

$L_- L_z Y = b L_- Y.$

Then, we substitute $L_- L_z$ by $[L_-, L_z] + L_z L_-$, 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

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

Consequently,

$(\hbar L_- + L_z L_-)Y = b L_- Y,$

and,

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

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

... $b - 3\hbar$ $b - 2\hbar$ $b - \hbar$ b $b + \hbar$ $b + 2\hbar$ $b + 3\hbar$ ...

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. (110)).

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 bound:

$$L_z Y_k = b_k Y_k,$$

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

Therefore,

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

$L^2 Y_k = a Y_k,$

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

$\Longrightarrow (a - b_k^2)$ has to be positive:

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

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

In order to avoid contradictions,

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

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

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

Therefore,

$$a - b_{min}^2 + \hbar b_{min} = 0, \tag{112}$$

because,

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

Analogously,

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

$\Downarrow$

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

$$a - b_{max}^2 - \hbar b_{max} = 0. \tag{113}$$

Eqs. (112) and (113) 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,

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

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

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

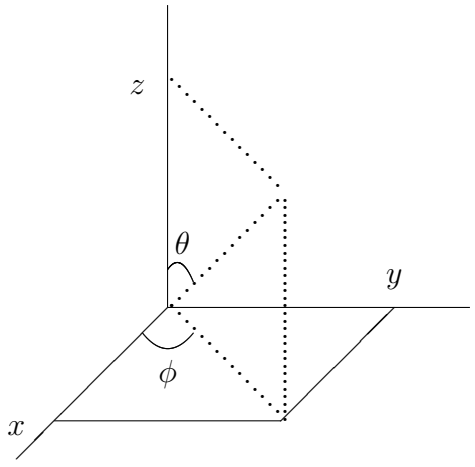
Spherical coordinates are defined as follows,

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

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

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

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



23.3 Exercise 23

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

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

$$\left(\frac{\partial \text{tan}\phi}{\partial x}\right)_{y,z} = \frac{1}{\text{Cos}^2\phi}\left(\frac{\partial \phi}{\partial x}\right)_{y,z} = -\frac{y}{x^2} \Rightarrow \left(\frac{\partial \phi}{\partial x}\right)_{y,z} = -\frac{r\text{Sin}\theta\text{Sin}\phi\text{Cos}^2\phi}{r^2\text{Sin}^2\theta\text{Cos}^2\phi},$$

$$\left(\frac{\partial r}{\partial x}\right)_{y,z} = \frac{1}{2}\frac{2x}{r} \Rightarrow \left(\frac{\partial r}{\partial x}\right)_{y,z} = \frac{r\text{Sin}\theta\text{Cos}\phi}{r}.$$

23.4 Exercise 24

Show that,

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

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

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,

$$L_z Y = bY.$$

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

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

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

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

Therefore, $\boxed{b = m\hbar}$, 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, $A = A(\theta)$:

$$L^2 Y = -\hbar^2\left(\frac{\partial^2 A}{\partial\theta^2} + \frac{\text{Cos}\theta}{\text{Sin}\theta}\frac{\partial A}{\partial\theta} + \frac{1}{\text{Sin}^2\theta}\left(-\frac{b^2}{\hbar^2}\right)A\right)\exp\left(\frac{ib\phi}{\hbar}\right) = aA(\theta)\text{exp}\left(\frac{ib\phi}{\hbar}\right),$$

$$-\hbar^2\left(Sin^2\theta\frac{\partial^2 A}{\partial\theta^2} + \text{Sin}\theta\text{Cos}\theta\frac{\partial A}{\partial\theta} - \frac{b^2}{\hbar^2}A\right) = aA(\theta)\text{Sin}^2\theta. \tag{114}$$

Making the substitution $x = \text{Cos}\theta$ we obtain,

$$(1 - x^2)\frac{d^2 A}{dx^2} - 2x\frac{dA}{dx} + \left(\frac{a}{\hbar^2} - \frac{m^2}{1 - x^2}\right)A = 0. \tag{115}$$

23.5 Exercise 25

Obtain Eq. (115) from Eq. (114).
Solution: Since $x = cos\theta$, then $sin\theta = (1 - x^2)^{1/2}$ and $\partial x/\partial\theta = -sin\theta = -(1 - x^2)^{1/2}$. Therefore,

$$\frac{\partial}{\partial\theta} = \frac{\partial x}{\partial\theta}\frac{\partial}{\partial x},$$
$$= -sin\theta = -(1 - x^2)^{1/2}\frac{\partial}{\partial x},$$

and

$$\begin{aligned}\frac{\partial^2}{\partial\theta^2} &= \frac{\partial x}{\partial\theta}\frac{\partial}{\partial x}\left[-(1-x^2)^{1/2}\frac{\partial}{\partial x}\right], \\ &= -(1-x^2)^{1/2}\frac{\partial}{\partial x}\left[-(1-x^2)^{1/2}\frac{\partial}{\partial x}\right], \\ &= (1-x^2)^{1/2}\left[(1-x^2)^{1/2}\frac{\partial^2}{\partial x^2}+\frac{1}{2}(1-x^2)^{-1/2}(-2x)\frac{\partial}{\partial x}\right], \\ &= (1-x^2)\frac{\partial^2}{\partial x^2}-x\frac{\partial}{\partial x}.\end{aligned}$$

In addition,

$$\begin{aligned}sin\theta cos\theta\frac{\partial}{\partial\theta} &= x(1-x^2)^{1/2}\frac{\partial}{\partial\theta}, \\ &= -x(1-x^2)\frac{\partial}{\partial x}.\end{aligned}$$

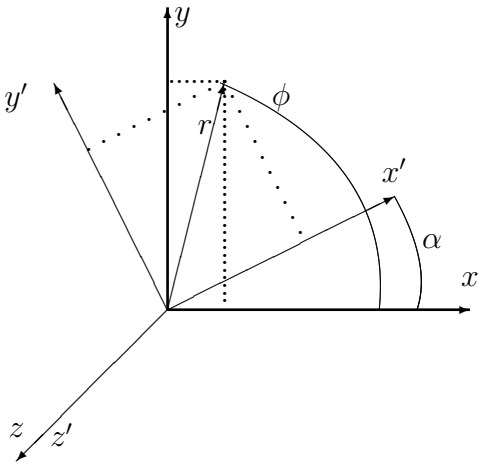
Eq. (115) is the *associated Legendre equation*, whose solutions exist only for $a = \hbar^2 l(l+1)$, and $b = -l\hbar, (-l+1)\hbar, ..., l\hbar$ (i.e., the quantum number l is an *integer* greater or equal to zero, with $|m| \leq l$). The solutions of the associated Legendre equations are the *associated Legendre polynomials* , $A(l,m) = P_l^{|m|}(\text{Cos}\theta)$,
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,

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

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,

$$\boxed{\bar{r}' = R(\alpha, z)\bar{r}}, \tag{116}$$

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

$$\alpha: \text{ Angle}, \qquad z: \text{Rotation axis}$$

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

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:

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

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

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 $n \to \infty$, and $\delta \to 0$.

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

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:

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

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

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

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, $\bar{r}' = R\bar{r}$, whenever the operator associated with the coordinate transformation commutes with the Hamiltonian, $[\hat{P}_R, H] = 0$.

24 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 $\boxed{S \times S = i\hbar S}$. 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. 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 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,

$$\sum_{m_s=-1/2}^{1/2} |\alpha(m_s)|^2 = 1, \qquad \sum_{m_s=-1/2}^{1/2} |\beta(m_s)|^2 = 1, \tag{117}$$

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:

$$\sum_{m_s=-1/2}^{1/2} \alpha^*(m_s)\beta(m_s) = 0. \tag{118}$$

In order to satisfy the conditions imposed by Eqs. (117) and (118),

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

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. (117) we obtain,

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

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,

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

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

$|c|^2 = \sum_{m_s} \beta^* S_- S_+ \beta$,
$|c|^2 = \sum_{m_s} \beta^* (S^2 - S_z^2 - \hbar S_z)\beta$,
$|c|^2 = \sum_{m_s} \beta^* (\frac{3}{4}\hbar^2 - \frac{\hbar^2}{4} + \frac{\hbar^2}{2})\beta$,
$|c|^2 = \hbar^2$.
Since the phase of c is arbitrary, we can choose c=$\hbar$.
Similarly, we obtain $\boxed{S_-\alpha = \hbar\beta}$.
Since α is the eigenfunction with highest eigenvalue, the operator S_+ acting on it must annihilate it as follows,

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

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

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

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

$<\lvert S_x\rvert>$	α	β
α	0	$\hbar/2$
β	$\hbar/2$	0

$<\lvert S_y\rvert>$	α	β
α	0	$-i\hbar/2$
β	$+i\hbar/2$	0

$<\lvert S_z\rvert>$	α	β
α	$\hbar/2$	0
β	0	$-\hbar/2$

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

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

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

24.1 Exercise 26

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:

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

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

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

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 $\begin{pmatrix} \alpha_+ \\ \alpha_- \end{pmatrix}$.

24.2 Exercise 27

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

24.3 Exercise 28

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:

$$\psi_j^m = \sum_{l_1,m_1,l_2,m_2} \underbrace{C(jm, l_1 m_1\ l_2 m_2)}\, \phi_{l_1}^{m_1} \phi_{l_2}^{m_2},$$

Clebsch-Gordan Coefficients

where,

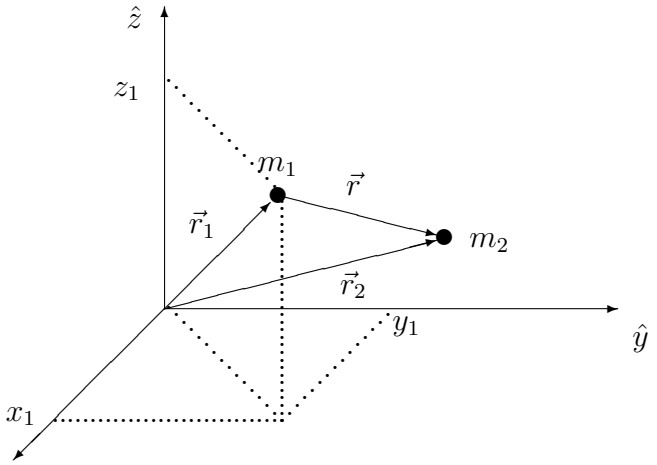
$$J^2 \psi_{jm} = \hbar^2 j(j+1)\psi_{jm},$$
$$J_z \psi_{jm} = \hbar m \psi_{jm}.$$

24.4 Exercise 29

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

25 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 $|\bar{r}| = \sqrt{x^2 + y^2 + z^2}$, 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,

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

we obtain,

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

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,

$$-\frac{\hbar^2}{2M}\frac{1}{\psi_M}{\nabla_R}^2\psi_M = E_M, \tag{119}$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{\psi_\mu}{\nabla_r}^2\psi_\mu + V(|\vec{r}|) = E_\mu, \qquad \text{with} \quad E_M + E_\mu = E. \tag{120}$$

Eq. (120) is the Schrödinger equation for a free particle with mass M. The solution of such equation is,

$$\psi_M(R) = (2\pi\hbar)^{-3/2}e^{i\bar{k}\bar{R}}, \quad \text{where } \frac{|\bar{k}|^2\hbar^2}{2M} = E_M. \tag{121}$$

According to Eq. (121), the energy E_μ is found by solving the equation,

$$\boxed{-\frac{\hbar^2}{2\mu}{\nabla_r}^2\psi_\mu + V(|\bar{r}|)\psi_\mu = E_\mu\psi_\mu}. \tag{122}$$

Equations ((121)) and ((122)) have separated the problem of two particles interacting according to a central potential $V(|\bar{r}_2 - \bar{r}_1|)$ 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. (122), 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.

25.1 Exercise 30

Prove that the Laplacian ∇^2 can written in spherical coordinates as follows,

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

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:

$\hat{H}\psi_\mu = E_\mu\psi_\mu$,
$\hat{L}^2\psi_\mu = \hbar^2 l(l+1)\psi_\mu, \qquad l = 0, 1, 2, ...$
$\hat{L}_z\psi_\mu = \hbar m\psi_\mu, \qquad m = -l, -l+1, ..., l.$

Substituting these results into Eq. (122) 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,

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r}\right) + \frac{\hbar^2}{2\mu r^2}l(l+1)R + V(|\bar{r}|)R = E_\mu R. \tag{123}$$

26 Two-Particle Rigid-Rotor

The *rigid-rotor* is a system of two particles for which the distance between them $|\bar{r}| = d$ is constant. The Hamiltonian of the system is described by Eq. (123), 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.

26.1 Exercise 31

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:

$$E_\mu = \frac{\hbar^2}{2I} l(l+1), \text{ with } l = 0, 1, 2, ... \tag{124}$$

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

27 Problem Set

27.1 Exercise 32

32.1. Solve problems 6.5 and 6.6 of reference 1.
32.2. Prove that the angular momentum operator $L = r \times p$ is hermitian.

27.2 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.

27.3 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 $< \psi_n | [\hat{Q}, \hat{H}] | \psi_k >= 0$, for any arbitrary operator $\hat{Q}$, when $n = k$.

27.4 Exercise 35

Prove that,

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

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

27.5 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 $L^2 Y_l^m = \hbar^2 l(l+1)Y_l^m$.

27.6 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 $H_{jk} =< \psi_j|\hat{H}|\psi_k >$. 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 $t >> \tau$.

28 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 $m_e << m_n$. 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,

$$\hat{H}^{el}\psi_{el} = E_{el}\psi_{el}. \tag{125}$$

Eq. (125) is the eigenvalue problem of a one particle central-potential. We consider the factorizable solution,

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

where $R(r)$ satisfies the equation,

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} - \frac{\hbar^2}{\hbar^2 r^2}l(l+1)R\right] - \frac{Ze^2 R}{r} = ER. \tag{126}$$

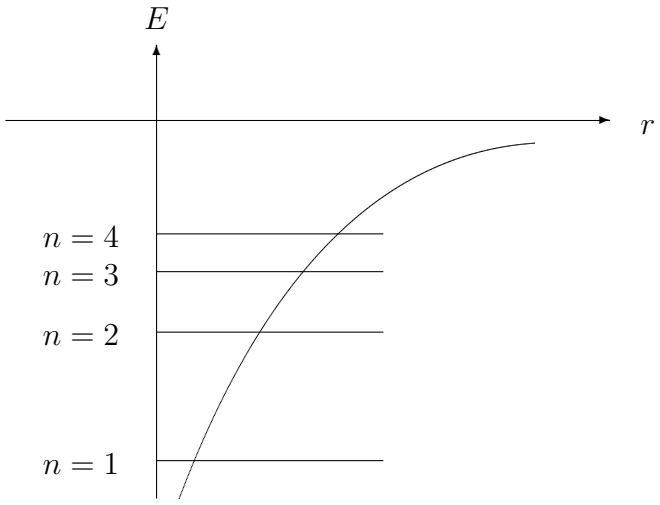
This equation could be solved by first transforming it into the *associated Laguerre equation*, for which solutions are well-known. Here, however, we limit the presentation to note that Eq. (126) has solutions that are finite, single valued and square integrable only when

$$E = -\frac{Z^2\mu e^4}{2\hbar^2 n^2}, \quad \text{or} \quad E = -\frac{Z^2 e^2}{2an^2}, \tag{127}$$

where $n = 1, 2, 3, ...$, 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

$$\bar{\omega} = \frac{E_2 - E_1}{hc} = -\frac{Z^2\mu e^4}{hc2\hbar^2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right).$$

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, ...
l=0, 1, 2, ... n-1 } these are n states
m=-l, -l+1, ..., 0, 1, 2, ...l } these are 2 l + 1 states

28.1 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* and $R_{nl}(r)$ are the *Laguerre associated polynomials*,

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

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,

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

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

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

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

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

ψ_{200} ψ_{210}, ψ_{211} ψ_{21-1},

28.2 Exercise 39

Show that,

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

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

28.3 Exercise 40

Compute the ionization energy of He^+.

28.4 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 $\omega = -\beta\vec{L}.\vec{B}$, 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,

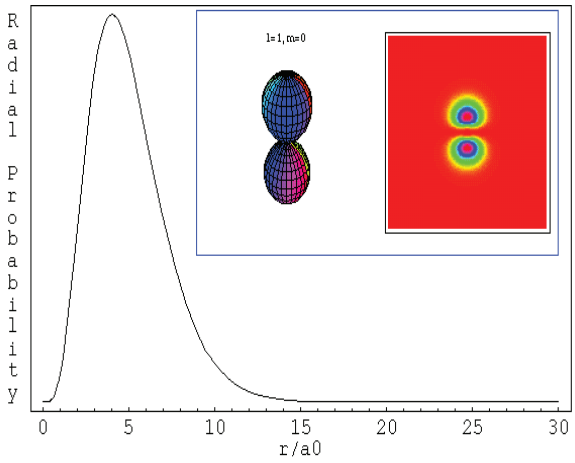
$$P = R^*(r)R(r)Y_l^m(\theta)^*Y_l^m(\theta)r^2\text{sin}\theta dr d\theta d\phi.$$

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

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

where $\int_0^\pi d\theta \int_0^{2\pi} d\phi Y_l^m(\theta)^*Y_l^m(\theta)\text{sin}\theta = 1$. For example, the radial probability for m=0 and l=1, can be visualized as follows:

Pictures of atomic orbitals with n $\leq$ 10 are available here .



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 $l = 1$,

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

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

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

are real and mutually orthogonal eigenfunctions.

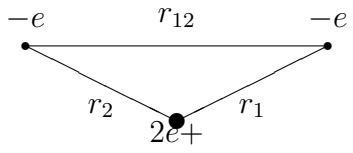
Function ψ_{2P_z} is zero in the xy plane, positive above such plane, and negative below it. Functions ψ_{2P_x} and ψ_{2P_y} are zero at the zy and xz planes, respectively. $\psi_{2P_{-1}}$ and ψ_{2P_1} are eigenfunctions of $\hat{L}^2$ with eigenvalue $2\hbar^2$. However, since $\psi_{2P_{-1}}$ and 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.

28.5 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 $\hat{V}$.

29 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,

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

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,

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

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

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

and the eigenvalues are,

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

Exercise 43 Prove that,

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

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,

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

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 $< \tilde{\psi} | \hat{H} | \tilde{\psi} >$ is always higher than the ground state energy. Therefore, the optimum coefficient z' minimizes the expectation value,

$$\tilde{E}(z') = < \tilde{\psi} | \hat{H} | \tilde{\psi} >, \qquad \text{where}$$

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

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,

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

30 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:

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

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.,

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

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.

31 Pauli Exclusion Principle

Pauli observed that relativistic quantum field theory requires that particles with *half-integer* spin (s=1/2, 3/2, ...) must have *antisymmetric* wave functions and particles with *integer* spin (s=0, 1, ...) 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,

$$\psi = 1S(1)1S(2)\frac{1}{\sqrt{2}} \left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]. \tag{128}$$

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

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

32 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,

$$\chi = \frac{1}{\sqrt{6}} \begin{vmatrix} \alpha(1) & \beta(1) & \alpha(1) \\ \alpha(2) & \beta(2) & \alpha(2) \\ \alpha(3) & \beta(3) & \alpha(3) \end{vmatrix}. \tag{129}$$

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:

$$\psi^{(0)} = 1S(1)\ 1S(2)\ 1S(3) \tag{130}$$

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,

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

where ψ is the product of hydrogenlike functions of Eq. (130).

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),

$$\psi^{(0)} = \frac{1}{\sqrt{6}} \begin{vmatrix} 1S(1)\alpha(1) & 1S(1)\beta(1) & 2S(1)\alpha(1) \\ 1S(2)\alpha(2) & 1S(2)\beta(2) & 2S(2)\alpha(2) \\ 1S(3)\alpha(3) & 1S(3)\beta(3) & 2S(3)\alpha(3) \end{vmatrix}, \tag{131}$$

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. (131) 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.

32.1 Exercise 44

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

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

and,

$$E^{(1)} = 2 < 1S(1)2S(2)|\frac{e^2}{r_{12}}|1S(1)2S(2) > + < 1S(1)1S(2)|\frac{e^2}{r_{12}}|1S(1)1S(2) >$$

$$- < 1S(1)2S(2)|\frac{e^2}{r_{12}}|2S(1)1S(2) > .$$

33 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,

$$\hat{H}_{SO} = \frac{1}{2m_e c^2}\frac{1}{r}\left(\frac{\partial V}{\partial r}\right)\hat{L}\cdot\hat{S} = \xi\hat{L}\cdot\hat{S}, \tag{132}$$

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. (132) 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 for each electron i in the total electric field of electrons and nuclear charges. Then, we can compute the sum over *all* electrons as follows,

$$\hat{H}_{SO} \approx \frac{1}{2m_e c^2} \sum_i \frac{1}{r_i} \frac{\partial V_i}{\partial r_i} \hat{L}_i \cdot \hat{S}_i = \sum_i \xi_i \hat{L}_i \cdot \hat{S}_i. \tag{133}$$

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 $\mid \Psi\rangle$ for a one-electron atom is,

$$E^{(1)}_{S.O.} \approx \langle \Psi \mid \xi \hat{L} \cdot \hat{S} \mid \Psi \rangle. \tag{134}$$

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,

$$L \cdot S|\psi >= \frac{1}{2}\hbar^2(J(J+1) - L(L+1) - S(S+1))|\psi > .$$

Therefore,

$$E_{S.O.} \approx \frac{1}{2}\hbar^2 < \xi > [J(J+1) - L(L+1) - S(S+1)] .$$

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, ..., L-S).

The spin orbit interaction is, therefore, responsible for the splitting of spectroscopic lines in atomic spectra.

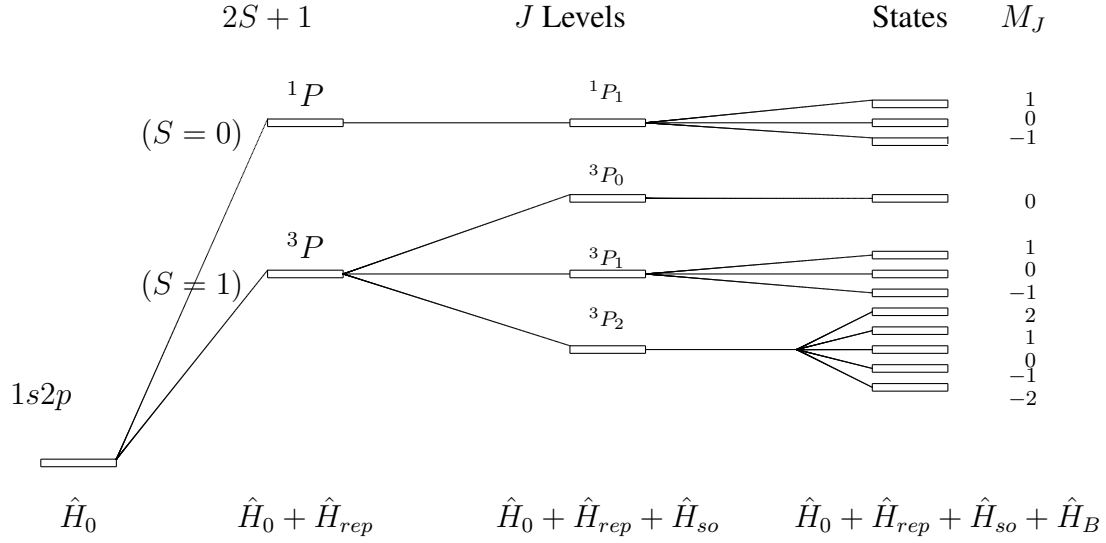
It is possible to remove the degeneracy of energy levels by applying an external magnetic field that perturbs the system as follows, $H_B = -m \cdot B$, where $m = m_L + m_S$, with $m_L = -\frac{e}{2m_e}L$, and $m_S = -\frac{e}{m_e}S$. The external perturbation is, therefore, described by the following 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:

$$E_B = -\frac{e}{2m_e} B(\hbar M_J + < S_z >) = ABM_J,$$

where $< S_z >= \hbar M_J \frac{J(J+1)-L(L+1)+S(S+1)}{2J(J+1)}$ and A is a proportionality constant. Therefore, the perturbation of an external magnetic field splits the 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:



33.1 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 $E_B =< \psi | \hat{H}_B | \psi >= \beta_e B M_J g$, with $g = 1 + \frac{J(J+1)-L(L+1)+S(S+1)}{2J(J+1)}$.

34 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.,

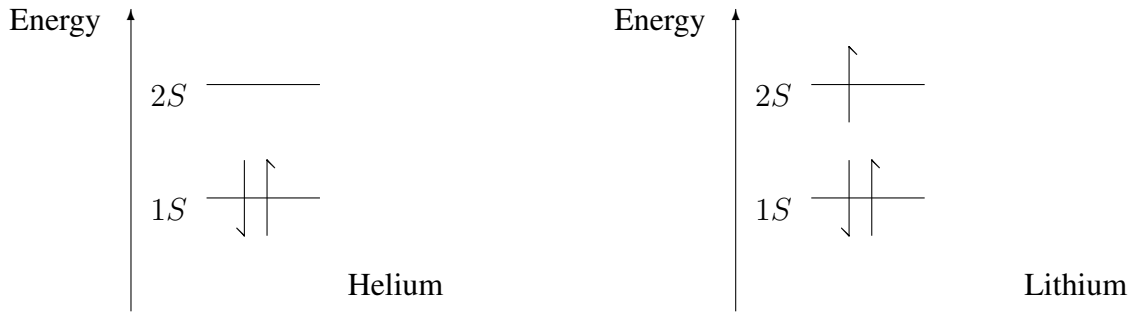
$$\psi_{He}^{gr} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1S(1)\alpha(1) & 1S(1)\beta(1) \\ 1S(2)\alpha(2) & 1S(2)\beta(2) \end{vmatrix} = 1S(1)1S(2)\frac{1}{\sqrt{2}} \left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right],$$

$$\psi_{Li}^{gr} = \frac{1}{\sqrt{6}} \begin{vmatrix} 1S(1)\alpha(1) & 1S(1)\beta(1) & 2S(1)\alpha(1) \\ 1S(2)\alpha(2) & 1S(2)\beta(2) & 2S(2)\alpha(2) \\ 1S(3)\alpha(3) & 1S(3)\beta(3) & 2S(3)\alpha(3) \end{vmatrix},$$

with zeroth order energies,

$$E_{He}^{(0)} = 2E(1S), \qquad \text{and} \qquad E_{Li}^{(0)} = 2E(1S) + E(2S),$$

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,

$$\psi^{gr} = \frac{1}{\sqrt{6}} \begin{vmatrix} 1S(1)\alpha(1) & 1S(1)\beta(1) & 2S(1)\alpha(1) \\ 1S(2)\alpha(2) & 1S(2)\beta(2) & 2S(2)\alpha(2) \\ 1S(3)\alpha(3) & 1S(3)\beta(3) & 2S(3)\alpha(3) \end{vmatrix}, \tag{135}$$

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, $E_n = -\frac{z^2e^2}{2an^2}$, 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}.

34.1 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 $J_{\phi_1,\phi_2} =< \phi_1^{(i)}\phi_2^{(j)}|\frac{e}{r_{ij}}|\phi_1^{(i)}\phi_2^{(j)} >\equiv$ Coulomb Intergral,
and $K_{\phi_1,\phi_2} =< \phi_1^{(i)}\phi_2^{(j)}|\frac{e}{r_{ij}}|\phi_2^{(i)}\phi_1^{(j)} >\equiv$ Exchange Integral.

34.2 Exercise 47

Use Hund's Rules to predict that the ground states of nitrogen, oxygen and fluorine atoms are ${}^4S$, ${}^3P$ and ${}^2P$, respectively.

35 Problem Set

35.1 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,

$$\phi(x) = \sqrt[4]{\frac{\alpha}{\pi}}\text{exp}^{-\frac{\alpha}{2}x^2}.$$

From tables,

$$\int_{-\infty}^{\infty} dx x^4 e^{-\alpha x^2} = \frac{3}{4\alpha^2}\sqrt{\frac{\pi}{\alpha}};\ \int_{-\infty}^{\infty} dx e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}};\ \int_{-\infty}^{\infty} dx x^2 e^{-\alpha x^2} = \frac{1}{2\alpha}\sqrt{\frac{\pi}{\alpha}}.$$

35.2 Exercise 49

Compute the eigenvalues and normalized eigenvectors of $\sigma = \sigma_y + \sigma_z$, where,

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

35.3 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?

35.4 Exercise 51

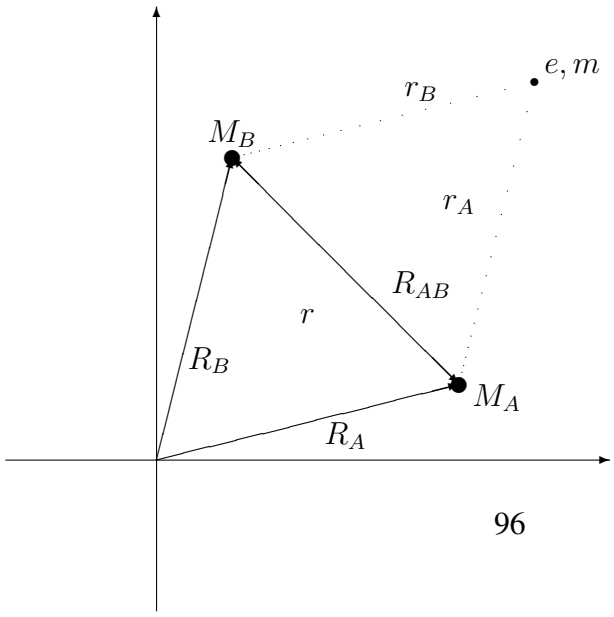
Consider a spin 1/2 represented by the spinor,

$$\chi = \begin{pmatrix} \text{Cos}\alpha \\ \text{sin}\alpha \quad e^{i\beta} \end{pmatrix}.$$

What is the probability that a measurement of S_y would yield the value $-\frac{\hbar}{2}$ when the spin is described by χ?

36 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)**

$$\hat{H} = -\frac{\hbar^2}{2M_A}\nabla^2_{R_A} - \frac{\hbar^2}{2M_B}\nabla^2_{R_B} + H_{el}, \tag{136}$$

where,

$$\hat{H}_{el} = -\frac{\hbar^2}{2m}\nabla^2_r - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R_{AB}}. \tag{137}$$

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. (137) 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,

$$\mid \Psi >= C_A \mid \phi_A > + C_B \mid \phi_B >,$$

where $\mid \phi_A >$, and $\mid \phi_B >$, 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,

$$< E >= \frac{<\psi|\hat{H'}_{el}|\psi>}{<\psi|\psi>} = \frac{C_A^2 H_{AA} + 2C_A C_B H_{AB} + C_B^2 H_{BB}}{C_A^2 S_{AA} + 2C_A C_B S_{AB} + C_B^2 S_{BB}},$$

with respect to C_A and C_B. Here, $H_{jk} =< \phi_j|\hat{H'}_{el}|\phi_k >$, $S_{jk} =< \phi_j|\phi_k >$, and

$$\hat{H'}_{el} = -\frac{\hbar^2}{2m}\nabla^2_r - \frac{e^2}{r_A} - \frac{e^2}{r_B}.$$

36.1 Exercise 52

Show that the condition,

$\left(\frac{\partial<E>}{\partial C_A}\right)_{C_B} = 0$ implies $(H_{AA} - < E > S_{AA})C_A + (H_{AB} - < E > S_{AB})C_B = 0$,

and

$\left(\frac{\partial<E>}{\partial C_B}\right)_{C_A} = 0$ implies $(H_{AB} - < E > S_{AB})C_A + (H_{BB} - < E > S_{BB})C_B = 0$,

with $S_{jj} = \langle\phi_j|\phi_j\rangle = 1$.

In matrix form, these equations (called *secular equations*) can be written in compact form, as follows:

$$(\mathbf{H} - \mathbf{ES})\mathbf{C} = 0, \tag{138}$$

where $\mathbf{H}$ is the Hamiltonian matrix, $\mathbf{C}$ is the matrix of column eigenvectors, $\mathbf{E}$ is the diagonal matrix of eigenvalues, and $\mathbf{S}$ is the overlap matrix.

The secular equations have a nontrivial solution (*i.e.*, a solution different from the trivial solution $C_A = 0$, $C_B = 0$), when the determinant of $(\mathbf{H} - \mathbf{ES})$ (*i.e.*, the so-called *secular determinant*) vanishes:

$$\begin{vmatrix} H_{AA} - < E > & H_{AB} - S_{AB} < E > \\ H_{BA} - S_{BA} < E > & H_{BB} - < E > \end{vmatrix} = 0.$$

Since $\mid \phi_A >$ and $\mid \phi_B >$ are 1S orbitals, $H_{AA} = H_{BB}$, and $S_{AB} = S_{BA} = S$. Therefore,

$$(H_{AA} - < E >)^2 - (H_{AB} - S < E >)^2 = 0,$$

and

$$E_{\pm} = \frac{H_{AA} \pm H_{AB}}{1 \pm S}.$$

Substituting $< E >_+$ in the secular equations we obtain,

$$C_{A\pm} = \pm C_{B\pm}.$$

Therefore,

$\psi_+ = C_{A+}(\phi_A + \phi_B)$, where $C_{A+} = \frac{1}{\sqrt{2+2S}}$,

$\psi_- = C_{A-}(\phi_A - \phi_B)$, 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 $\mid \Psi >$ 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 $< E >_\pm$ 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:

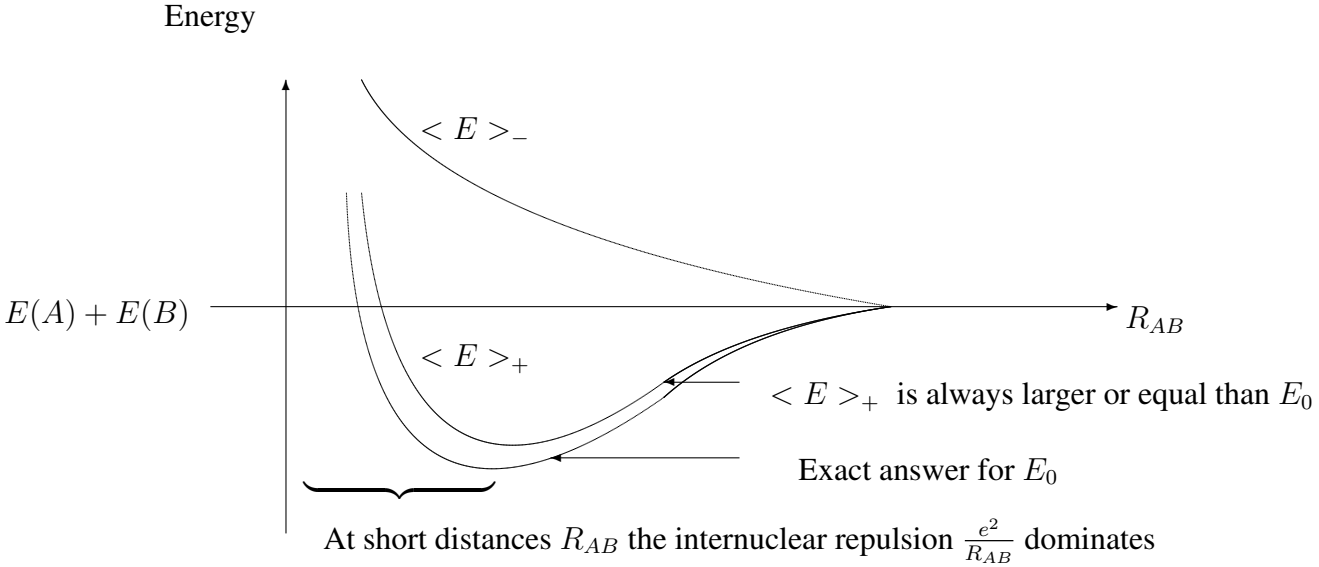
$$H_{AA} = \int d\tau \phi_A^* \left[-\frac{\hbar^2}{2m}\nabla_r^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} \right] \phi_A = E_{1S}(H) - \int d\tau \phi_A^* \frac{e^2}{r_B} \phi_A. \tag{139}$$

As the nuclei A and B are brought closer together, the second term in Eq. (139) (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,

$$H_{AB} = \int d\tau \phi_A^* \left(-\frac{\hbar^2}{2m} \nabla_r^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} \right) \phi_B, \tag{140}$$

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 $< E >_\pm$ can be represented as a function of R_{AB} by the following diagram:



Note that $< E >_+$ is lower than $< E >_-$ 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,

$$\phi_{A/B} = \frac{(\frac{\xi}{2a})^{3/2}}{\sqrt{\pi}} e^{-\frac{\xi r_{A/B}}{2a}}. \tag{141}$$

Such variational correction of the effective nuclear charge is known as *scaling*.

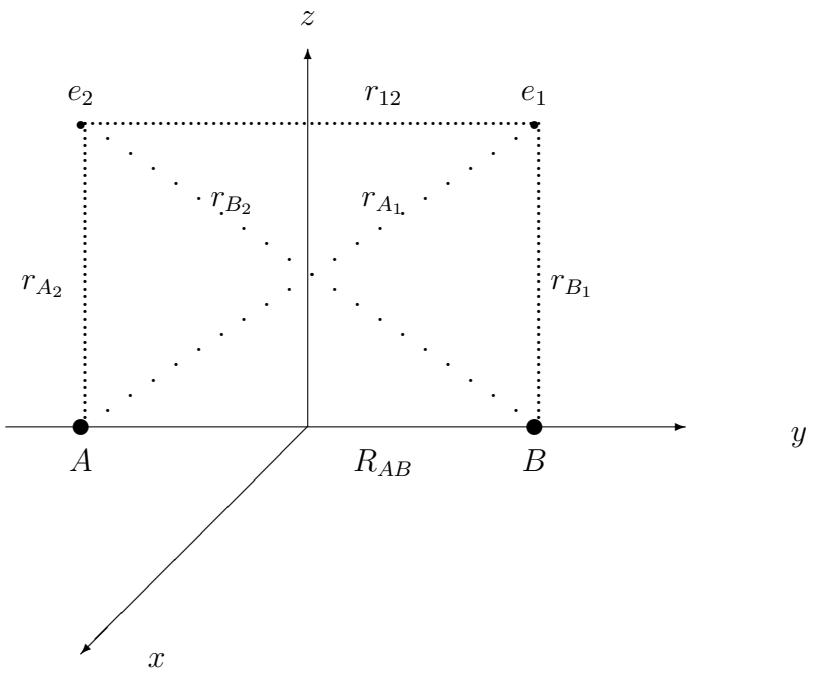
36.2 Exercise 53

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.

37 H_2 Molecule

The H_2 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,

$$\hat{H} = -\frac{\hbar^2}{2M_A}\nabla^2_{R_A} - \frac{\hbar^2}{2M_B}\nabla^2_{R_B} + \hat{H}_{el},$$

where

$$\hat{H}_{el} = -\frac{\hbar^2}{2m}\nabla^2_1 - \frac{e^2}{r_{A1}} - \frac{e^2}{r_{B1}} - \frac{\hbar^2}{2m}\nabla^2_2 - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B2}} + \frac{e^2}{r_{12}} + \frac{e^2}{R_{AB}}.$$

In analogy to the He atom, it is possible to identify one-electron Hamiltonians (i.e., associated with electrons 1 and 2),

$$H_2^+(1) = -\frac{\hbar^2}{2m}\nabla^2_1 - \frac{e^2}{r_{A1}} - \frac{e^2}{r_{B1}},$$

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,

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

as the product

$$\mid \psi >= A \mid \Phi_1 > \mid \Phi_2 >, \tag{142}$$

where $\mid \Phi_1 >$ and $\mid \phi_2 >$ are eigenstates of the H_2^+ Hamiltonian and A is the anti-symmetrizing spin wave function,

$$A = \frac{1}{N\sqrt{2}} \left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right].$$

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,

$$E = 2E_{H_2^+}(R_{AB}) + < \psi | \frac{e^2}{r_{12}} | \psi > - \frac{e^2}{R_{AB}}. \tag{143}$$

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. (143), we obtain the minimum energy of the H_2 molecule.
The complete ground state of H_2 is described as follows,

$$\psi = \frac{1}{N\sqrt{2}} \left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \left[1S_A(1)1S_A(2) + 1S_A(1)1S_B(2) + 1S_B(1)1S_A(2) + 1S_B(1)1S_B(2)\right], \tag{144}$$

where N is a normalization factor, obtained by substituting $\mid \Phi_1 >$ and $\mid \Phi_2 >$ in Eq. (144), by the ground state wave function of H_2^+,

$$\Phi_j = \frac{1}{\sqrt{N}} \left[1S_A(j) + 1S_B(j)\right]. \tag{145}$$

According to Eq. (145), 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. (145), predicts the same probability for ionic and covalent configurations, $H_A^+H_B^-$, $H_A^-\ H_B^+$, and H_AH_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.

37.1 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,

$$\psi_{HL} = \frac{1}{N'\sqrt{2}} \left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \left[1S_A(1)1S_B(2) + 1S_B(1)1S_A(2)\right].$$

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.

37.2 Exercise 54

Prove that, according to the HL approach,

$$E = \frac{J + K}{1 + S^2},$$

with

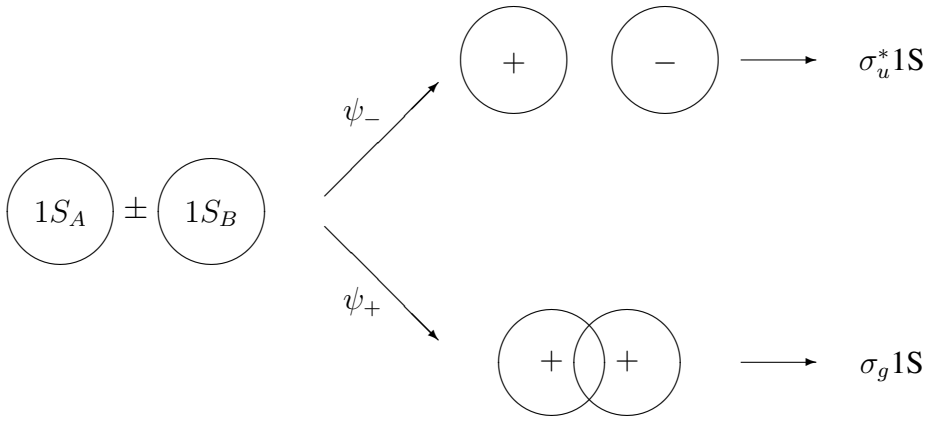
$$J =< 1S_A(1)1S_B(2)|H|1S_A(1)1S_B(2) >,$$

and

$$K =< 1S_A(1)1S_B(2)|H|1S_B(1)1S_A(2) > .$$

38 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:

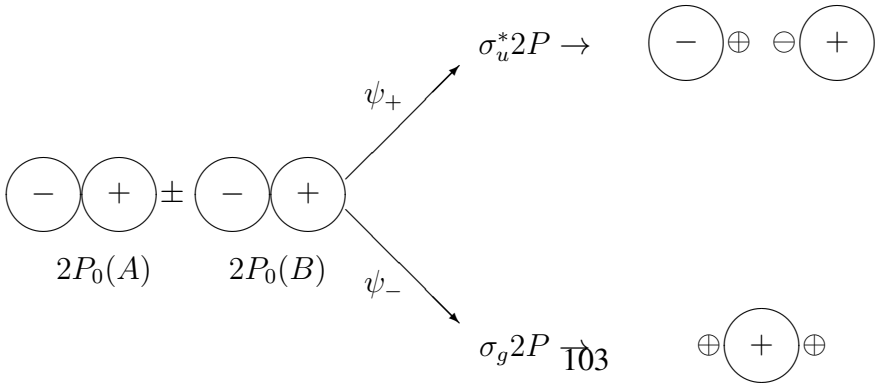
1. Nature of the atomic orbitals in the linear combination (e.g., 1S orbitals in the study of the H_2^+ molecules).

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:

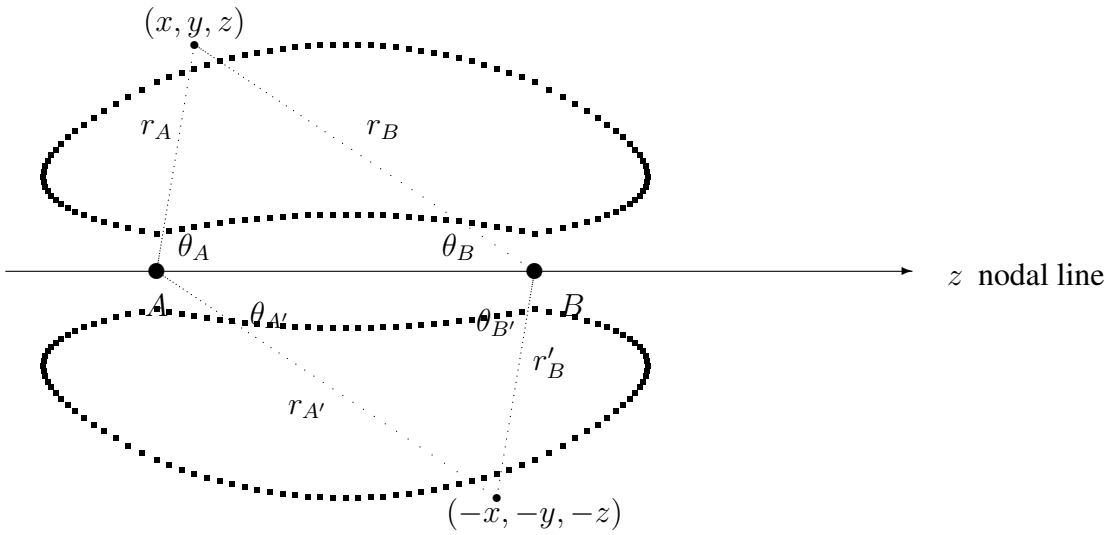
m= 1:	$2P_{+1}(A) \pm 2P_{+1}(B)$,	$\overbrace{\pi_u 2P_{+1}}^{\oplus}$,	$\overbrace{\pi_g^* 2P_{+1}}^{\ominus}$,
m=-1:	$2P_{-1}(A) \pm 2P_{-1}(B)$,	$\pi_u 2P_{-1}$,	$\pi_g^* 2P_{-1}$.

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,

$$\pi_u 2P_{+1} = 2P_{+1}(A) + 2P_{+1}(B) = \frac{1}{8\sqrt{\pi}}(\frac{z}{a})^{5/2}(e^{i\phi_A}e^{-\frac{zr_A}{2a}}r_A \text{sin}\theta_A + e^{i\phi_B}e^{-\frac{zr_B}{2a}}r_B \text{sin}\theta_B),$$

which is represented by the following diagram:

$\pi_u 2P_{+1}$ orbital



This diagram shows that under inversion through the origin, coordinates are transformed as follows,

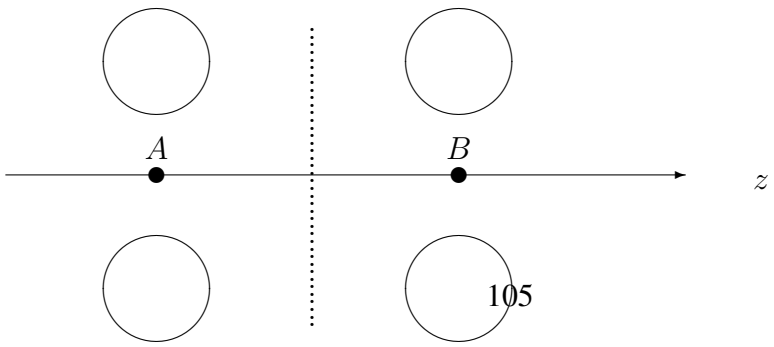
$r_A \to r_B, \qquad \theta_A \to \theta_B,$
$r_B \to r_A, \qquad \theta_B \to \theta_A,$
$\phi_A = \phi_B = \phi,$
$\phi \to \phi + \pi,$
$e^{i(\phi+\pi)} = e^{i\phi}e^{i\pi} = -e^{i\phi}$, because $\quad e^{i\pi} = \underbrace{\text{Cos}\pi}_{-1} + i\underbrace{\text{Sin}\pi}_{0}.$

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,

$$\pi_g^* 2P_{+1} = \frac{1}{8\sqrt{\pi}}(\frac{z}{a})^{5/2} e^{i\phi}(e^{-\frac{zr_A}{2a}} r_A \text{sin}\theta_A + e^{-\frac{zr_B}{2a}} r_B \text{sin}\theta_B).$$

This function has a nodal xy plane and is described by the following diagram:

nodal xy plane



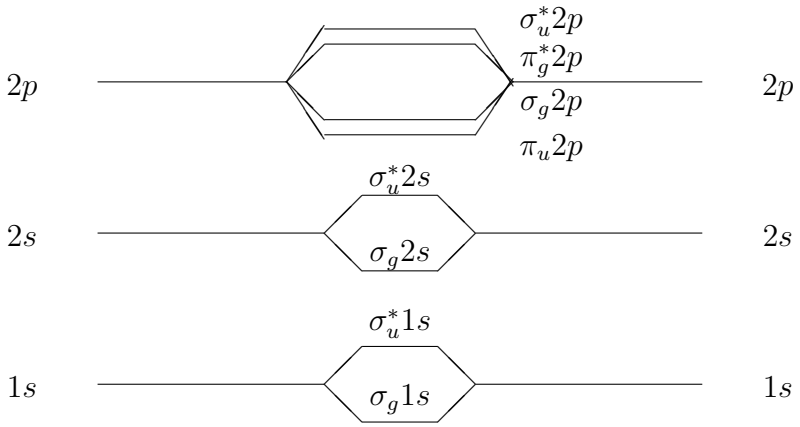
Since atomic orbitals $2p_x$, and $2p_y$ are linear combinations of atomic orbitals $2p_{+1}$ and $2p_{-1}$ molecular orbitals $\pi_u 2p_{+1}$ and $\pi_u 2p_{-1}$ can be combined to construct molecular orbitals $\pi_u 2p_x$, and $\pi_u 2p_y$ as follows,

$\pi_u 2p_x = 2p_x(A) + 2p_x(B)$,

$\pi_u 2p_y = 2p_y(A) + 2p_y(B)$.

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.

38.1 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.

39 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:

$$\hat{H}_\pi = \sum_{i=1}^{n_\pi} \hat{h}_{core}(i) + \sum_{i=1}^{n_\pi} \sum_{k>i}^{n_\pi} \frac{e^2}{r_{ik}}, \tag{146}$$

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. (146), and by approximating the Hamiltonian of the system as follows,

$$\hat{H}_\pi^{(0)} \approx \sum_{i=1}^{n_\pi} H_{\text{eff}}(i), \qquad \text{where} \qquad \hat{H}_{\text{eff}}(j) = -\frac{\hbar^2}{2m_j} \nabla_{r_j}^2 - \sum_{k=1}^{N} \frac{z'_k e^2}{r_{kj}}. \tag{147}$$

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,

$$\hat{H}_\pi^{(0)} | \psi_\pi > = E_\pi | \psi_\pi >,$$

according to the factorizable solution $|\psi_\pi > = \prod_{j=1}^{n_\pi} |\phi_j >$, where,

$$\hat{H}_{\text{eff}}(j) \mid \phi_j > = \epsilon_j \mid \phi_j > . \tag{148}$$

The energy E_π is obtained by using the Pauli exclusion principle to fill up the molecular orbitals, after finding the eigenvalues ϵ_j.

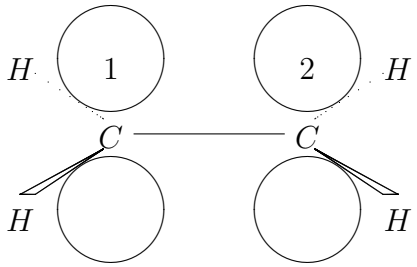
Eq. (148) is solved by implementing the variational method, assuming that $\mid \phi_j >$ can be written according to a linear combination of atomic orbitals,

$$|\phi_j >= \sum_{k=1}^{N} C_{jk}|\chi_k >,$$

where $|\chi_k >$ 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,

$$\mid \phi_j >= c_{j1} \mid \chi_1 > + c_{j2} \mid \chi_2 > . \tag{149}$$

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*).

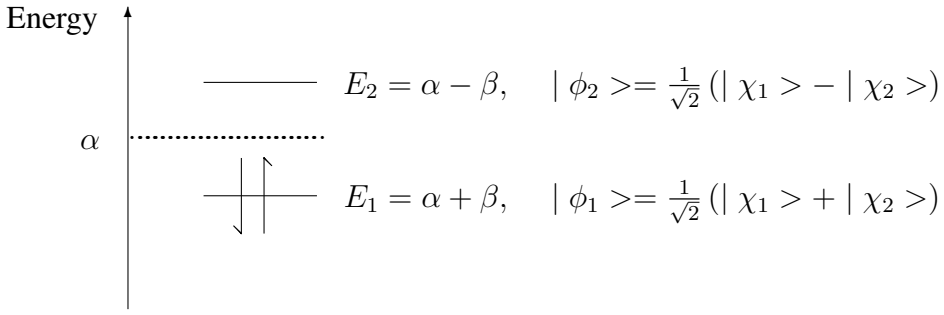
2. $H_{jk} = \beta$, when $j = k \pm 1$; and $H_{jk} = 0$, otherwise. The constant β is also an empirical parameter (*vide infra*).

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:



$$E_\pi = 2E_1 = 2\alpha + 2\beta, \quad | \phi_\pi >= \frac{1}{\sqrt{2}} | \phi_1(1) > | \phi_1(2) > (\alpha\beta - \beta\alpha) .$$

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.

An interactive program to perform electronic structure calculations within the "Simple Huckel Molecular Orbital" approximation can be found here .

A tutorial to perform electronic structure calculations and simulations of electronic dynamics within the "Extended Huckel Molecular Orbital" method approximation can be found here .

40 Self-Consistent Field Hartree-Fock Method

The self-consistent field (SCF) Hartree-Fock (HF) method is a variational approach for finding the Slater determinant of a system of n-electrons,

$$|\Phi\rangle = |\chi_1 \chi_2 \cdots \chi_n\rangle \tag{150}$$

that minimizes the expectation value of the energy:

$$\bar{E} = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle},$$

for a fixed nuclear configuration.

The one-electron basis functions χ_i are typically expressed as linear combinations of spin orbitals ϕ_k, as follows:

$$\chi_i = \sum_k c_{ki}\phi_k, \tag{151}$$

allowing for the variational approach to minimize $\bar{E}$ with respect to the expansion coefficients c_{ki}.

The energy is computed according to the usual Hamiltonian of a system of N nuclei and n electrons, with a fixed nuclear configuration:

$$\hat{H}_{el} = \sum_{i=1}^{n} \hat{h}^{(i)} + \sum_{i}^{n}\sum_{k>i}^{n} \frac{e^2}{r_{ik}}, \tag{152}$$

where the spin-orbit coupling interactions are neglected. The first term in Eq. (152) is the sum of 1-electron *core Hamiltonians*,

$$\hat{h}^{(i)} = -\frac{\hbar^2}{2m_e}\nabla^2_{r_i} - \sum_{j=1}^{N} \frac{z_j e^2}{r_{ji}}, \tag{153}$$

describing a system of n non-interacting electrons in the electrostatic potential of the nuclei. The second term in Eq. (152) is the sum of electron-electron interactions.

As a simple example, we consider the H_2 molecule with $n = 2$, $N = 2$ and $\langle \mathbf{r}_1, \mathbf{r}_2|\Phi\rangle = 2^{-1/2}\left(\langle \mathbf{r}_1|\chi_1\rangle\langle \mathbf{r}_2|\chi_2\rangle - \langle \mathbf{r}_1|\chi_2\rangle\langle \mathbf{r}_2|\chi_1\rangle\right)$,

$$\begin{aligned}\langle \mathbf{r}_1, \mathbf{r}_2|\hat{H}_{el}|\Phi\rangle \;&= 2^{-1/2}\Big[\langle \mathbf{r}_2|\chi_2\rangle\langle \mathbf{r}_1|\hat{h}^{(1)}|\chi_1\rangle - \langle \mathbf{r}_2|\chi_1\rangle\langle \mathbf{r}_1|\hat{h}^{(1)}|\chi_2\rangle + \langle \mathbf{r}_1|\chi_1\rangle\langle \mathbf{r}_2|\hat{h}^{(2)}|\chi_2\rangle \\ &\quad -\langle \mathbf{r}_1|\chi_2\rangle\langle \mathbf{r}_2|\hat{h}^{(2)}|\chi_1\rangle + \tfrac{e^2}{r_{12}}[\langle \mathbf{r}_1|\chi_1\rangle\langle \mathbf{r}_2|\chi_2\rangle - \langle \mathbf{r}_1|\chi_2\rangle\langle \mathbf{r}_2|\chi_1\rangle]\Big]\end{aligned} \tag{154}$$

and the energy expectation value

$$\begin{aligned}\bar{E} \;&= \langle\Phi|\hat{H}_{el}|\Phi\rangle \\ &= \tfrac{1}{2}\Big[\langle\chi_1|\hat{h}^{(1)}|\chi_1\rangle + \langle\chi_2|\hat{h}^{(1)}|\chi_2\rangle + \langle\chi_2|\hat{h}^{(1)}|\chi_2\rangle + \langle\chi_1|\hat{h}^{(1)}|\chi_1\rangle + \\ &\quad +[\langle\chi_1\chi_2| - \langle\chi_2\chi_1|]\tfrac{e^2}{r_{12}}[|\chi_1\chi_2\rangle - |\chi_2\chi_1\rangle]\Big] \\ &= \langle\chi_1|\hat{h}^{(1)}|\chi_1\rangle + \langle\chi_2|\hat{h}^{(1)}|\chi_2\rangle + \tfrac{1}{2}[\langle\chi_1\chi_2|\tfrac{e^2}{r_{12}}|\chi_1\chi_2\rangle \\ &\quad -\langle\chi_1\chi_2|\tfrac{e^2}{r_{12}}|\chi_2\chi_1\rangle - \langle\chi_2\chi_1|\tfrac{e^2}{r_{12}}|\chi_1\chi_2\rangle + \langle\chi_2\chi_1|\tfrac{e^2}{r_{12}}|\chi_2\chi_1\rangle]\end{aligned} \tag{155}$$

since $\hat{h}^{(1)} = \hat{h}^{(2)}$, according to Eq. (153). In general,

$$\bar{E} = \sum_{j=1}^{n}\langle\chi_j|\hat{h}^{(1)}|\chi_j\rangle + \frac{1}{2}\sum_{j=1}^{n}\sum_{k\neq j}\langle\chi_j\chi_k|\frac{e^2}{r_{12}}|\chi_j\chi_k\rangle - \langle\chi_j\chi_k|\frac{e^2}{r_{12}}|\chi_k\chi_j\rangle, \tag{156}$$

or

$$\bar{E} = \sum_{j=1}^{n}\langle\chi_j|\hat{h}^{(1)}|\chi_j\rangle + \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}\langle\chi_j\chi_k|\frac{e^2}{r_{12}}|\chi_j\chi_k\rangle - \langle\chi_j\chi_k|\frac{e^2}{r_{12}}|\chi_k\chi_j\rangle, \tag{157}$$

since $\langle\chi_j\chi_k|\frac{e^2}{r_{12}}|\chi_j\chi_k\rangle - \langle\chi_j\chi_k|\frac{e^2}{r_{12}}|\chi_k\chi_j\rangle = 0$, when $j = k$.

To minimize $\bar{E}$ with respect to χ_j, subject to the constraint of orthonormal orbitals, we apply the Lagrange multiplier method for the following functional:

$$L(\chi_1, ..., \chi_n) = \bar{E} + \sum_j \sum_k \epsilon_{jk}[\langle\chi_j|\chi_k\rangle - \delta_{jk}], \tag{158}$$

where ϵ_{jk} are the Lagrange multipliers. Varying the spin orbitals χ_j in an infinitesimal amount δ_j, with respect to the expansion coefficients c_{kj}, we obtain:

$$\delta L(\chi_1, ..., \chi_n) = \delta\bar{E} + \sum_{j=1}^{n}\sum_{k=1}^{n} \epsilon_{jk}[\langle\delta\chi_j|\chi_k\rangle + \langle\chi_j|\delta\chi_k\rangle], \tag{159}$$

where

$$\begin{aligned}\delta\bar{E} \;&= \textstyle\sum_{j=1}^{n}\langle\delta\chi_j|\hat{h}^{(1)}|\chi_j\rangle + \langle\chi_j|\hat{h}^{(1)}|\delta\chi_j\rangle \\ &+\tfrac{1}{2}\textstyle\sum_{j=1}^{n}\sum_{k=1}^{n}\langle\delta\chi_j\chi_k|\frac{e^2}{r_{12}}|\chi_j\chi_k\rangle + \langle\chi_j\delta\chi_k|\frac{e^2}{r_{12}}|\chi_j\chi_k\rangle \\ &+\langle\chi_j\chi_k|\frac{e^2}{r_{12}}|\delta\chi_j\chi_k\rangle + \langle\chi_j\chi_k|\frac{e^2}{r_{12}}|\chi_j\delta\chi_k\rangle \\ &-\langle\delta\chi_j\chi_k|\frac{e^2}{r_{12}}|\chi_k\chi_j\rangle - \langle\chi_j\delta\chi_k|\frac{e^2}{r_{12}}|\chi_k\chi_j\rangle \\ &-\langle\chi_j\chi_k|\frac{e^2}{r_{12}}|\delta\chi_k\chi_j\rangle - \langle\chi_j\chi_k|\frac{e^2}{r_{12}}|\chi_k\delta\chi_j\rangle\end{aligned} \tag{160}$$

Substituting Eq. (160) into Eq. (159) and simplifying, we obtain:

$$\begin{aligned}\delta L \;&= \textstyle\sum_{j=1}^{n}\langle\delta\chi_j|\hat{h}^{(1)}|\chi_j\rangle + \sum_{j=1}^{n}\sum_{k=1}^{n}\langle\delta\chi_j\chi_k|\frac{e^2}{r_{12}}|\chi_j\chi_k\rangle - \langle\delta\chi_j\chi_k|\frac{e^2}{r_{12}}|\chi_k\chi_j\rangle \\ &+\textstyle\sum_{j=1}^{n}\sum_{k=1}^{n}\epsilon_{jk}\langle\delta\chi_j|\chi_k\rangle + c.c.\end{aligned} \tag{161}$$

which gives,

$$\begin{aligned}\delta L \;&= \textstyle\sum_{j=1}^{n}\langle\delta\chi_j(1)|\Big[\hat{h}^{(1)}|\chi_j(1)\rangle + \sum_{k=1}^{n}\langle\chi_k(2)|\frac{e^2}{r_{12}}|\chi_k(2)\rangle|\chi_j(1)\rangle \\ &-\langle\chi_k(2)|\frac{e^2}{r_{12}}|\chi_j(2)\rangle|\chi_k(1)\rangle + \textstyle\sum_{j=1}^{n}\sum_{k=1}^{n}\epsilon_{jk}|\chi_k\rangle\Big] + c.c. = 0\end{aligned} \tag{162}$$

Since $\delta\chi_j$ is arbitrary, it must be that the expression in square brackets is equal to zero for all j:

$$\left[\hat{h}^{(1)} + \sum_{k=1}^{n}\langle\chi_k(2)|\frac{e^2}{r_{12}}[1 - \hat{P}_{12}]|\chi_k(2)\rangle\right]|\chi_j(1)\rangle = \sum_{j=1}^{n}\sum_{k=1}^{n}\epsilon_{jk}|\chi_k\rangle \tag{163}$$

where the operator $\hat{P}_{12}$ permutes the states of electrons 1 and 2.

To write Eq. (163) in the canonical eigenvalue form, we change the basis set according to the unitary transformation,

$$|\chi'_j\rangle = \sum_k |\chi_k\rangle\Gamma_{kj}, \tag{164}$$

with $\mathbf{\Gamma}\mathbf{\Gamma}^\dagger = 1$. Considering that the Lagrange multipliers matrix ϵ is Hermitian (since the functional L is real), it is always possible to find a $\mathbf{\Gamma}$ that diagonalizes ϵ according to the similarity transformation:

$$\epsilon' = \mathbf{\Gamma}^\dagger\epsilon\mathbf{\Gamma} \tag{165}$$

Such a transformation defines the set of *canonical spin orbitals* $|\chi'_j\rangle$ for which

$$\hat{f}^{(1)}|\chi'_j\rangle = \epsilon'_{jj}|\chi'_j\rangle. \tag{166}$$

for $j = 1 - n$, where $\hat{f}^{(1)}$ is the *Fock* operator,

$$\hat{f}^{(1)} = \hat{h}^{(1)} + \hat{V}_1^{HF}, \tag{167}$$

where $\hat{V}_1^{HF}$ is the *Hartree-Fock potential* describing the electron-electron interactions, as follows:

$$\hat{V}_1^{HF} = J_1(r_1) - \hat{X}_1(r_1), \tag{168}$$

where $J_1(r_1)$ is the Coulomb mean-field potential,

$$J_1(r_1) = \sum_{k=1}^{n} \langle \chi'_k | \frac{e^2}{r_{12}} | \chi'_k \rangle. \tag{169}$$

The matrix elements in Eq. (169) are integrals over the spatial and spin coordinates of electron 2. Analogously, $\hat{X}_1(r_1)$ is defined as the *exchange operator*,

$$\hat{X}_1(r_1) = \sum_{k \neq j}^{n} \langle \chi'_k(2) | \frac{e^2}{r_{12}} \hat{P}_{12} | \chi'_k(2) \rangle. \tag{170}$$

Equation (166) defines a self-consistent field (SCF) problem since the operator $\hat{f}^{(1)}$, required to find the solutions χ'_j, depends on those functions through J_1 and $\hat{X}_1$. To solve this SCF problem, we first obtain approximate solutions χ'_j by approximating $\hat{f}^{(1)}$ by $\hat{h}^{(1)}$ (i.e., neglecting the electron-electron interactions introduced by J_1 and $\hat{X}_1$), or by using a semiempirical method (like the Hueckel method described later in these lectures). These approximate functions χ'_j are then used to compute J_1 and $\hat{X}_1$, giving an approximate $\hat{f}^{(1)}$ that can be used to obtain improved functions χ'_j. The process is repeated until convergence.

To solve the Hartree-Fock Eq. (166) by solving a set of matrix equations, we substitute χ'_j by a linear combination of atomic orbitals, analogous Eq. (151): $|\chi'_j\rangle = \sum_k C_{kj}|\psi_k\rangle$. Making the substitution and multiplying from the left with $\langle\psi_{k'}|$, we obtain:

$$\sum_k \langle \psi_{k'} | \hat{f}(j) | \psi_k \rangle C_{kj} = \epsilon_{jj} \sum_k \langle \psi_{k'} | \psi_j \rangle C_{kj}, \tag{171}$$

or, in matrix form,

$$\mathbf{FC} = \mathbf{SC}\epsilon' \tag{172}$$

where we have introduced the overlap matrix $S_{jk} = \langle \psi_j | \psi_k \rangle$, the Fock matrix $F_{jk} = \langle \psi_j | \hat{f} | \psi_k \rangle$, and the matrix of column eigenvectors C_{kj} defining the canonical molecular orbitals χ'_j, with energies ϵ_{jj}, expressed in the basis of atomic orbitals $|\psi_k\rangle$.

40.1 Restricted Closed Shell Hartree-Fock

The so-called *closed-shell restricted* Hartree-Fock method is essentially the Hartree-Fock approach implemented for systems with an *even* number n of electrons, with each orbital j populated by 2 electrons with opposite spins (one with spin α, described by ψ_j, and the other one with spin β, described by $\bar{\psi}_j$). It is called *restricted* to indicate that the spin states are restricted to be either α or β, and *closed shell* to indicate that each shell ψ_j is full with 2 electrons. The system is described by the Slater determinant,

$$\begin{aligned} |\Phi\rangle &= |\chi_1\chi_2 \cdots \chi_n\rangle \\ &= |\psi_1\bar{\psi}_1 \ldots \psi_{n/2}\bar{\psi}_{n/2}\rangle \end{aligned} \tag{173}$$

where $\chi_1 = \psi_1$, $\chi_2 = \bar{\psi}_1$, ..., $\chi_{n-1} = \psi_{n/2}$, $\chi_n = \bar{\psi}_{n/2}$.

The energy of this *closed-shell restricted* Hartree-Fock wave function is computed, according to Eq. (157), by replacing the sums over n spin-orbitals χ_j by sums over $n/2$ spin-orbitals with spin α, ψ_j and $n/2$ spin-orbitals with spin β, $\bar{\psi}_j$, as follows:

$$\begin{aligned} \bar{E} &= \textstyle\sum_{j=1}^{n/2}\langle\psi_j|\hat{h}^{(1)}|\psi_j\rangle + \frac{1}{2}\sum_{j=1}^{n/2}\sum_{k=1}^{n/2}\langle\psi_j\psi_k|\frac{e^2}{r_{12}}|\psi_j\psi_k\rangle - \langle\psi_j\psi_k|\frac{e^2}{r_{12}}|\psi_k\psi_j\rangle \\ &+\frac{1}{2}\sum_{j=1}^{n/2}\sum_{k=1}^{n/2}\langle\psi_j\bar{\psi}_k|\frac{e^2}{r_{12}}|\psi_j\bar{\psi}_k\rangle - \cancel{\langle\psi_j\bar{\psi}_k|\frac{e^2}{r_{12}}|\bar{\psi}_k\psi_j\rangle} \\ &+\sum_{j=1}^{n/2}\langle\bar{\psi}_j|\hat{h}^{(1)}|\bar{\psi}_j\rangle + \frac{1}{2}\sum_{j=1}^{n/2}\sum_{k=1}^{n}\langle\bar{\psi}_j\psi_k|\frac{e^2}{r_{12}}|\bar{\psi}_j\psi_k\rangle - \cancel{\langle\bar{\psi}_j\psi_k|\frac{e^2}{r_{12}}|\psi_k\bar{\psi}_j\rangle} \\ &+\frac{1}{2}\sum_{j=1}^{n/2}\sum_{k=1}^{n/2}\langle\bar{\psi}_j\bar{\psi}_k|\frac{e^2}{r_{12}}|\bar{\psi}_j\bar{\psi}_k\rangle - \langle\bar{\psi}_j\bar{\psi}_k|\frac{e^2}{r_{12}}|\bar{\psi}_k\bar{\psi}_j\rangle, \end{aligned} \tag{174}$$

where we can cross out the terms that cancel upon integration over the spin variable to obtain:

$$\bar{E} = 2\sum_{j=1}^{n/2}\langle\psi_j|\hat{h}^{(1)}|\psi_j\rangle + \sum_{j=1}^{n/2}\sum_{k=1}^{n/2} 2\langle\psi_j\psi_k|\frac{e^2}{r_{12}}|\psi_j\psi_k\rangle - \langle\psi_j\psi_k|\frac{e^2}{r_{12}}|\psi_k\psi_j\rangle. \tag{175}$$

Analogously to the general case, we minimize $\bar{E}$ with respect to ψ_j, subject to the constraint of orthonormal orbitals by applying the Lagrange multiplier method for the following functional:

$$L(\psi_1, ..., \psi_n) = \bar{E} + \sum_j \sum_k \epsilon_{jk}[\langle\psi_j|\psi_k\rangle - \delta_{jk}], \tag{176}$$

where ϵ_{jk} are the Lagrange multipliers. Varying the spin orbitals ψ_j in an infinitesimal amount δ_j, with respect to expansion coefficients c_{kj}, we obtain:

$$\delta L(\psi_1, ..., \psi_n) = \delta\bar{E} + \sum_{j=1}^{n}\sum_{k=1}^{n}\epsilon_{jk}[\langle\delta\psi_j|\psi_k\rangle + \langle\psi_j|\delta\psi_k\rangle]. \tag{177}$$

Varying the spatial orbitals ψ_j in an infinitesimal amount δ_j with respect to the expansion coefficients c_j, we obtain:

$$\begin{aligned} \delta\bar{E} &= 2\textstyle\sum_{j=1}^{n/2}\langle\delta\psi_j|\hat{h}^{(1)}|\psi_j\rangle + \sum_{j=1}^{n/2}\sum_{k=1}^{n/2} 2\langle\delta\psi_j\psi_k|\frac{e^2}{r_{12}}|\psi_j\psi_k\rangle - \langle\delta\psi_j\psi_k|\frac{e^2}{r_{12}}|\psi_k\psi_j\rangle \\ &+\sum_{j=1}^{n/2}\sum_{k=1}^{n/2} 2\langle\psi_j\delta\psi_k|\frac{e^2}{r_{12}}|\psi_j\psi_k\rangle - \langle\psi_j\delta\psi_k|\frac{e^2}{r_{12}}|\psi_k\psi_j\rangle \\ &+2\sum_{j=1}^{n/2}\langle\psi_j|\hat{h}^{(1)}|\delta\psi_j\rangle + \sum_{j=1}^{n/2}\sum_{k=1}^{n/2} 2\langle\psi_j\psi_k|\frac{e^2}{r_{12}}|\delta\psi_j\psi_k\rangle - \langle\psi_j\psi_k|\frac{e^2}{r_{12}}|\delta\psi_k\psi_j\rangle \\ &+\sum_{j=1}^{n/2}\sum_{k=1}^{n/2} 2\langle\psi_j\psi_k|\frac{e^2}{r_{12}}|\psi_j\delta\psi_k\rangle - \langle\psi_j\psi_k|\frac{e^2}{r_{12}}|\psi_k\delta\psi_j\rangle \end{aligned} \tag{178}$$

which gives

$$\delta\bar{E} \quad = 2\sum_{j=1}^{n/2}\langle\delta\psi_j|\hat{h}^{(1)}|\psi_j\rangle + 2\sum_{j=1}^{n/2}\sum_{k=1}^{n/2} 2\langle\delta\psi_j\psi_k|\tfrac{e^2}{r_{12}}|\psi_j\psi_k\rangle - \langle\delta\psi_j\psi_k|\tfrac{e^2}{r_{12}}|\psi_k\psi_j\rangle + c.c. \tag{179}$$

Substituting Eq. (179) into Eq. (177), we obtain:

$$\delta L = 2\sum_{j=1}^{n/2}\langle\delta\psi_j|\left[\hat{h}^{(1)}|\psi_j\rangle + \sum_{k=1}^{n/2} 2\langle\psi_k|\frac{e^2}{r_{12}}|\psi_k\rangle|\psi_j\rangle - \langle\psi_k|\frac{e^2}{r_{12}}\hat{P}_{12}|\psi_k\rangle|\psi_j\rangle + \epsilon_{jk}|\psi_k\rangle\right] + c.c. = 0, \tag{180}$$

which is satisfied when

$$\left[\hat{h}^{(1)} + \sum_{k=1}^{n/2}\langle\psi_k|\frac{e^2}{r_{12}}[2-\hat{P}_{12}]|\psi_k\rangle\right]|\psi_j\rangle = \epsilon_{jk}|\psi_k\rangle. \tag{181}$$

To write Eq. (181) in the canonical eigenvalue form, we change the basis set according to the unitary transformation,

$$|\psi'_j\rangle = \sum_k |\psi_k\rangle\Gamma_{kj}, \tag{182}$$

with $\mathbf{\Gamma}\mathbf{\Gamma}^\dagger = 1$. Considering that the Lagrange multipliers matrix ϵ is Hermitian (since the functional L is real), it is always possible to find a $\mathbf{\Gamma}$ that diagonalizes ϵ according to the similarity transformation:

$$\epsilon' = \mathbf{\Gamma}^\dagger\epsilon\mathbf{\Gamma} \tag{183}$$

Such a transformation defines the set of *canonical orbitals* $|\psi'_j\rangle$ for which

$$\hat{f}^{(1)}_{rhf}|\psi'_j\rangle = \epsilon'_{jj}|\psi'_j\rangle, \tag{184}$$

for $j = 1 - n/2$, where $\hat{f}^{(1)}_{rhf}$ is the *closed-shell restricted Hartree-Fock* operator,

$$\hat{f}^{(1)}_{rhf} = \hat{h}^{(1)} + \hat{V}_1^{rhf}, \tag{185}$$

where $\hat{V}_j^{rhf}$ is the *restricted Hartree-Fock potential* describing the interactions between electrons of the same spin, as follows:

$$\hat{V}_1^{rhf} = 2J_1(r_1) - \hat{X}_1(r_1), \tag{186}$$

where $J_1(r_1)$ is the Coulombic mean-field potential due to the presence of other electrons of the same spin,

$$J_1(r_1) = \sum_{k=1}^{n/2}\langle\psi'_k(2)|\frac{e^2}{r_{12}}|\psi'_k(2)\rangle. \tag{187}$$

Analogously, $\hat{X}_1(r_1)$ is defined as the *exchange operator*,

$$\hat{X}_1(r_1) = \sum_{k=1}^{n/2}\langle\psi'_k(2)|\frac{e^2}{r_{12}}\hat{P}_{12}|\psi'_k(2)\rangle, \tag{188}$$

where the permutation operator $\hat{P}_{12}$ interchanges electrons 1 and 2.

Equation (184) defines a self-consistent field (SCF) problem since $\hat{f}^{(1)}_{rhf}$ depends on ψ_j through $\hat{V}^{rhf}_1$. To solve this SCF problem, we first obtain approximate solutions ψ_j by approximating $\hat{f}^{(1)}_{rhf}$ by $\hat{h}_j$ (i.e., neglecting the electron-electron interactions introduced by J_1 and $\hat{X}_1$), or by using a semiempirical method (like the Hückel method described in these lectures). The resulting approximate solutions ψ_j are then used to compute J_1 and $\hat{X}_1$, giving a better approximation to $\hat{f}^{(1)}_{rhf}$ that can be used to obtain improved functions ψ_j. The process is repeated until convergence.

In practice, the restricted Hartree-Fock eigenvalue problem, introduced by Eq. (184), is solved with a set of matrix equations, obtained by substituting ${\psi'}_j$ by a linear combination of atomic orbitals, analogous Eq. (151): $|{\psi'}_j\rangle = \sum_{k=1}^{n/2} C_{kj}|\zeta_k\rangle$. Making the substitution and multiplying from the left with $\langle\zeta_{k'}|$, we obtain:

$$\sum_{k=1}^{n/2}\langle\zeta_{k'}|\hat{f}^{(1)}_{rhf}|\zeta_k\rangle C_{kj} = \epsilon_{jj}\sum_{k=1}^{n/2}\langle\zeta_{k'}|\zeta_j\rangle C_{kj}, \tag{189}$$

or, in matrix form,

$$\mathbf{F}^{rhf}\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon' \tag{190}$$

where we have introduced the overlap matrix $S_{jk} = \langle\zeta_j|\zeta_k\rangle$, the restricted Hartree Fock matrix

$$F^{rhf}_{jk} = \langle\zeta_j|\hat{f}^{(1)}_{rhf}|\zeta_k\rangle, \tag{191}$$

and the matrix of column eigenvectors C_{kj} defining the canonical orbitals ${\psi'}_j$, with energies ϵ_{jj}, in the basis of atomic orbitals $|\zeta_k\rangle$.

The electronic density $\rho(\mathbf{r})$ of the system with 2 electrons per orbital, populating the lowest $n/2$ states (*i.e.*, closed-shell Hartree-Fock density) can be computed, as follows:

$$\begin{array}{ll}\rho(\mathbf{r}) & = 2\sum_{k=1}^{n/2}{\psi'}_k^*(\mathbf{r}){\psi'}_k(\mathbf{r}) \\ & = 2\sum_{lm}\zeta_l^*(\mathbf{r})\zeta_m(\mathbf{r})\sum_{k=1}^{n/2}C^*_{kl}C_{mk} \\ & = 2\sum_{lm}\zeta_l^*(\mathbf{r})\zeta_m(\mathbf{r})P_{lm}\end{array} \tag{192}$$

where

$$P_{lm} = \sum_{k=1}^{n/2} C^*_{kl}C_{mk} \tag{193}$$

define the elements of the electronic *density matrix* $\mathbf{P}$.

The elements of the density matrix, P_{lm}, are thus computed from the solution of the eigenvalue problem, introduced by Eq. (190). The resulting elements of the density matrix P_{lm} can be used to compute not only the density, according to Eq. (192), but also the restricted Hartree-Fock matrix, according to Eq. (191) since $\hat{f}^{(1)}_{rhf} = \hat{h}^{(1)} + \hat{V}^{rhf}_1$, with $\hat{V}^{rhf}_1 = 2J_1(\mathbf{r}_1) - \hat{X}(\mathbf{r}_1)$, where

$$\begin{array}{ll}J_1(\mathbf{r}_1) & = \sum_{k=1}^{n/2}\int d\mathbf{r}_2{\psi'}^*_k(\mathbf{r}_2)\frac{e^2}{r_{12}}{\psi'}_k(\mathbf{r}_2) \\ & = \sum_{k=1}^{n/2}\int d\mathbf{r}_2\sum_{l=1}^{n/2}\sum_{m=1}^{n/2}C^*_{km}\zeta^*_m(\mathbf{r}_2)\frac{e^2}{r_{12}}C_{lk}\zeta_l(\mathbf{r}_2) \\ & = \sum_{l=1}^{n/2}\sum_{m=1}^{n/2}\sum_{k=1}^{n/2}C^*_{km}C_{lk}\int d\mathbf{r}_2\zeta^*_m(\mathbf{r}_2)\frac{e^2}{r_{12}}\zeta_l(\mathbf{r}_2) \\ & = \sum_{l=1}^{n/2}\sum_{m=1}^{n/2}P_{ml}\int d\mathbf{r}_2\zeta^*_m(\mathbf{r}_2)\frac{e^2}{r_{12}}\zeta_l(\mathbf{r}_2)\end{array} \tag{194}$$

and

$$\begin{aligned}\hat{X}_1(r_1) &= \sum_{k=1}^{n/2}\langle\psi'_k|\frac{e^2}{r_{jk}}\hat{P}_{kj}|\psi'_k\rangle, \\ &= \sum_{l=1}^{n/2}\sum_{m=1}^{n/2} P_{ml}\int d\mathbf{r}_2\zeta_m^*(\mathbf{r}_2)\frac{e^2}{r_{12}}\hat{P}_{12}\zeta_l(\mathbf{r}_2).\end{aligned} \tag{195}$$

Therefore,

$$\hat{f}_{rhf}^{(1)}(\mathbf{r}_1) = \hat{h}^{(1)} + \sum_{l=1}^{n/2}\sum_{m=1}^{n/2} P_{ml}\left[2\langle\zeta_m(\mathbf{r}_2)|\frac{e^2}{r_{12}}|\zeta_l(\mathbf{r}_2)\rangle - \langle\zeta_m(\mathbf{r}_2)|\frac{e^2}{r_{12}}\hat{P}_{12}|\zeta_l(\mathbf{r}_2)\rangle\right], \tag{196}$$

and

$$\begin{aligned}F_{jk}^{rhf} &= \langle\zeta_j|\hat{f}_{rhf}^{(1)}|\zeta_k\rangle, \\ &= H_{jk}^{core} + G_{jk},\end{aligned} \tag{197}$$

with

$$H_{jk}^{core} = \langle\zeta_j(1)|\hat{h}^{(1)}|\zeta_k(1)\rangle, \tag{198}$$

and

$$G_{jk} = \sum_{l=1}^{n/2}\sum_{m=1}^{n/2} P_{ml}\left[2\langle\zeta_j(\mathbf{r}_1)\zeta_m(\mathbf{r}_2)|\frac{e^2}{r_{12}}|\zeta_l(\mathbf{r}_2)\zeta_k(\mathbf{r}_1)\rangle - \langle\zeta_j(\mathbf{r}_1)\zeta_m(\mathbf{r}_2)|\frac{e^2}{r_{12}}\hat{P}_{12}|\zeta_l(\mathbf{r}_2)\zeta_k(\mathbf{r}_1)\rangle\right]. \tag{199}$$

To solve Eq. (190), we first diagonalize the overlap matrix by computing the matrix $\mathbf{X} = \mathbf{S}^{-1/2}$ that transforms the overlap matrix into the identity matrix, as follows: $\mathbf{X}^\dagger\mathbf{S}\mathbf{X} = \mathbf{1}$. Then, we introduce the matrix $\tilde{\mathbf{C}}$, as follows:

$$\mathbf{C} = \mathbf{X}\tilde{\mathbf{C}}, \tag{200}$$

that, according to Eq. (190), satisfies the eigenvalue problem:

$$\mathbf{F}^{rhf}\mathbf{X}\tilde{\mathbf{C}} = \mathbf{S}\mathbf{X}\tilde{\mathbf{C}}\epsilon' \tag{201}$$

or

$$\tilde{\mathbf{F}}^{rhf}\tilde{\mathbf{C}} = \tilde{\mathbf{C}}\epsilon' \tag{202}$$

with

$$\tilde{\mathbf{F}}^{rhf} = \mathbf{X}^\dagger\mathbf{F}^{rhf}\mathbf{X}. \tag{203}$$

These equations allow for the implementation of the self-consistent-field restricted Hartree-Fock (SCF RHF) method, for a fixed nuclear configuration, as follows:

1. Calculate the matrix elements S_{jk}, H_{jk}^{core} and the 2-electron integrals $\langle\zeta_j(\mathbf{r}_1)\zeta_m(\mathbf{r}_2)|\frac{e^2}{r_{12}}|\zeta_l(\mathbf{r}_2)\zeta_k(\mathbf{r}_1)\rangle$ and $\langle\zeta_j(\mathbf{r}_1)\zeta_m(\mathbf{r}_2)|\frac{e^2}{r_{12}}|\zeta_l(\mathbf{r}_1)\zeta_k(\mathbf{r}_2)\rangle$.
2. Diagonalize S_{jk} to obtain X_{jk}
3. Obtain an approximate density matrix P_{jk}, according to Eq. (193), by solving Eq. (190) with $\hat{f}^{(1)} \approx \hat{h}^{(1)}$, or $\hat{f}^{(1)} \approx \hat{h}_{EH}^{(1)}$, where $\hat{h}_{EH}^{(1)}$ is the semiempirical extended-Hückel Hamiltonian of the system.

4. Compute the matrix elements G_{jk}, according to Eq. (199), using P_{jk} and the 2-electron integrals.

5. Compute the Fock matrix F_{jk}^{rhf}, according to Eq. (197), by using H_{jk}^{core}, P_{jk} and the 2-electron integrals.

6. Compute the transformed Fock matrix $\tilde{F}_{jk}^{rhf}$ by using F_{jk}^{rhf} and X_{jk}, according to Eq. (203).

7. Obtain $\tilde{\mathbf{C}}$ and ϵ' by solving Eq. (202).

8. Calculate $\mathbf{C}$ by using Eq. (200).

9. Compute a new density matrix $\mathbf{P}$, according to Eq. (193), based on $\mathbf{C}$ obtained in (8).

10. If $\mathbf{P}$ has changed more than a given tolerance, relative to the previous iteration, go to (4). Otherwise, the SCF calculation has converged and the solution is given by the current eigenvectors $\mathbf{C}$ and eigenvalues ϵ.

The total energy provided by Hartree-Fock theory is usually satisfactory since it is dominated by high-density inner-shell electrons that are well described by HF. However, the description of low-density valence electrons provided by HF theory is usually unsatisfactoy since it neglects important correlation energy terms. While correlation effects can be addressed through configuration-interaction corrections, the complexity of the corrections, their sensitivity to the choice of basis functions, and the increase in effort required with the decrease in spacing between energy levels, preclude application to large systems. In addition, the long range of the Coulomb interaction produces unrealistic features in the HF energy eigenvalues, such as vanishing density of states at the Fermi level in metals, and unphysically large band gaps in insulators. The density-functional theory, described in the following section, provides an alternative approach.

40.2 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*.

40.3 Supplement: Green's Function

The goal of this supplementary section is to explain how to compute a function $f(\mathbf{A})$ of a hermitian matrix $\mathbf{A}$ and subsequently introduce the Green's function. Analogously to the function $f(x)$ of simple variable x, $f(\mathbf{A})$ can be expanded in powers of $\mathbf{A}$:

$$f(\mathbf{A}) = \sum_{n=0}^{\infty} \alpha_n \mathbf{A}^n. \tag{204}$$

with $\alpha_n = \frac{1}{n!}\left.\frac{\partial f(x)}{\partial x}\right|_{x=0}$. Equation (204) shows how to compute a function of a matrix as a sum of products of such matrix.

Note that when the matrix is diagonal

$$\mathbf{A} = \begin{pmatrix} a_1 & 0 & \cdots & 0 \\ 0 & a_2 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & a_N \end{pmatrix}, \tag{205}$$

then

$$\mathbf{A}^n = \begin{pmatrix} a_1^n & 0 & \cdots & 0 \\ 0 & a_2^n & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & a_N^n \end{pmatrix}. \tag{206}$$

When $\mathbf{A}$ is not diagonal, it can be diagonalized by the similarity transformation $\mathbf{a} = \mathbf{c}^\dagger \mathbf{A} \mathbf{c}$, where $\mathbf{a}$ is the diagonal matrix of eigenvalues $a_1, a_2, \cdots, a_N$ and $\mathbf{c}$ is the matrix of column eigenvectors of $\mathbf{A}$. Therefore,

$$\begin{aligned} \mathbf{A}^n &= [\mathbf{c}\mathbf{a}\mathbf{c}^\dagger]^n, \\ &= \mathbf{c}\mathbf{a}^n\mathbf{c}^\dagger \end{aligned} \tag{207}$$

since $\mathbf{c}^\dagger\mathbf{c} = 1$. Substituting Eq. (207) into Eq. (204), we obtain:

$$f(\mathbf{A}) = \mathbf{c} f(\mathbf{a}) \mathbf{c}^\dagger. \tag{208}$$

Optional Exercise: (A) Show that the matrix elements of the Green's function $\mathbf{G_0} = (E\mathbf{1} - \mathbf{H}_0)^{-1}$ can be computed, according to Eq. (208), as follows:

$$[\mathbf{G_0}]_{ik} = \sum_{j=1}^{N} \frac{c_j^{(i)} c_j^{(k)*}}{E - E_j^{(0)}}, \tag{209}$$

where $E_j^{(0)}$ is the j-th eigenvalue of $\mathbf{H}_0$ associated with the eigenvector $\mathbf{c}_j = (c_j^{(1)}, c_j^{(2)}, \cdots, c_j^{(N)})$.

(B) Show that the Green's function

$$\mathbf{G} = (E\mathbf{1} - (\mathbf{H}_0 + \mathbf{V}))^{-1}, \tag{210}$$

obeys the *Dyson equation*:

$$\mathbf{G} = \mathbf{G_0} + \mathbf{G_0}\mathbf{V}\mathbf{G}. \tag{211}$$

Hint: Note that by multiplying both sides of Eq. (210) by $\mathbf{G_0}(E\mathbf{1} - (\mathbf{H}_0 + \mathbf{V}))$, we obtain:

$$\mathbf{G_0}(E\mathbf{1} - (\mathbf{H}_0 + \mathbf{V}))\mathbf{G} = \mathbf{G_0}. \tag{212}$$

As an application of the Green's function, we consider the eigenvalue problem:

$$\left[\hat{H}_0 + \hat{V}\right] \psi_E(x) = E\psi_E(x), \tag{213}$$

which can be re-written, as follows:

$$(E \hat{-} H_0)\psi_E(x) = \phi(x), \tag{214}$$

with $\phi(x) = \hat{V}\psi_E(x)$. Expanding $\psi_E(x)$ and $\phi(x)$ in the basis of eigenfunctions of $\hat{H}_0$:

$$\hat{H}_0\psi_\alpha(x) = E_\alpha^{(0)}\psi_\alpha(x), \tag{215}$$

we obtain:

$$\psi_E(x) = \sum_\alpha a_{\alpha,E}\psi_\alpha(x), \tag{216}$$

and

$$\phi(x) = \sum_\alpha b_\alpha\psi_\alpha(x), \tag{217}$$

where

$$b_\alpha = \int dx\psi_\alpha^*(x)\phi(x). \tag{218}$$

In addition, substituting Eqs. (216) and (217) into Eq. (214), we obtain:

$$\sum_\beta a_{\beta,E}(E - E_\beta^{(0)})\psi_\beta(x) = \sum_\beta b_\beta\psi_\beta(x), \tag{219}$$

and multiplying both sides of Eq. (219) by $\psi_\alpha^*(x)$ and integrating over x, we obtain:

$$\begin{aligned} a_{\alpha,E} &= \frac{b_\alpha}{E - E_\alpha^{(0)}}, \\ &= \frac{1}{E - E_\alpha^{(0)}}\int dx'\psi_\alpha^*(x')\phi(x'). \end{aligned} \tag{220}$$

Substituting Eq. (220) into Eq. (216), we obtain:

$$\begin{aligned} \psi_E(x) &= \int dx' \sum_\alpha \frac{\psi_\alpha^*(x')\psi_\alpha(x)}{E - E_\alpha^{(0)}}\phi(x'), \\ &= \int dx' G_0(x, x'; E)V(x')\psi_E(x'), \end{aligned} \tag{221}$$

where $G_0(x, x'; E) = \sum_\alpha \frac{\psi_\alpha^*(x')\psi_\alpha(x)}{E - E_\alpha^{(0)}}$ has poles at values of E equal to the eigenvalues of $\hat{H}_0$.

As a by-product of Eq. (221), we note that in the particular case of $\phi(x') = \delta(x' - x'')$, we obtain:

$$\begin{aligned} \psi_E(x) &= \sum_\alpha \frac{\psi_\alpha^*(x'')\psi_\alpha(x)}{E - E_\alpha^{(0)}}, \\ &= G_0(x, x''; E). \end{aligned} \tag{222}$$

Substituting Eq. (222) into Eq. (214), we obtain:

$$(E \hat{-} H_0)G_0(x, x''; E) = \delta(x - x''), \tag{223}$$

or in matrix form,

$$(E\mathbf{1} - \mathbf{H}_0)\mathbf{G_0}(E) = \mathbf{1}. \tag{224}$$

Equation (222) shows that the Green's function can be computed in terms of the eigenfunctions $\psi_\alpha(x)$ and eigenvalues E_α of $\hat{H}_0$.

Analogously, we obtain the Green's function of $\hat{H} = \hat{H}_0 + \hat{V}$:

$$(E - \hat{H}_0 - V)G(x, x''; E) = \delta(x - x''), \tag{225}$$

or in matrix form,

$$(E\mathbf{1} - \mathbf{H}_0 - V)\mathbf{G}(E) = \mathbf{1}, \tag{226}$$

which, according to Eq. (211), obeys the Dyson integral equation:

$$G(x, x''; E) = G_0(x, x''; E) + \int dx' G_0(x, x'; E)V(x')G(x', x''; E), \tag{227}$$

and has poles at values of E equal to the eigenvalues of $\hat{H}$.

It is important to note that the Green's function can be used to compute several functions, including the density matrix $\rho(x, x'') = \sum_\alpha n_\alpha \psi^*_\alpha(x'')\psi_\alpha(x)$, as follows:

$$\rho(x, x'') = \frac{i}{\pi}\int_{-\infty}^{\infty} dE\; n(E)G(x, x''; E). \tag{228}$$

To prove Eq. (228), we compute the integral

$$I(x, x'') = \int_{-\infty}^{\infty} dE\; n(E)G(x, x''; E). \tag{229}$$

Substituting Eq. (222) into Eq. (229), we obtain:

$$\begin{aligned} I(x, x'') &= \sum_\alpha \psi^*_\alpha(x'')\psi_\alpha(x) \int_{-\infty}^{\infty} dE\; \frac{n(E)}{E - E^{(0)}_\alpha} \\ &= \int_{-\infty}^{\infty} dE\; f(E) \end{aligned} \tag{230}$$

with $f(E) = \sum_\alpha \psi^*_\alpha(x'')\psi_\alpha(x)n(E)/(E - E^{(0)}_\alpha)$. Note that the argument $f(E)$ of this integral, introduced by Eq. (230), has singularities (poles) at the energy values $E = E^{(0)}_\alpha$. To evaluate that integral we introduce the complex 'energy' $Z = Z_r + iZ_i$, with $Z_r = E$, and the Cauchy principal value $P[f(Z)]$ (*i.e.*, integral over the real axis excluding each singularity with an exclusion radius ϵ), which converges to the desired integral in the limit with $\epsilon \to 0$ (see Fig. (1)). We note that according to the residue theorem , $\oint_C dZ f(Z) = 0$, since the overall integration contour C (*i.e.*,

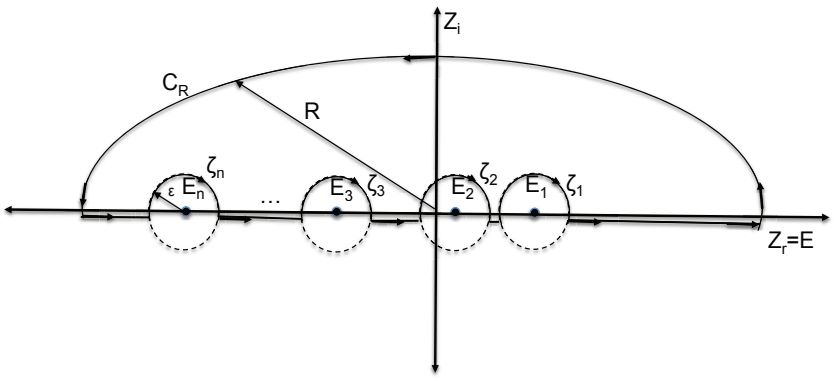


Figure 1: Poles of the integrand of Eq. (230) at $E = E_\alpha^{(0)}$ and integration contour.

including the real axis excluding the singularities, the half-circles around the singularities and the big half-circle C_R) encloses an area without singularities. In addition,

$$\oint_C dZ f(Z) = P[f(Z)] + \frac{1}{2}\sum_\alpha \oint_{\zeta_\alpha} dZ f(Z) + \oint_{C_R} dZ f(Z). \tag{231}$$

Since the full-circle contour integrals around the poles are:

$$\oint_{\zeta_\alpha} f(Z) dZ = 2\pi i \,\text{Res}[f, E_\alpha], \tag{232}$$

with $\text{Res}[f, E_\alpha] = n(E_\alpha)\psi_\alpha^*(x'')\psi_\alpha(x)$ and the integral over C_R vanishes for $R \to \infty$, we obtain:

$$\begin{aligned} \int_{-\infty}^{\infty} dE\, n(E) G(x, x''; E) &= P[f(Z)] \\ &= -i\pi \sum_\alpha \text{Res}[f, E_\alpha] \\ &= -i\pi \sum_\alpha n(E_\alpha)\psi_\alpha^*(x'')\psi_\alpha(x) \\ &= -i\pi\rho(x, x'') \end{aligned} \tag{233}$$

which is equivalent to Eq. (228).

41 Second Quantization Mapping

The goal of this section is to introduce the single-particle basis $\{\psi_{\nu_1}(\mathbf{r}), \psi_{\nu_2}(\mathbf{r}), \psi_{\nu_3}(\mathbf{r}), \cdots\}$ for representation of the N-particle state $\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$ in terms of symmetrized product states $\hat{S}_{\pm} \prod_{j=1}^{N} \psi_{\nu_j}(\mathbf{r}_j)$, and its correspondence to the occupation number representation $|n_{\nu_1}, n_{\nu_2}, n_{\nu_3}, \cdots\rangle$, where n_{ν_j} is the number of particles in state $\psi_{\nu_j}(\mathbf{r})$ in the product state representation. Furthermore, we introduce the creation $\hat{a}_j^{\dagger}$ and anihilation $\hat{a}_j$ operators (i.e., operators that raise or lower the occupation numbers n_{ν_j} by one unit) and we show that any single particle operator $\hat{A}$ can be expressed in terms of $\hat{a}_j^{\dagger}$ and $\hat{a}_j$, as follows: $\hat{A} = \sum_{\nu_j,\nu_k} A_{\nu_j,\nu_k} \hat{a}_j^{\dagger} \hat{a}_k$, with $A_{\nu_j,\nu_k} = \langle \nu_j | \hat{A} | \nu_k \rangle$.

41.1 Single-Particle Basis

The state of the N-particle system $\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$ can be represented in a complete orthonormal basis composed of single-particle states $\{\psi_{\nu_j}(\mathbf{r})\}$, satisfying that

$$\sum_{\nu_j} \psi_{\nu_j}(\mathbf{r}')^* \psi_{\nu_j}(\mathbf{r}) = \delta(\mathbf{r}' - \mathbf{r}), \tag{234}$$

and

$$\int d\mathbf{r}\, \psi_{\nu_j}(\mathbf{r})^* \psi_{\nu_k}(\mathbf{r}) = \delta_{\nu_j \nu_k}. \tag{235}$$

To represent $\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$, we first project the state along the basis set of $\mathbf{r}_1$, as follows:

$$\Psi(\mathbf{r}_1, \mathbf{r'}_2, \cdots, \mathbf{r'}_N) = \sum_{\nu_1} \psi_{\nu_1}(\mathbf{r}_1) \int d\mathbf{r'}_1 \psi_{\nu_1}(\mathbf{r'}_1)^* \Psi(\mathbf{r'}_1, \mathbf{r'}_2, \cdots, \mathbf{r'}_N), \tag{236}$$

and then we proceed analogously with the other coordinates, so we obtain:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \sum_{\nu_1, \cdots, \nu_N} c_{\nu_1, \cdots, \nu_N} \prod_{j=1}^{N} \psi_{\nu_j}(\mathbf{r}_j), \tag{237}$$

with

$$c_{\nu_1, \cdots, \nu_N} = \int d\mathbf{r'}_1 \psi_{\nu_1}(\mathbf{r'}_1)^* \cdots \int d\mathbf{r'}_N \psi_{\nu_N}(\mathbf{r'}_N)^* \Psi(\mathbf{r'}_1, \mathbf{r'}_2, \cdots, \mathbf{r'}_N). \tag{238}$$

While the product states $\prod_{j=1}^{N} \psi_{\nu_j}(\mathbf{r}_j)$ form a complete basis for the N-particle Hilbert space, they do not necessarily fulfill the indistinguishability requirement of bosons (or fermions) so they need to be symmetrized (or anti-symmetrized). Applying the bosonic symmetrization $\hat{S}_+$ (or the fermionic anti-symmetrization $\hat{S}_-$) operator, we obtain linear combinations of product states with the proper symmetry to describe systems of N-bosons (or fermions), according to the following normalized

permanents (or *Slater determinants*):

$$\hat{S}_{\pm}\prod_{j=1}^{N}\psi_{\nu_j}(\mathbf{r}_j) = \frac{1}{\prod_\nu \sqrt{n_\nu!}}\frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{\nu_1}(\mathbf{r}_1) & \psi_{\nu_1}(\mathbf{r}_2) & \cdots & \psi_{\nu_1}(\mathbf{r}_N) \\ \psi_{\nu_2}(\mathbf{r}_1) & \psi_{\nu_2}(\mathbf{r}_2) & \cdots & \psi_{\nu_2}(\mathbf{r}_N) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_{\nu_N}(\mathbf{r}_1) & \psi_{\nu_N}(\mathbf{r}_2) & \cdots & \psi_{\nu_N}(\mathbf{r}_N) \end{vmatrix}_{\pm}, \tag{239}$$
$$= \langle \mathbf{r}|\psi_{\nu_1}\psi_{\nu_2}\cdots\psi_{\nu_N}\rangle,$$

which are linear combinations of product states corresponding to all possible permutation on the set of N coordinates. Each term of the Slater determinant has a sign $(-1)^p$, corresponding to the number of permutations p, while the bosonic permanent terms are all sing-less.

41.2 Occupation Number Basis

The product states, introduced by Eq. (239), are linear combinations of occupied single-particle states. The occupation number representation $|n_{\nu_1}, n_{\nu_2}, n_{\nu_3}, \cdots\rangle$, simply lists the number of particles n_{ν_j} in each occupied state ν_j, with $\sum_j n_{\nu_j} = N$. Such states are eigenstates of the number operators,

$$\hat{n}_{\nu_k}|n_{\nu_1}, n_{\nu_2}, n_{\nu_3}, \cdots\rangle = n_{\nu_k}|n_{\nu_1}, n_{\nu_2}, n_{\nu_3}, \cdots\rangle. \tag{240}$$

For fermions, $n_{\nu_k} = 0, 1$ while for bosons $n_{\nu_k} = 0, 1, 2, \cdots$ is a positive integer.

41.3 Creation and Anihilation Operators

Bosons: The creation and anihilation operators of bosons, $\hat{b}_j^\dagger$ and $\hat{b}_j$, are defined to ensure that the number operator $\hat{n}_{\nu_j} = \hat{b}_j^\dagger\hat{b}_j$ gives the number of bosons in state ν_j as follows:

$$\hat{n}_{\nu_j}|n_{\nu_1}, n_{\nu_2}, \cdots n_{\nu_j}, \cdots\rangle = n_{\nu_j}|n_{\nu_1}, n_{\nu_2}, \cdots n_{\nu_j}, \cdots\rangle, \tag{241}$$

and raise or lower the occupation of that state, as follows:

$$\begin{aligned} \hat{b}_j^\dagger|n_{\nu_1}, n_{\nu_2}, \cdots n_{\nu_j}, \cdots\rangle &= B_+(n_{\nu_j})|n_{\nu_1}, n_{\nu_2}, \cdots (n_{\nu_j}+1), \cdots\rangle, \\ \hat{b}_j|n_{\nu_1}, n_{\nu_2}, \cdots n_{\nu_j}, \cdots\rangle &= B_-(n_{\nu_j})|n_{\nu_1}, n_{\nu_2}, \cdots (n_{\nu_j}-1), \cdots\rangle, \end{aligned} \tag{242}$$

where $B_+(n_{\nu_j})$ and $B_-(n_{\nu_j})$ are normalization constants. We further demand that the occupation number of an unoccupied state (e.g., $n_{\nu_j} = 0$) cannot be further reduced, which is equivalent to demand that $\hat{b}_j|n_{\nu_1}, n_{\nu_2}, \cdots 0, \cdots\rangle = 0$. Furthermore, we define the normalization constants $B_+(0) = 1$ and $B_-(1) = 1$ so that

$$\begin{aligned} \hat{b}_j^\dagger|n_{\nu_1}, n_{\nu_2}, \cdots 0, \cdots\rangle &= |n_{\nu_1}, n_{\nu_2}, \cdots 1, \cdots\rangle, \\ \hat{b}_j|n_{\nu_1}, n_{\nu_2}, \cdots 1, \cdots\rangle &= |n_{\nu_1}, n_{\nu_2}, \cdots 0, \cdots\rangle. \end{aligned} \tag{243}$$

Therefore,

$$\begin{aligned} \hat{b}_j\hat{b}_j^\dagger|n_{\nu_1}, n_{\nu_2}, \cdots 0, \cdots\rangle &= |n_{\nu_1}, n_{\nu_2}, \cdots 0, \cdots\rangle, \\ \hat{b}_j^\dagger\hat{b}_j|n_{\nu_1}, n_{\nu_2}, \cdots 0, \cdots\rangle &= 0, \end{aligned} \tag{244}$$

which can be summarized as $\hat{b}_j\hat{b}_j^\dagger = \hat{n}_{\nu_j} + 1$ and $[\hat{b}_j, \hat{b}_j^\dagger] = 1$. When $j \neq k$, however, $[\hat{b}_j, \hat{b}_k^\dagger] = 0$. The normalization constants for other states are found from Eq. (241), as follows:

$$\begin{aligned}\langle n_{\nu_1}, n_{\nu_2}, \cdots n_{\nu_j}, \cdots | \hat{b}_j^\dagger \hat{b}_j | n_{\nu_1}, n_{\nu_2}, \cdots n_{\nu_j}, \cdots \rangle &= n_{\nu_j}, \\ \langle n_{\nu_1}, n_{\nu_2}, \cdots n_{\nu_j}, \cdots | \hat{b}_j^\dagger \hat{b}_j | n_{\nu_1}, n_{\nu_2}, \cdots n_{\nu_j}, \cdots \rangle &= B_-(n_{\nu_j})^2,\end{aligned} \tag{245}$$

so $B_-(n_{\nu_j}) = \sqrt{n_{\nu_j}}$. Analogously, we obtain

$$\begin{aligned}\langle n_{\nu_1}, n_{\nu_2}, \cdots n_{\nu_j}, \cdots | \hat{b}_j \hat{b}_j^\dagger | n_{\nu_1}, n_{\nu_2}, \cdots n_{\nu_j}, \cdots \rangle &= B_+(n_{\nu_j})^2, \\ (n_{\nu_j} + 1) &= B_+(n_{\nu_j})^2,\end{aligned} \tag{246}$$

$B_+(n_{\nu_j}) = \sqrt{n_{\nu_j} + 1}$. Therefore,

$$(\hat{b}_j^\dagger)^{n_\nu} | n_{\nu_1}, n_{\nu_2}, \cdots 0, \cdots \rangle = \sqrt{n_\nu!} | n_{\nu_1}, n_{\nu_2}, \cdots n_\nu, \cdots \rangle. \tag{247}$$

or

$$| n_{\nu_1}, n_{\nu_2}, n_{\nu_3}, \cdots \rangle = \prod_j \frac{(\hat{b}_j^\dagger)^{n_{\nu_j}}}{\sqrt{n_\nu!}} | 0, 0, 0, \cdots \rangle. \tag{248}$$

Fermions: The creation and anihilation operators of fermions, $\hat{c}_j^\dagger$ and $\hat{c}_j$, are defined to ensure that the number operator $\hat{n}_{\nu_j} = \hat{c}_j^\dagger \hat{c}_j$ gives the number of fermions $n_{\nu_j} = 0, 1$ in state ν_j. This requires that $\hat{c}_j^\dagger |1\rangle = 0$, $\hat{c}_j^\dagger |0\rangle = |1\rangle$, $\hat{c}_j |0\rangle = 0$, and $\hat{c}_j^\dagger |0\rangle = |1\rangle$. Therefore, $\hat{c}_j \hat{c}_j^\dagger |0\rangle = |0\rangle$ and $\hat{c}_j \hat{c}_j^\dagger |0\rangle = |0\rangle$, or $\hat{c}_j \hat{c}_j^\dagger + \hat{c}_j^\dagger \hat{c}_j = 0$.

41.4 Operators in Second Quantization

In this subsection we show that any single particle operator $\hat{A}$ can be expressed in terms of $\hat{b}_j^\dagger$ and $\hat{b}_j$, as follows: $\hat{A} = \sum_{\nu_j, \nu_k} A_{\nu_j, \nu_k} \hat{b}_j^\dagger \hat{b}_k$, with $A_{\nu_j, \nu_k} = \langle \nu_j | \hat{A} | \nu_k \rangle$. As an example of a single particle operator, we consider the kinetic energy $\hat{T} = \sum_{k=1}^N \hat{T}_k$, with $\hat{T}_k = \frac{\hat{p}_k^2}{2m_k}$:

$$\begin{aligned}\langle \mathbf{r} | \hat{T} | \psi_{\nu_1} \psi_{\nu_2} \cdots \psi_{\nu_N} \rangle &= \sum_{\nu_j} \langle \mathbf{r} | \psi_{\nu_j} \rangle \langle \psi_{\nu_j} | \hat{T} | \psi_{\nu_1} \psi_{\nu_2} \cdots \psi_{\nu_N} \rangle \\ &= \sum_{\nu_j} \langle \mathbf{r} | \psi_{\nu_j} \rangle \sum_{k=1}^N \langle \psi_{\nu_j} | \hat{T}_k | \psi_{\nu_1} \psi_{\nu_2} \cdots \psi_{\nu_N} \rangle \\ &= \sum_{\nu_j} \langle \mathbf{r} | \psi_{\nu_j} \rangle \sum_{k=1}^N \langle \psi_{\nu_j} | \hat{T}_k | \psi_{\nu_k} \rangle \langle \mathbf{r} | \hat{b}_{\nu_k} | \psi_{\nu_1} \psi_{\nu_2} \cdots \psi_{\nu_N} \rangle \\ &= \sum_{k=1}^N \sum_{\nu_j, \nu_l} \langle \mathbf{r} | \psi_{\nu_j} \rangle \delta_{\nu_l, \nu_k} T_{\nu_j, \nu_l} \langle \mathbf{r} | \hat{b}_{\nu_k} | \psi_{\nu_1} \psi_{\nu_2} \cdots \psi_{\nu_N} \rangle \\ &= \sum_{k=1}^N \sum_{\nu_j, \nu_l} \delta_{\nu_l, \nu_k} T_{\nu_j, \nu_l} \langle \mathbf{r} | \hat{b}_{\nu_j}^\dagger \hat{b}_{\nu_k} | \psi_{\nu_1} \psi_{\nu_2} \cdots \psi_{\nu_N} \rangle\end{aligned} \tag{249}$$

Therefore,

$$\begin{aligned}
\hat{T}\left[\hat{b}^\dagger_{\nu_1}\cdots\hat{b}^\dagger_{\nu_N}|0\rangle\right] &= \sum_{k=1}^{N}\sum_{\nu_j,\nu_l}\delta_{\nu_l,\nu_k}T_{\nu_j,\nu_l}\hat{b}^\dagger_{\nu_j}\hat{b}_{\nu_k}\hat{b}^\dagger_{\nu_1}\cdots\hat{b}^\dagger_{\nu_N}|0\rangle \\
&= \sum_{k=1}^{N}\sum_{\nu_j,\nu_l}\delta_{\nu_l,\nu_k}T_{\nu_j,\nu_l}\hat{b}^\dagger_{\nu_j}\frac{\hat{n}_{\nu_k}}{n_{\nu_k}}\hat{b}_{\nu_k}\hat{b}^\dagger_{\nu_1}\cdots\hat{b}^\dagger_{\nu_N}|0\rangle \\
&= \sum_{k=1}^{N}\sum_{\nu_j,\nu_l}\delta_{\nu_l,\nu_k}T_{\nu_j,\nu_l}\frac{\hat{b}^\dagger_{\nu_j}\hat{b}_{\nu_k}}{n_{\nu_k}}\left[\hat{b}^\dagger_{\nu_k}\hat{b}_{\nu_k}\hat{b}^\dagger_{\nu_1}\cdots\hat{b}^\dagger_{\nu_N}|0\rangle\right] \\
&= \sum_{\nu_j,\nu_l}T_{\nu_j,\nu_l}\sum_{k=1}^{N}\delta_{\nu_l,\nu_k}\frac{\hat{b}^\dagger_{\nu_j}\hat{b}_{\nu_k}}{n_{\nu_k}}\left[\hat{b}^\dagger_{\nu_1}\cdots\hat{b}^\dagger_{\nu_N}|0\rangle\right] \\
&= \sum_{\nu_j,\nu_l}T_{\nu_j,\nu_l}\hat{b}^\dagger_{\nu_j}\hat{b}_{\nu_l}\sum_{k=1}^{N}\frac{\delta_{\nu_l,\nu_k}}{n_{\nu_k}}\left[\hat{b}^\dagger_{\nu_1}\cdots\hat{b}^\dagger_{\nu_N}|0\rangle\right] \\
&= \sum_{\nu_j,\nu_l}T_{\nu_j,\nu_l}\hat{b}^\dagger_{\nu_j}\hat{b}_{\nu_l}\frac{1}{n_{\nu_l}}\sum_{k=1}^{N}\delta_{\nu_l,\nu_k}\left[\hat{b}^\dagger_{\nu_1}\cdots\hat{b}^\dagger_{\nu_N}|0\rangle\right] \\
&= \sum_{\nu_j,\nu_l}T_{\nu_j,\nu_l}\hat{b}^\dagger_{\nu_j}\hat{b}_{\nu_l}\left[\hat{b}^\dagger_{\nu_1}\cdots\hat{b}^\dagger_{\nu_N}|0\rangle\right]
\end{aligned} \tag{250}$$

where p is the number of particles in state state ψ_{ν_k} for the N-particle system described by state $|\psi_{\nu_1}\psi_{\nu_2}\cdots\psi_{\nu_N}\rangle = \hat{b}^\dagger_{\nu_1}\cdots\hat{b}^\dagger_{\nu_N}|0\rangle$, so according to Eq. (246), $\langle\psi_{\nu_1}\psi_{\nu_2}\cdots\psi_{\nu_N}|\hat{b}_{\nu_k}\hat{b}^\dagger_{\nu_k}|\psi_{\nu_1}\psi_{\nu_2}\cdots\psi_{\nu_N}\rangle = (n_{\nu_k}+1)$. Therefore,

$$\hat{T} = \sum_{\nu_j,\nu_l}T_{\nu_j,\nu_l}\hat{b}^\dagger_{\nu_j}\hat{b}_{\nu_l}. \tag{251}$$

Analogously, any 2-particle operator $\hat{V}$ such as the pair-wise additive potential,

$$\hat{V} = \frac{1}{2}\sum_{j=1}^{N}\sum_{k\neq j}V(x_j,x_k), \tag{252}$$

can be written in second quantization, as follows:

$$\hat{V} = \sum_{\nu_j,\nu_i,\nu_l,\nu_k}V_{\nu_j,\nu_i,\nu_l,\nu_k}\hat{b}^\dagger_{\nu_j}\hat{b}^\dagger_{\nu_i}\hat{b}_{\nu_l}\hat{b}_{\nu_k} \tag{253}$$

where $V_{\nu_j,\nu_i,\nu_l,\nu_k} = \langle\psi_{\nu_j}\psi_{\nu_i}|V(x_1,x_2)|\psi_{\nu_l}\psi_{\nu_k}\rangle$.

41.5 Change of basis in Second Quantization

We consider two different complete and ordered single-particle basis sets $\{|\psi_{\nu_j}\rangle\}$ and $\{|\psi_{\mu_j}\rangle\}$ with $j = 1$–N. Using the completeness relationship we can write any element of one basis set as a linear combination of elements of the other basis set, as follows:

$$|\psi_{\mu_j}\rangle = \sum_k |\psi_{\nu_k}\rangle\langle\psi_{\nu_k}|\psi_{\mu_j}\rangle, \tag{254}$$

where $\psi_{\nu_k}\rangle = \hat{a}^\dagger_{\nu_k}|0\rangle$ and $\psi_{\mu_j}\rangle = \hat{a}^\dagger_{\mu_j}|0\rangle$. Therefore,

$$\hat{a}_{\mu_j}|0\rangle = \sum_k \langle\psi_{\nu_k}|\psi_{\mu_j}\rangle\hat{a}_{\nu_k}|0\rangle, \tag{255}$$

or

$$\hat{a}_{\mu_j} = \sum_k \langle\psi_{\nu_k}|\psi_{\mu_j}\rangle\hat{a}_{\nu_k}, \tag{256}$$

and

$$\hat{a}^\dagger_{\mu_j} = \sum_k \langle\psi_{\nu_k}|\psi_{\mu_j}\rangle^*\hat{a}^\dagger_{\nu_k}, \tag{257}$$

41.6 Mapping into Cartesian Coordinates

Introducing the Cartesian operators $\tilde{x}_{\nu_j} = \frac{1}{\sqrt{2}}[\hat{b}^\dagger_{\nu_j} + \hat{b}_{\nu_j}]$ and $\tilde{p}_{\nu_j} = \frac{i}{\sqrt{2}}[\hat{b}^\dagger_{\nu_j} - \hat{b}_{\nu_j}]$, with $[\tilde{x}_{\nu_j}, \tilde{p}_{\nu_j}] = i$, since $\tilde{x}_{\nu_j} = \hat{x}\sqrt{\frac{m\omega}{\hbar}}$, $\tilde{p}_{\nu_j} = \hat{p}/\sqrt{m\omega\hbar}$ and $[\hat{x}_{\nu_j}, \hat{p}_{\nu_j}] = i\hbar$, for the harmonic oscillator Hamiltonian

$$\begin{aligned} H &= \frac{\hat{p_{\nu_j}}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2, \\ &= \frac{\tilde{p_{\nu_j}}^2}{2m}m\omega\hbar + \frac{1}{2}m\omega^2\frac{\hbar}{m\omega}\tilde{x_{\nu_j}}^2, \\ &= \frac{\hbar\omega}{2}\left[\tilde{p}^2_{\nu_j} + \tilde{x}^2_{\nu_j}\right]. \end{aligned} \tag{258}$$

Considering that

$$\begin{aligned} \hat{n}_{\nu_j} &= \hat{b}^\dagger_{\nu_j}\hat{b}_{\nu_j}, \\ \hat{b}^\dagger_{\nu_j} &= \frac{1}{\sqrt{2}}\left[\tilde{x}_{\nu_j} - i\tilde{p}_{\nu_j}\right], \\ \hat{b}_{\nu_j} &= \frac{1}{\sqrt{2}}\left[\tilde{x}_{\nu_j} + i\tilde{p}_{\nu_j}\right]. \end{aligned} \tag{259}$$

we obtain,

$$\begin{aligned} \hat{n}_{\nu_j} &= \frac{1}{2}(\tilde{x}_{\nu_j} - i\tilde{p}_{\nu_j})(\tilde{x}_{\nu_j} + i\tilde{p}_{\nu_j}) \\ &= \frac{1}{2}(\tilde{x}^2_{\nu_j} + i[\tilde{x}_{\nu_j}, \tilde{p}_{\nu_j}] + \tilde{p}^2_{\nu_j}) \\ &= \frac{1}{2}(\tilde{x}^2_{\nu_j} + \tilde{p}^2_{\nu_j} - 1) \end{aligned} \tag{260}$$

and

$$H = \hbar\omega \left(\hat{n}_{\nu_j} + \frac{1}{2} \right). \tag{261}$$

Substituting the Cartesian expressions of b_{ν_j} and $b^{\dagger}_{\nu_j}$ into Eq. (251), we obtain:

$$\begin{aligned} \hat{T} &= \frac{1}{2} \sum_{\nu_j,\nu_l} T_{\nu_j,\nu_l} \left[\tilde{x}_{\nu_j} - i\tilde{p}_{\nu_j} \right] \left[\tilde{x}_{\nu_l} + i\tilde{p}_{\nu_l} \right], \\ &= \frac{1}{2} \sum_{\nu_j} T_{\nu_j,\nu_j} (\tilde{x}^2_{\nu_j} + \tilde{p}^2_{\nu_j} - 1) + \frac{1}{2} \sum_{\nu_j} \sum_{\nu_l \neq \nu_j} T_{\nu_j,\nu_l} \left[\tilde{x}_{\nu_j} - i\tilde{p}_{\nu_j} \right] \left[\tilde{x}_{\nu_l} + i\tilde{p}_{\nu_l} \right] \\ &= \frac{1}{2} \sum_{\nu_j} T_{\nu_j,\nu_j} (\tilde{x}^2_{\nu_j} + \tilde{p}^2_{\nu_j} - 1) + \frac{1}{2} \sum_{\nu_j} \sum_{\nu_l \neq \nu_j} T_{\nu_j,\nu_l} \left[\tilde{x}_{\nu_j} \tilde{x}_{\nu_l} + \tilde{p}_{\nu_j} \tilde{p}_{\nu_l} \right] \end{aligned} \tag{262}$$

since $[\tilde{x}_{\nu_j}, \tilde{p}_{\nu_l}] = i\delta_{\nu_l,\nu_j}$ while $[\tilde{x}_{\nu_j}, \tilde{x}_{\nu_l}] = 0$ and $[\tilde{p}_{\nu_j}, \tilde{p}_{\nu_l}] = 0$.

42 Density Functional Theory

In the Kohn-Sham formulation of density functional theory (DFT), the total electronic energy is expressed as a sum of electronic kinetic energy T, electron-nuclear interaction V, Coulomb self-interaction U of the electron density ρ and the remaining part of the electron-electron repulsion energy due to exchange-correlation E^{XC}, all expressed as functionals of the density ρ, as follows:

$$E = T + V + U + E^{XC}. \tag{263}$$

Considering a spin-unrestricted format, as described by Pople , α and β electrons are assigned to sets of orthonormal orbitals ψ_i^α with $i = 1, .., n_\alpha$ and ψ_i^β with $i = 1, .., n_\beta$, respectively, defining a single Slater determinant. The corresponding total density is then obtained as the sum of the α and β densities,

$$\rho = \rho^\alpha + \rho^\beta, \tag{264}$$

with

$$\begin{aligned} \rho_\alpha &= \sum_{i=1}^{n_\alpha} |\psi_i^\alpha|^2, \\ \rho_\beta &= \sum_{j=1}^{n_\beta} |\psi_j^\beta|^2. \end{aligned} \tag{265}$$

The energies T, V and U are defined, as follows:

$$T = -\frac{1}{2}\sum_{i=1}^{n_\alpha} \langle \psi_i^\alpha | \nabla^2 | \psi_i^\alpha \rangle - \frac{1}{2}\sum_{j=1}^{n_\beta} \langle \psi_j^\beta | \nabla^2 | \psi_j^\beta \rangle, \tag{266}$$

$$V = -\sum_{j=1}^{N_{nucl}} Z_j \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_j|} d\mathbf{r}, \tag{267}$$

$$U = \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|} d\mathbf{r}_1 d\mathbf{r}_2. \tag{268}$$

The exchange-correlation energy E^{XC} is typically approximated by a functional f of the densities and their gradients, as follows:

$$E^{XC} = \int f(\rho_\alpha, \rho_\beta, \gamma_{\alpha\alpha}, \gamma_{\alpha\beta}, \gamma_{\beta\beta}) d\mathbf{r}, \tag{269}$$

where

$$\gamma_{jk} = \nabla\rho_j \cdot \nabla\rho_k. \tag{270}$$

Expanding the orthonormal orbitals ψ_i^α in the basis of atomic orbitals (AOs) ϕ_μ,

$$\psi_i^\alpha = \sum_\mu c_{\mu,i}^\alpha \phi_\mu, \tag{271}$$

we obtain:

$$\begin{aligned} \rho_\alpha &= \sum_{i=1}^{n_\alpha} \sum_\mu \sum_\nu (c_{\mu i}^\alpha)^* c_{\nu i}^\alpha \phi_\mu^* \phi_\nu, \\ &= \sum_\mu \sum_\nu P_{\mu,\nu}^\alpha \phi_\mu^* \phi_\nu, \end{aligned} \tag{272}$$

and similarly for ρ^β, where $P_{\mu,\nu}^\alpha$ in Eq. (272) is the AO density matrix of α electrons. Substituting these expressions into Eq. (263) and then minimizing with respect to the expansion coefficients, as done for the Hartree-Fock method, we obtain the equations,

$$\sum_\nu (F_{\mu\nu}^\alpha - \epsilon_i^\alpha S_{\mu\nu}) c_{\nu i}^\alpha = 0, \tag{273}$$

analogous to the Roothaan-Hall Eqs. (190) of Hartree-Fock theory. The only difference is that the Fock matrix is replaced by the Fock-type matrices,

$$\begin{aligned} F_{\mu\nu}^\alpha &= H_{\mu\nu}^{core} + J_{\mu\nu} + F_{\mu\nu}^{XC\alpha}, \\ F_{\mu\nu}^\beta &= H_{\mu\nu}^{core} + J_{\mu\nu} + F_{\mu\nu}^{XC\beta}. \end{aligned} \tag{274}$$

Here, $S_{\mu\nu}$ and $H_{\mu\nu}^{core}$ are the overlap and bare nucleus Hamiltonian matrices, $J_{\mu\nu}$ is the Coulomb matrix

$$J_{\mu\nu} = \sum_{\lambda\sigma} \left(P_{\lambda\sigma}^\alpha + P_{\lambda\sigma}^\beta \right) \langle \mu\nu | \lambda\sigma \rangle. \tag{275}$$

and $F_{\mu\nu}^{XC\alpha}$ are given, as follows:

$$F_{\mu\nu}^{XC\alpha} = \int d\mathbf{r} \left[\frac{\partial f}{\partial \rho_\alpha} \phi_\mu \phi_\nu + \left(2 \frac{\partial f}{\partial \gamma_{\alpha\alpha}} \nabla \rho_\alpha + \frac{\partial f}{\partial \gamma_{\alpha\beta}} \nabla \rho_\beta \right) \cdot \nabla (\phi_\mu \phi_\nu) \right]. \tag{276}$$

Expressions and Fortran codes for various versions of proposed f, defining popular functionals such as LDA, PBE, B3LYP, etc., and the corresponding derivatives $\frac{\partial f}{\partial \rho_\alpha}$, $\frac{\partial f}{\partial \gamma_{\alpha\alpha}}$ and $\frac{\partial f}{\partial \gamma_{\alpha\beta}}$ are available at the CCLRC DFT repository . The Fortran codes were automatically generated with dfauto from Maple expressions.

Once the equations have been solved to find the expansion coefficients $c_{\nu i}^\alpha$ through an iterative self-consistent procedure, the Kohn-Sham energy is obtained from Eq. (263), as follows:

$$E = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{core} + \frac{1}{2} \sum_{\mu\nu} \sum_{\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \langle \mu\nu | \lambda\sigma \rangle + E^{XC}. \tag{277}$$

42.1 Hohenberg and Kohn Theorems

The underlying concept, introduced by Eq. (263), is that the minimum energy is a unique functional of the ground state density (*i.e.*, the minimum energy of a non-degenerate state is uniquely determined by the ground state density). Such concept is a consequence of the Hohenberg and Kohn first theorem : '*For any system of interacting particles in an external potential V, the ground state density is uniquely determined (*i.e.*, the potential is a unique functional of the density, to within an additive constant)*'.

The theorem is demonstrated by considering two external potentials V and V', differing by more than a constant, giving the same ground state density ρ:

$$\begin{aligned} E' &= \langle\psi'|H'|\psi'\rangle < \langle\psi|H'|\psi\rangle = \langle\psi|H + (V' - V)|\psi\rangle, \\ E' &< E + \int d\mathbf{r}\rho(\mathbf{r})(V'(\mathbf{r}) - V(\mathbf{r})), \end{aligned} \tag{278}$$

where the inequality is strict because ψ and ψ' are different (*i.e.*, eigenstates of different Hamiltonians). Exchanging the primed and unprimed quantities, and assuming $\rho = \rho'$, we obtain:

$$\begin{aligned} E &= \langle\psi|H|\psi\rangle < \langle\psi'|H|\psi'\rangle = \langle\psi'|H' + (V - V')|\psi'\rangle, \\ E &< E' + \int d\mathbf{r}\rho(\mathbf{r})(V(\mathbf{r}) - V'(\mathbf{r})), \end{aligned} \tag{279}$$

Summing Eqs. (278) and (279), we obtain: $E' + E < E + E'$ which is an absurd. Therefore, two potentials that differ in more than a constant value cannot define the same density, so the density defines a unique potential (except for a constant).

As mentioned above, a straightforward consequence of the first theorem is Hohenberg and Kohn second theorem stating that *the ground state energy E_0 is uniquely determined by a functional of the density*, as follows:

$$E = F[\rho] + \int d\mathbf{r}\rho(\mathbf{r})V(\mathbf{r}), \tag{280}$$

where $F[\rho]$ is a a universal functional valid for any number of particles and any external potential V. The second theorem can be proved by using the variational theorem with a trial state ψ, as follows:

$$\langle\psi|\hat{H}|\psi\rangle = F[\rho] + \int d\mathbf{r}\rho(\mathbf{r})V(\mathbf{r}) \geqslant E_0. \tag{281}$$

where the equality holds only when ψ is the ground state for $V(\mathbf{r})$. Note that one can write the energy as a functional of the density because the external potential is uniquely determined by the density and since the potential in turn uniquely (except in degenerate situations) determines the ground state wavefunction, all the other observables of the system such as kinetic energy are uniquely determined.

42.2 Kohn Sham Equations

Kohn and Sham mapped the system of interacting electrons onto a fictitious system of non-interacting 'electrons', and wrote the variational problem for the Hohenberg-Kohn density-functional by introducing a Lagrange multiplier μ that constrains the number of electrons to N, as follows:

$$\delta \left[F[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) V(\mathbf{r}) - \mu \left(\int d\mathbf{r} \rho(\mathbf{r}) - N \right) \right] = 0. \tag{282}$$

$F[\rho]$ is separated into the kinetic energy $T[\rho]$ of the non-interacting electron gas with density ρ, the classical electrostatic potential, and the non-classical term due to exchange-correlation accounting for the difference between the kinetic energies of the interacting and non-interacting electrons, as follows:

$$F[\rho] = T[\rho] + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{XC}[\rho]. \tag{283}$$

The first two terms are simple and 'classical' while the third term describes the complex behaviour of correlated electrons and is usually approximated by using proper interpolation between asymptotic limits.

Substituting Eq. (283) into Eq. (282), we obtain:

$$\frac{\delta T[\rho]}{\delta \rho(\mathbf{r})} + V_{KS}(\mathbf{r}) = \mu, \tag{284}$$

where the Kohn-Sham potential $V_{KS}(\mathbf{r})$ is defined, as follows:

$$V_{KS}(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{XC}(\mathbf{r}) + V(\mathbf{r}). \tag{285}$$

Here, we have introduced the exchange-correlation potential $V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[\rho]}{\delta \rho(\mathbf{r})}$.

Equation (284) is equivalent to the description of a system of non-interacting electrons in an external potential $V_{KS}(\mathbf{r})$ for which the ground state can be found by solving the one-electron Schrödinger equation:

$$H_{KS}\psi_j(\mathbf{r}) = E_j \psi_j(\mathbf{r}), \tag{286}$$

where we have introduced the *Kohn-Sham orbitals* ψ_j that are eigenstates of the DFT Hamiltonian,

$$H_{KS} = -\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}). \tag{287}$$

The density can be computed, as follows:

$$\rho(\mathbf{r}) = 2 \sum_{j=1}^{N/2} \psi_j(\mathbf{r})^* \psi_j(\mathbf{r}), \tag{288}$$

after obtaining the *Kohn-Sham orbitals*. However, to obtain the *Kohn-Sham orbitals* we need the density since, according to Eq. (285), $V_{KS}(\mathbf{r})$ depends on the density $\rho(\mathbf{r})$. So, it is necessary to

solve Eq. (286) self-consistently. Having an initial guess for the density, approximate Kohn-Sham orbitals ψ_j are found by solving Eq. (286) and the density $\rho(\mathbf{r})$ is updated according to Eq. (288). The procedure is repeated multiple times until the input and output densities are the same.

The total energy of the system of interacting electrons,

$$E = T[\rho] + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int d\mathbf{r}\rho(\mathbf{r})V(\mathbf{r}) + E_{XC}[\rho], \tag{289}$$

can be computed from the energy $E^{non-int}$ of the non-interacting system,

$$\begin{aligned} E^{non-int} = 2\sum_{j=1}^{N/2} E_j &= T[\rho] + \int d\mathbf{r}\rho(\mathbf{r})V_{KS}(\mathbf{r}), \\ &= T[\rho] + \int d\mathbf{r}\int d\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int d\mathbf{r}\rho(\mathbf{r})[V_{XC}(\mathbf{r}) + V(\mathbf{r})], \end{aligned} \tag{290}$$

as follows:

$$E = E^{non-int} - \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \int d\mathbf{r}\rho(\mathbf{r})V_{XC}(\mathbf{r}) + E_{XC}[\rho]. \tag{291}$$

42.3 Thomas-Fermi Functional

The Thomas-Fermi model functional assumes a uniform distribution of electrons in phase space, with 2 electrons per element of phase-space volume h^3. According to such uniform phase-space distribution, the number of electrons $\Delta N(\mathbf{r})$ in a volume ΔV at $\mathbf{r}$ is

$$\Delta N(\mathbf{r}) = \frac{2}{h^3}\Delta V\frac{4}{3}\pi p_F(\mathbf{r})^3, \tag{292}$$

where $p_F(\mathbf{r})$ is the maximum value of momentum for electrons in ΔV, as determined by the local density $\rho(\mathbf{r})$, as follows:

$$\rho(\mathbf{r}) = \frac{2}{h^3}\frac{4}{3}\pi p_F(\mathbf{r})^3. \tag{293}$$

The local density $\rho(\mathbf{r})$ also determines the *Wigner-Seitz radius* $r_s(\mathbf{r})$, defined as the radius of a sphere with the mean volume per electron (or, mean volume per atom in metals where each atom contributes with a single electron to the electronic structure of interest), as follows:

$$\frac{4}{3}\pi r_s^3 = \rho(\mathbf{r}). \tag{294}$$

The fraction of electrons with momentum between p and $p+dp$ is $4\pi p^2 dp/(\frac{4}{3}\pi p_F(\mathbf{r})^3)$, since $4\pi p^2$ is the surface of a sphere of momentum p, while $4\pi p^2 dp$ is the volume between the surfaces of

momentum p and $p+dp$ and $4/3\pi p_F^3$ is the total volume of mometum in the element of phase-space volume h^3. Therefore, the kinetic energy per unit volume is

$$\begin{aligned} T(\mathbf{r}) &= \rho(\mathbf{r}) \int_0^{p_F} dp \frac{p^2}{2m_e} \frac{4\pi p^2}{\frac{4}{3}\pi p_F(\mathbf{r})^3}, \\ &= \int_0^{p_F} dp \frac{p^2}{2m_e} \frac{8\pi p^2}{h^3}, \\ &= \frac{p_F^5}{10m_e} \frac{8\pi}{h^3}, \\ &= \left(\frac{3h^3\rho(\mathbf{r})}{8\pi}\right)^{5/3} \frac{1}{10m_e} \frac{8\pi}{h^3}, \\ &= \left(\frac{3}{8\pi}\right)^{2/3} \frac{3h^2}{10m_e} \rho(\mathbf{r})^{5/3}. \end{aligned} \tag{295}$$

giving the total kinetic energy as a functional of the density,

$$T = \left(\frac{3}{8\pi}\right)^{2/3} \frac{3h^2}{10m_e} \int d\mathbf{r} \rho(\mathbf{r})^{5/3}. \tag{296}$$

The complete energy, can now be written as a functional of the density, as follows:

$$E[\rho] = \left(\frac{3}{8\pi}\right)^{2/3} \frac{3h^2}{10m_e} \int d\mathbf{r} \rho(\mathbf{r})^{5/3} + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \sum_{j=1}^{N_{nucl}} Z_j \int \frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}_j|} d\mathbf{r} + \cancel{E^{XC}[\rho]}. \tag{297}$$

The *Thomas-Fermi model functional* neglects the E_{XC} term in Eq (297). However, such an approximation usually introduces significant errors. For example, in the one-electron limit (i.e., for one-electron systems), $E_C = 0$. Therefore, $E_{XC} = E_X$, with $E_X = -U$ according to Hartree-Fock theory (see, Eq. (**??**)). Neglecting E_{XC} would thus introduce error since the self-interaction energy U would no longer cancel out with the exchange term. *Self-interaction corrections* (SIC) can be introduced to avoid that error. The earliest SIC was proposed by E. Fermi and E. Amaldi [Accad. Ital. Rome 6, 119 (1934)], who replaced $U[\rho]$ by $U[\rho] - NU[\rho/N]$, where N is the number of electrons in the system, giving the so-called *Thomas-Fermi-Amaldi* (TFA) functional:

$$E^{TFA} = \left(\frac{3}{8\pi}\right)^{2/3} \frac{3h^2}{10m_e} \int d\mathbf{r} \rho(\mathbf{r})^{5/3} + \frac{1}{2}\frac{N-1}{N} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \sum_{j=1}^{N_{nucl}} Z_j \int \frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}_j|} d\mathbf{r}. \tag{298}$$

42.4 Local Density Approximation

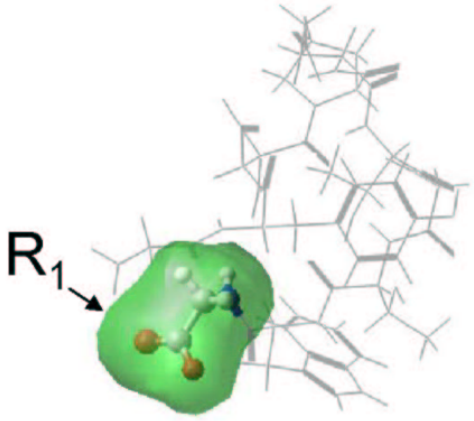
The local density approximation (LDA) states that if the charge density is sufficiently slowly varying, the exchange correlation energy is approximately

$$E_{XC}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) E_{XC}^{HEG}(\rho(\mathbf{r})), \tag{299}$$

where $E_{XC}^{HEG}(\rho(\mathbf{r}))$ is the exchange-correlation energy of a homogeneous electron gas (HEG) with the same local charge density $\rho(\mathbf{r})$.

43 Quantum Mechanics/Molecular Mechanics Methods

A practical approach for describing the electronic structure of a molecular fragment in a complex molecular environment is the so-called quantum mechanics/molecular mechanics (QM/MM) approach, where the environment (represented by sticks in the figure) is described in terms of a sum of classical potentials V_{MM} described by a molecular mechanics (MM) force field, while the molecular fragment (R_1 in the Figure below) is described by quantum chemistry (QM) methods, as for example by a Slater determinant obtained according to the Hartree-Fock method. The interaction



between the molecular fragment and the environment is usually defined as the sum of the electrostatic interaction between the atomic charges of the environment and the nuclear and electronic charges in molecular fragment. If the fragment is covalently bound to the environment, the bond is broken and the covalency is completed with a link atom (usually a H atom).

The interaction between the fragment and the environment is included as an additional term in the one-electron core Hamiltonian $\hat{h}^{(1)}$, as follows:

$$\hat{h}^{(i)} = -\frac{\hbar^2}{2m_e}\nabla^2_{r_i} - \sum_{j=1}^{N}\frac{z_j e^2}{r_{ji}} + \sum_{j=1}^{N}\sum_{j'=1}^{N}\frac{z_{j'} z_j e^2}{r_{jj'}} + \hat{h}^{(i)}_{QM/MM}, \tag{300}$$

with

$$\hat{h}^{(i)}_{QM/MM} = -\sum_{k=1}^{N_e}\frac{z_k e^2}{r_{ki}} + \sum_{j=1}^{N}\sum_{k=1}^{N_e}\frac{z_k z_j e^2}{r_{ki}} + \sum_{k=1}^{N_e} V_{vdw}(r_{ki}), \tag{301}$$

where we have considered a molecular fragment with N nuclei embedded in an environment with N_e electrostatic potential atomic charges. The third term in Eq. (301) is a van der Waals potential that accounts for the interaction of the electrons in the molecular fragment with electrons in the environment that are not explicitly considered. Implementing the Hartree-Fock method with the one-electron core-Hamiltonian, introduced by Eq. (300), we obtain the Hartree Fock energy E_{QM} of the molecular fragment in the electrostatic field of the surrounding environment yielding the total QM/MM energy of the system, as follows:

$$E^{QM/MM} = E_{QM} + V_{MM}. \tag{302}$$

In this simple form, the molecular fragment is polarized by the surrounding environment. Polarization of the environment due to the distribution of charges in the molecular fragment can be included by using a polarizable molecular mechanics force field, or a moving domain QM/MM approach, where the charges in the environment are obtained self-consistently.

Another QM/MM approach is the ONIOM methodology, as implemented in Gaussian, where the total energy is computed, as follows:

$$E^{ONIOM} = E_{QM} + V_{MM}^{system} - V_{MM}^{fragment}, \tag{303}$$

where V_{MM}^{system} and $V_{MM}^{fragment}$ are the energies of the complete system and the fragment as described by the molecular mechanics force field.

The force fields are usually parametrized to match the experimental or ab-initio ground state potential energy surfaces as a function of nuclear coordinates. The following section illustrates the parametrization of the potential energy surface for diatomic molecules.

44 Empirical Parametrization of Diatomic Molecules

The main features of chemical bonding by electron pairs are properly described by the HL model of H_2. 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

$$^1E_+ = <^1 \psi_{HL}|H|^1\psi_{HL}> = \frac{J+K}{1+S^2},$$

where $H = h(1) + h(2) + e^2/r_{12}$, with

$h(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}}$,

$h(2) = -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}}$,

$J = < \chi_A(1)\chi_B(2)|H|\chi_A(1)\chi_B(2) >$ Coulomb integral

$K = < \chi_A(1)\chi_B(2)|H|\chi_A(2)\chi_B(1) >$ Exchange integral

$S^2 = < \chi_A(1)\chi_B(2)|\chi_A(2)\chi_B(1) >$.

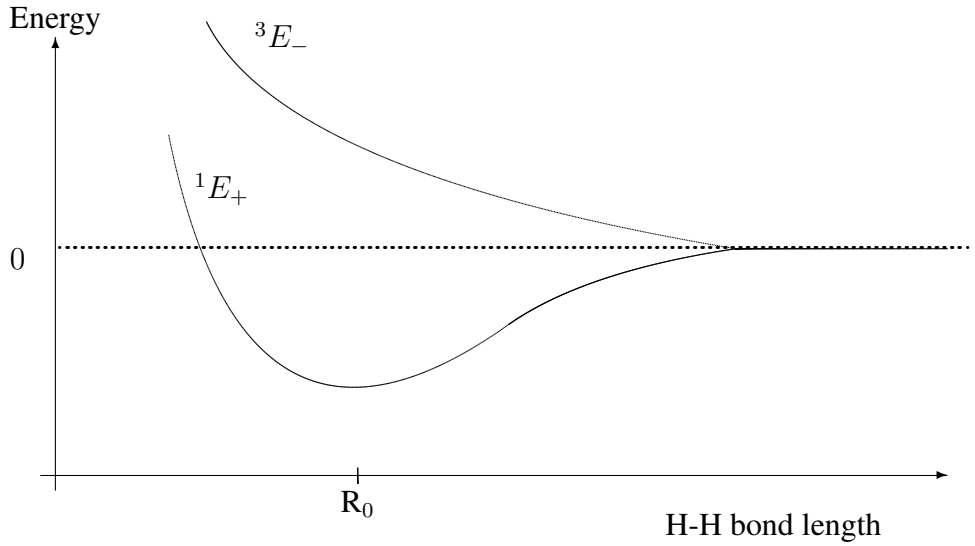
Similarly, the triplet state is described as follows,

$$^3\psi_{HL} = N_3[\chi_A(1)\chi_B(2) - \chi_B(1)\chi_A(2)] \begin{cases} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \end{cases},$$

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:

$$^1E_+ \approx D\left[e^{-2a(R-R_0)} - 2e^{-a(R-R_0)}\right] \equiv M(R),$$

$$^3E_- \approx \frac{D}{2}\left[e^{-2a(R-R_0)} + 2e^{-a(R-R_0)}\right] \equiv M^*(R).$$

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

$\psi_1 = [\alpha(1)\beta(2) - \beta(1)\alpha(2)](\chi_A(1)\chi_B(2) + \chi_A(2)\chi_B)$,

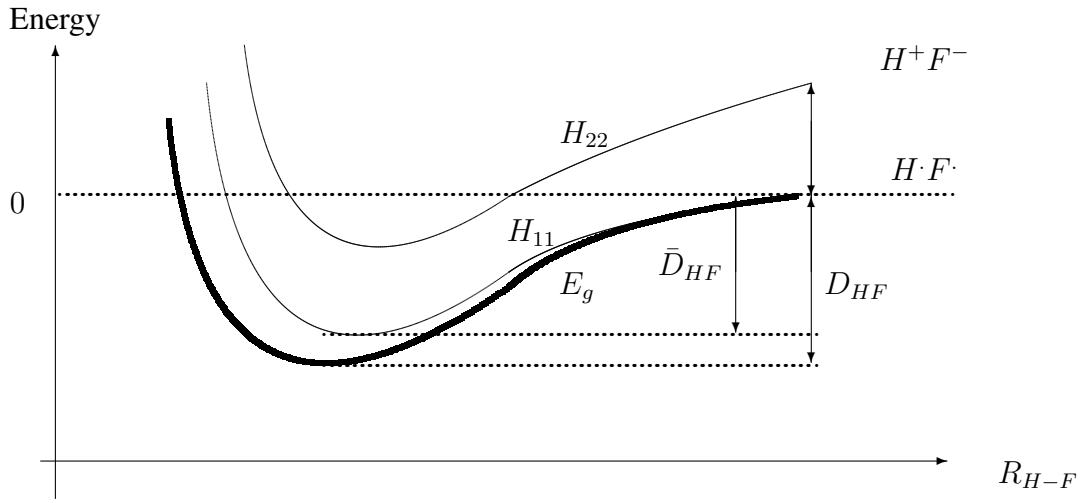
and the ionic wave function is

$\psi_2 = [\alpha(1)\beta(2) - \beta(1)\alpha(2)][\chi_A(1)\chi_A(2)\xi_1 + \chi_B(1)\chi_B(2)(1-\xi_1)]$,

where the parameter ξ_1 is determined by the relative electronegativity of the two atoms. For example, consider the HF molecule. For such molecule ξ_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,

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} = 0. \tag{304}$$

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 $\bar{D}_{HF} = \sqrt{D_{HH}D_{FF}}and\delta = 0.05\mathring{A}$. 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,

$$\mu_g = < \psi_g|\hat{\mu}|\psi_g >,$$

where

$$\hat{\mu} = -\sum_i er_i + \sum_j ez_j R_j.$$

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,

$$\mu_g = C_1^2 \underbrace{< \psi_1|\hat{\mu}|\psi_1 >}_{0} + C_2^2 \underbrace{< \psi_2|\hat{\mu}|\psi_2 >}_{eR_0} + 2C_1C_2 \underbrace{< \psi_1|\hat{\mu}|\psi_2 >}_{0},$$

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.

44.1 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),

D=134; $\bar{D}$=61; R_0=0.92; a=2.27;
A=640; b=2.5; C=20; I=313; EA=83.

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,

$$E'_g = \frac{1}{2}\left[(H'_{22} + H_{11}) - ((H'_{22} - H_{11}) + 4H_{12}^2)^{1/2}\right].$$

44.2 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,

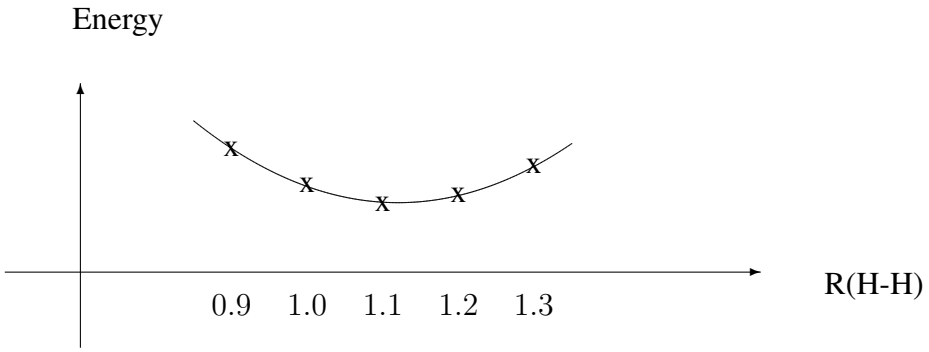
#hf/6-31G scan

potential scan for H_2

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:


Energy
R(H-H)
0.9
1.0
1.1
1.2
1.3

45 Discrete Variable Representation

The goal of this section is to introduce a generic discrete variable representation (DVR) method, introduced by Colbert and Miller [*J. Chem. Phys.* (1992) **96**:1982-1991] to solve the time-independent Schrödinger equation,

$$HC_j - C_j E_j = 0. \tag{305}$$

The method obtains the eigenstates $\chi_j(x)$ in a grid-based representation: $\chi(x) = \sum_j C_j \delta(x - x_j)$ and the corresponding eigenvalues E_j by simple diagonalization of the Hamiltonian matrix H by using standard numerical diagonalization methods –*e.g.*, TRED2, TQLI and EIGSRT, as described in Numerical Recipes (Ch. 11, Numerical Recipes), or Lanczos-type (iterative linear algebra methods) that exploit the sparsity of H. The representation is based on delta functions $\delta(x - x_j)$, equally spaced at coordinates x_j as follows:

$$x_j = x_{min} + j\Delta, \text{ with } \Delta = (x_{max} - x_{min})/N, \tag{306}$$

with j = 1–N.

The rest of this section shows that the Hamiltonian matrix elements can be written in such a discrete (grid-based) representation, as follows:

$$H(j,j') = V(x_j)\delta_{jj'} + \frac{\hbar^2}{2m\Delta^2}(-1)^{j-j'}\left(\delta_{jj'}\frac{\pi^2}{3} + (1-\delta_{jj'})\frac{2}{(j-j')^2}\right), \tag{307}$$

when the delta functions $\delta(x - x_j)$ are placed on a grid $x_j = j * \Delta$ that extends over the interval $x = (-\infty, \infty)$ with $j = 1, 2, ...$ Furthermore, we show that for the particular case of a radial coordinate, defined in the interval $x = (0, \infty)$, the Hamiltonian matrix elements are:

$$H(j,j') = V(x_j)\delta_{jj'} + \frac{\hbar^2}{2m\Delta^2}(-1)^{j-j'}\left(\delta_{jj'}\left(\frac{\pi^2}{3} - \frac{1}{2j^2}\right) + (1-\delta_{jj'})\left(\frac{2}{(j-j')^2} - \frac{2}{(j+j')^2}\right)\right). \tag{308}$$

To derive Eq. (307) and Eq. (308), we consider the Hamiltonian,

$$\hat{H} = \hat{T} + V(\hat{x}), \tag{309}$$

where $V(\hat{x})$ and $\hat{T} = \frac{\hat{p}^2}{2m}$ are the potential energy and kinetic energy operators, respectively. The potential energy matrix $V^{(\delta)}$ is diagonal, with matrix elements defined as follows:

$$\begin{aligned} V^{(\delta)}(j,k) &= \langle j|V(\hat{x})|k\rangle = \int dx \delta^*(x - x_j)V(\hat{x})\delta(x - x_k), \\ &= V(x_k)\delta_{j,k}. \end{aligned} \tag{310}$$

The kinetic energy matrix $T^{(\delta)}$ is expressed in the same grid-based representation, by first obtaining the kinetic energy matrix $T^{(\phi)}$ in the representation of eigenstates $\phi_n(x)$ of the particle in the box

$x = (x_{min}, x_{max})$, and then rotating $T^{(\phi)}$ to the representation of delta functions by using the following similarity transformation:

$$T^{(\delta)} = \Gamma^{-1} T^{(\phi)} \Gamma, \tag{311}$$

where Γ is the transformation matrix defined by the linear combinations,

$$\phi_k(x) = \sum_j \Gamma(j,k)\delta(x - x_j)\Delta', \tag{312}$$

where

$$\Gamma(j,k) = \phi_k(x_j). \tag{313}$$

Considering that $1 = \int dx \phi_k^*(x)\phi_k(x) = (\Delta')^2 \int dx \sum_j \phi_k(x_j)\delta(x - x_j) \sum_{j'} \phi_k(x_{j'})\delta(x - x_{j'})$ we obtain that $\Delta' = \sqrt{\Delta}$ since $1 = (\Delta')^2/\Delta \sum_j \Delta \phi_k(x_j)\phi_k(x_j)$.

The eigenstates of the particle in the box are:

$$\phi_k(x) = \sqrt{\frac{2}{x_{max} - x_{min}}} \text{Sin}\left(k \frac{\pi(x - x_{min})}{(x_{max} - x_{min})}\right), \tag{314}$$

with $\phi_k(x_{min}) = 0$ and $\phi_k(x_{max}) = 0$. Therefore,

$$\hat{T}\phi_k(x) = \frac{(\hbar\pi k)^2}{2m}\phi_k(x), \tag{315}$$

and $T^{(\phi)}$ is diagonal with matrix elements,

$$\hat{T}^{(\phi)}(j,k) = \langle \phi_j | \hat{T} | \phi_k \rangle = \frac{(\hbar k)^2}{2m} \frac{\pi^2}{(x_{max} - x_{min})^2} \delta_{jk}. \tag{316}$$

Therefore, substituting Eq. (316) and Eq. (313) into Eq. (311) we obtain,

$$\begin{aligned} T^{(\delta)}(i,i') &= \sum_{j,k=1}^{N-1} \Gamma^{-1}(i,j) T^{(\phi)}(j,k) \Gamma(k,i') = \sum_{j,k=1}^{N-1} \Gamma(j,i) T^{(\phi)}(j,k) \Gamma(k,i'), \\ &= \frac{\Delta\pi^2}{(x_{max} - x_{min})^2} \sum_{j,k=1}^{N-1} \phi_j(x_i) \frac{(\hbar k)^2}{2m} \delta_{jk} \phi_k(x_i') = \frac{\Delta\pi^2}{(x_{max} - x_{min})^2} \sum_{k=1}^{N-1} \phi_k(x_i) \frac{(\hbar k)^2}{2m} \phi_k(x_i'), \\ &= \frac{\Delta\hbar^2\pi^2}{2m(x_{max} - x_{min})^2} \frac{2}{(x_{max} - x_{min})} \sum_{k=1}^{N-1} k^2 \text{Sin}\left(k\pi \frac{(x_i - x_{min})}{(x_{max} - x_{min})}\right) \text{Sin}\left(k\pi \frac{(x_{i'} - x_{min})}{(x_{max} - x_{min})}\right). \end{aligned} \tag{317}$$

Finally, substituting Eq. (306) into Eq. (317) we obtain:

$$T^{(\delta)}(j,j') = \frac{\hbar^2\pi^2}{2m(x_{max} - x_{min})^2} \frac{2}{N} \sum_{k=1}^{N-1} k^2 \text{Sin}\left(\frac{k\pi j}{N}\right) \text{Sin}\left(\frac{k\pi j'}{N}\right). \tag{318}$$

To calculate the finite series introduced by Eq. (318) we first note that,

$$\begin{aligned} 2\text{Sin}\left(\frac{k\pi j}{N}\right)\text{Sin}\left(\frac{k\pi j'}{N}\right) &= \text{Cos}\left(\frac{k\pi(j-j')}{N}\right) - \text{Cos}\left(\frac{k\pi(j+j')}{N}\right), \\ &= Re\left[\text{Exp}\left(i\frac{k\pi(j-j')}{N}\right) - \text{Exp}\left(i\frac{k\pi(j+j')}{N}\right)\right]. \end{aligned} \tag{319}$$

so that Eq. (318) can be written as follows:

$$T^{(\delta)}(j,j') = \frac{\hbar^2\pi^2}{2m(x_{max}-x_{min})^2}\frac{2}{N}\left[\text{Re}\sum_{k=1}^{N-1}k^2\text{Exp}\left(i\frac{k\pi(j-j'}{N}\right) - \text{Re}\sum_{k=1}^{N-1}k^2\text{Exp}\left(i\frac{k\pi(j+j')}{N}\right)\right]. \tag{320}$$

Then, we consider the geometric series $S_N = \sum_{k=0}^{N-1} x^k$ and we note that $S_N - xS_N = 1 - x^N$, therefore $S_N = (1-x^N)/(1-x)$. Also, we note that

$$\begin{aligned} x\frac{\partial}{\partial x}\sum_{k=0}^{N-1}x^k &= \sum_{k=0}^{N-1}kx^k, \\ x^2\frac{\partial^2}{\partial x^2}\sum_{k=0}^{N-1}x^k &= \sum_{k=0}^{N-1}k^2x^k - \sum_{k=0}^{N-1}kx^k, \end{aligned} \tag{321}$$

Therefore,

$$\sum_{k=1}^{N-1}k^2x^k = x^2\frac{\partial^2}{\partial x^2}\left(\frac{(1-x^N)}{(1-x)}\right) + x\frac{\partial}{\partial x}\left(\frac{(1-x^N)}{(1-x)}\right). \tag{322}$$

We evaluate the sums over k in Eq. (320) analytically to obtain:

$$T^{(\delta)}(j,j') = \frac{\hbar^2(-1)^{j-j'}}{2m(x_{max}-x_{min})^2}\frac{\pi^2}{2}\left[\frac{1}{\text{Sin}^2[\pi(j-j')/(2N)]} - \frac{1}{\text{Sin}^2[\pi(j+j')/(2N)]}\right], \tag{323}$$

for $j \neq j'$ and

$$T^{(\delta)}(j,j) = \frac{\hbar^2}{2m(x_{max}-x_{min})^2}\frac{\pi^2}{2}\left[\frac{(2N^2+1)}{3} - \frac{1}{\text{Sin}^2[\pi j/N]}\right]. \tag{324}$$

Equation (307) is obtained from Eq. (323) and Eq. (324), by taking the limit $x_{min} \to -\infty$, $x_{max} \to \infty$, at finite Δ. This requires $N \to \infty$. Furthermore, since $\Delta(j+j') = x_j + x_{j'} - 2x_{min}$ and $\Delta(j-j') = x_j - x_{j'}$, this limit implies $(j+j') \to \infty$ while $(j-j')$ remains finite.

Equation (308) is obtained from Eq. (323) and Eq. (324), by making $x_{min} = 0$, and taking the limit $x_{max} \to \infty$, at finite Δ. This requires $N \to \infty$. In this case, $\Delta(j+j') = x_j + x_{j'}$ and $\Delta(j-j') = x_j - x_{j'}$, and therefore both $(j+j')$ and $(j-j')$ remain finite.

45.1 Multidimensional DVR

The multidimensional version of the DVR is straightforward. For example, for three Cartesian degrees of freedom (x,y,z), the Hamiltonian matrix is defined, as follows:

$$H(ijk, i'j'k') = T_{ii'}\delta_{jj'}\delta_{kk'} + T_{jj'}\delta_{ii'}\delta_{kk'} + T_{kk'}\delta_{ii'}\delta_{jj'} + V(x_i, x_j, x_k)\delta_{ii'}\delta_{jj'}\delta_{kk'}. \quad (325)$$

A simple implementation of the multidimensional Hamiltonian, introduced by Eq. (325), reduces the three indices i, j, k to a single index $l = (j-1)n_k n_i + (i-1)n_k + k$ and the three indices i', j', k' to a single index $l' = (j'-1)n_k n_i + (i'-1)n_k + k'$. The three indices i, j, k can be calculated from l, by using the modulo function em mod, as follows: $k = mod(l, (n_k * n_i)$, giving the remainder after division of l by $n_k * n_i$. Analogously, $i = 1 + mod(l-k, n_k)$ and $j = 1 + abs(l-(i-1)n_k - k)$ where n_i, n_j and n_k are the number of grid points representing x, y and z, respectively.

45.2 Computational Problem 15

15.1 Write a program to solve the time independent Schrödinger equation by using the DVR method and apply it to find the first 4 eigenvalues and eigenfunctions of the Harmonic oscillator introduced by Eq. (28) with $m = 1$ and $\omega = 1$. Verify that the eigenvalues are $E(\nu) = (1/2 + \nu)\hbar\omega$, $\nu = 0$–10.
15.2 Change the potential of the code written in 15.1 to that of a Morse oscillator $V(\hat{x}) = De(1 - \exp(-a(\hat{x} - x_e)))^2$, with $x_e = 0$, $De = 8$, and $a = \sqrt{k/(2De)}$, where $k = m\omega^2$, and recompute the eigenvalues and eigenfunctions.
15.3 Generalize the program developed in 15.1 to solve the 2-dimensional Harmonic oscillator $V(x, y) = 1/2m\omega^2(x^2 + y^2)$ and apply it to find the first 4 eigenvalues and eigenfunctions of the Harmonic oscillator introduced by Eq. (28) with $m = 1$ and $\omega = 1$. Verify that the eigenvalues are $E(\nu) = (1 + \nu_1 + \nu_2)\hbar\omega$.
15.4 Change the potential of the code written in 15.3 to that of a 2-dimensional Morse oscillator $V(\hat{x}, \hat{y}) = De(1 - \exp(-a(\hat{x} - x_e)))^2 + De(1 - \exp(-a(\hat{y} - x_e)))^2$, with $x_e = 0$, $De = 8$, and $a = \sqrt{k/(2De)}$, where $k = m\omega^2$, and recompute the eigenvalues and eigenfunctions.
15.5 Propagate a 1-d or 2-d wavepacket, initialized as a superposition of ground ψ_0 and first excited state ψ_1, $\psi(0) = 1/\sqrt{2}\psi_0 - 1/\sqrt{2}\psi_1$ of the 1-d or 2-d Morse oscillator defined in 15.2 and 15.3, by using the DVR Hamiltonian of item 15.4 and the Lanczos propagation scheme in the Krylov basis as implemented in *Expokit* . Compare your results with the analytic solution, based on the eigenvalues and eigenvectors: $\psi(t) = 1/\sqrt{2}\psi_0 \exp(-iE_0 t) - 1/\sqrt{2}\psi_1 \exp(-iE_1 t)$.

46 Tunneling Current: Landauer Formula

We consider a 1-dimensional electron tunneling

$$\hat{H}\psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + eV(x)\right]\psi, \tag{326}$$

problem described by the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + eV(x), \tag{327}$$

where e is the charge of the electron and

$$V(x) = \begin{cases} V_l & \text{if} \quad x < 0, \\ V_b & \text{if} \quad 0 < x < a, \\ V_r & \text{if} \quad x > a, \end{cases} \tag{328}$$

where V_b defines the tunneling barrier, and $\Delta V = (V_l - V_r)$ defines the voltage drop across the barrier. Outside the tunneling interval $x_l < x < x_r$, the solutions of the Schrödinger equation are superpositions of plane waves since the potential is constant. For energy $E > eV_l$ and $E > eV_r$, there are two independent solutions ψ_l and ψ_r for incident electrons from the left and from the right, respectively.

Considering the solution for incidence from the left, we obtain:

$$\psi_l(x) = \begin{cases} \phi_l^+ + r_l\phi_l^- & \text{if} \quad x < 0 \\ Ae^{ik_b x} + Be^{-ik_b x} & \text{if} \quad 0 < x < a \\ t_r\phi_r^+ & \text{if} \quad x > a \end{cases} \tag{329}$$

where $\phi_j^{\pm} = k_j^{-1/2}e^{\pm ik_j x}$, are defined divided by the square root of k_j so they are normalized to carry the unit of current density $\hbar/m$, as shown below). The labels $j = l, r$ indicate the left (l) and right (r) side of the barrier, $k_l = \sqrt{2m(E - eV_l)/\hbar^2}$ and $k_r = \sqrt{2m(E - eV_r)/\hbar^2}$.

Applying the continuity conditions for ψ_l and $\partial\psi_l/\partial x$ at $x = 0$ and $x = a$, we obtain:

$$\begin{aligned} k_l^{-1/2} + k_l^{-1/2}r_l &= A + B, \\ Ae^{ik_b a} + Be^{-ik_b a} &= k_r^{-1/2}t_r e^{ik_r a}, \\ k_l^{1/2}(1 - r_l) &= k_b(A - B), \\ k_b(Ae^{ik_b a} - Be^{-ik_b a}) &= k_r^{1/2}t_r e^{ik_r a}. \end{aligned} \tag{330}$$

The transmission amplitude t_r, reflection amplitude r_l and coefficients A and B can be obtained by solving for them from Eq. (330).

The probability flux (or current density) of incoming electrons from the left, described by the incident wave $\psi_i(x,t) = k_l^{-1/2}e^{i(k_l x - wt)}$ with momentum k_l and energy $E(k_l) = eV_l + \hbar^2 k_l^2/(2m)$, is:

$$j_i(x,t) = \frac{\hbar}{2mi}\left(\psi_i^*(x,t)\frac{\partial\psi_i(x,t)}{\partial x} - \psi_i(x,t)\frac{\partial\psi_i^*(x,t)}{\partial x}\right), \tag{331}$$

or

$$\begin{aligned} j_i(x) &= \frac{1}{2}\psi_i^*(x,t)\left(-i\frac{\hbar}{m}\frac{\partial}{\partial x}\right)\psi_i(x,t) + c.c., \\ &= \frac{1}{2}\psi_i^*(x,t)\frac{\hat{p}}{m}\psi_i(x,t) + c.c., \\ &= \text{Re}[\psi_i^*(x,t)\hat{v}\psi_i(x,t)] = \frac{\hbar}{m}. \end{aligned} \tag{332}$$

The flux of transmitted electrons described by transmitted wave $\psi_t(x,t) = t_r k_r^{-1/2} e^{i(k_r x - wt)}$, with momentum k_r and energy $E(k_r) = eV_r + \hbar^2 k_r^2/(2m)$, is:

$$\begin{aligned} j_t(x) &= \frac{1}{2}\psi_t^*(x,t)\left(-i\frac{\hbar}{m}\frac{\partial}{\partial x}\right)\psi_t(x,t) + c.c., \\ &= |t_r|^2\frac{\hbar}{m}. \end{aligned} \tag{333}$$

Therefore, the transmission coefficient $T_l = j_t/j_i$, defined as the transmitted flux j_t over the incident flux at energy E is: $T_l = |t_r|^2$. The reflection coefficient $R_l = 1 - T_l$ is the reflected flux over the incident flux.

Analogously, we consider incidence from the right of the tunneling barrier, as follows:

$$\psi_r(x) = \begin{cases} \phi_r^- + r_r\phi_r^+ & \text{if} \quad x > a \\ Ae^{ik_b x} + Be^{-ik_b x} & \text{if} \quad 0 < x < a \\ t_l\phi_l^- & \text{if} \quad x < 0 \end{cases} \tag{334}$$

Solving for t_l, we obtained the transmission coefficient $T_r = |t_l|^2$, due to incidence from the right.

More generally, we can consider incoming waves from both left *and* right (ϕ_l^+ and ϕ_r^-, respectively) with amplitudes $\mathbf{c}_{in} = c_{in}^{(l)}, c_{in}^{(r)}$ that generate outgoing waves to the left and right (ϕ_l^- and ϕ_r^+, respectively) with amplitudes $\mathbf{c}_{out} = c_{out}^{(l)}, c_{out}^{(r)}$. The amplitudes of outgoing and incoming waves are related by the linear transformation defined by the scattering matrix (or, 'S-matrix') $\mathbf{S}$, as follows: $\mathbf{c}_{out} = \mathbf{S}\mathbf{c}_{in}$:

$$\begin{pmatrix} c_{out}^l \\ c_{out}^r \end{pmatrix} = \begin{pmatrix} r_l & t_l \\ t_r & r_r \end{pmatrix}\begin{pmatrix} c_{in}^l \\ c_{in}^r \end{pmatrix} \tag{335}$$

Due to the conservation of probability, the S-matrix must be unitary: $\mathbf{S}^{-1} = \mathbf{S}^\dagger$. Therefore, $\mathbf{S}\mathbf{S}^\dagger = 1$:

$$\begin{pmatrix} r_l & t_l \\ t_r & r_r \end{pmatrix}\begin{pmatrix} r_l^\dagger & t_r^\dagger \\ t_l^\dagger & r_r^\dagger \end{pmatrix} = 1 \tag{336}$$

which gives

$$r_l r_l^\dagger + t_l t_l^\dagger = 1. \tag{337}$$

In addition, $\mathbf{S}^\dagger\mathbf{S} = 1$:

$$\begin{pmatrix} r_l^\dagger & t_r^\dagger \\ t_l^\dagger & r_r^\dagger \end{pmatrix} \begin{pmatrix} r_l & t_l \\ t_r & r_r \end{pmatrix} = 1 \tag{338}$$

which gives

$$t_l^\dagger t_l + r_r^\dagger r_r = 1 \tag{339}$$

Therefore, according to Eqs. (337) and (339), we obtain: $1 - t_l t_l^\dagger = r_l r_l^\dagger = r_r^\dagger r_r$. For our 1-dimensional case, we obtain:

$$|r_l|^2 = |r_r|^2 = R. \tag{340}$$

Under stationary state, $\partial\rho/\partial t = 0$, with $\rho = |\psi^*\psi|$. Then, according to the continuity equation $\partial\rho/\partial t = -\partial j/\partial x$, we obtain: $\partial j/\partial x = 0$. Therefore, j_l for $x < 0$ must be equal to j_l for $x > a$. Also, j_r for $x < 0$ must be equal to j_r for $x > a$:

$$(1 - |r_l|^2) = |t_r|^2, \tag{341}$$

and

$$(1 - |r_r|^2) = |t_l|^2. \tag{342}$$

Dividing Eq. (341) by Eq. (342) and using (340), we obtain:

$$t_l = t_r. \tag{343}$$

Therefore,

$$\begin{aligned} T_l(E) &= |t_r|^2, \\ &= |t_l|^2 = T_r(E), \end{aligned} \tag{344}$$

so the transmission coefficient is the same for both directions of incidence and $R + T = 1$.

Considering that the number of electrons with energy E incident from the left and right of the barrier are $n_l(E)$ and $n_r(E)$, respectively, the net flux of charge from left to right is:

$$\begin{aligned} I &= 2e \int_0^\infty dk_l n_l(k_l) \frac{\hbar k_l}{m} T_l - 2e \int_0^\infty dk_r n_r(k_r) \frac{\hbar k_r}{m} T_r, \\ &= \frac{2e}{2\pi} \int_0^\infty dE\, T(E) \left(n_l(E) \frac{\hbar k_l}{m} \left| \frac{\partial k_l}{\partial E} \right| - n_r(E) \frac{\hbar k_r}{m} \left| \frac{\partial k_r}{\partial E} \right| \right), \\ &= \frac{2e}{2\pi} \int_0^\infty dE\, T(E) \left(n_l(E) \frac{\hbar k_l}{m} \left| \frac{m}{\hbar^2 k_l} \right| - n_r(E) \frac{\hbar k_r}{m} \left| \frac{m}{\hbar^2 k_r} \right| \right), \\ &= \frac{2e}{h} \int_0^\infty dE\, T(E) \left(n_l(E) - n_r(E) \right), \end{aligned} \tag{345}$$

where factor of 2 accounts for the two possible spin states, the first term on the r.h.s. accounts for the forward flux (i.e., from left to right) and the second term accounts for the backward flux

(i.e., from right to left). Note that in the second row of Eq. (345) we used the following equality: $\hat{1} = \int dE|E\rangle\langle E| = 2\pi \int dk|k\rangle\langle k|$.

At equilibrium, the population of energy levels is determined by the Fermi-Dirac distribution:

$$n(E) = \frac{1}{e^{\beta(E-E_F)}+1}, \tag{346}$$

where E_F is the Fermi level and the factor of 2 in the numerator accounts for the 2 possible spin states. Considering the potentials for electrons at either side of the barrier, we obtain $n_l(E) = n(E - eV_l)$ and $n_r(E) = n(E - eV_r)$. Therefore, we can expand these distributions, as follows:

$$\begin{aligned} n_l(E) &= n(E - E_F) + \frac{\partial n(E)}{\partial E} eV_l + \cdots, \\ n_r(E) &= n(E - E_F) + \frac{\partial n(E)}{\partial E} eV_r + \cdots, \end{aligned} \tag{347}$$

and write the Landauer formula, giving the current in the form of the Ohm's law, as follows:

$$\begin{aligned} I &= \frac{2e}{h} \int_0^\infty dE\, T(E)\, (n_l(E) - n_r(E))\,, \\ &= \frac{2e^2}{h} \int dE\, T(E) \frac{\partial n(E)}{\partial E} \Delta V, \\ &= G(E)\Delta V, \end{aligned} \tag{348}$$

where $G(E) = R^{-1} = G_0 \int dE\, T(E) \frac{\partial n(E)}{\partial E}$ is the conductance, or inverse of the resistance R, with $G_0 = \frac{2e^2}{h} = [12.906\ \mathrm{k}\Omega]^{-1}$ the quantum unit of conductance. Note that G_0 defines the maximum conductance (minimum resistance) per conduction channel with perfect transmission, $T(E) = 1$ (*i.e.*, if the transport through the channel is ballistic and therefore the probability for transmitting the electron that enters the channel is unity), as observed in experiments .

At low temperature (*i.e.*, $\beta \to \infty$), the Fermi-Dirac distributions become step functions $n_l(E) = 2H(E_F - (E - eV_l))$ and $n_r(E) = 2H(E_F - (E - eV_r))$, with $H(x)$ the Heaviside function equal to 1 for $x > 0$, and 0 for $x < 0$. Therefore, $\frac{\partial n(E)}{\partial E} = \delta(E_F - E)$, and

$$\begin{aligned} I &= \frac{2e^2}{h} \int dE\, T(E) \delta(E_F - E) \Delta V, \\ &= \frac{2e^2}{h}\, T(E_F) \Delta V. \end{aligned} \tag{349}$$

In this low-temperature limit, the conductance is the transmission times the quantum of conductance, $G(E) = \frac{2e^2}{h}\, T(E_F)$.

46.1 WKB Transmission

The goal of this subsection is to show that the transmission coefficient $T(E)$ can be estimated, under the WKB approximation, as follows:

$$T(E) = e^{-2\int_0^a dx \sqrt{2m|E-\xi(x)|/\hbar^2}}, \tag{350}$$

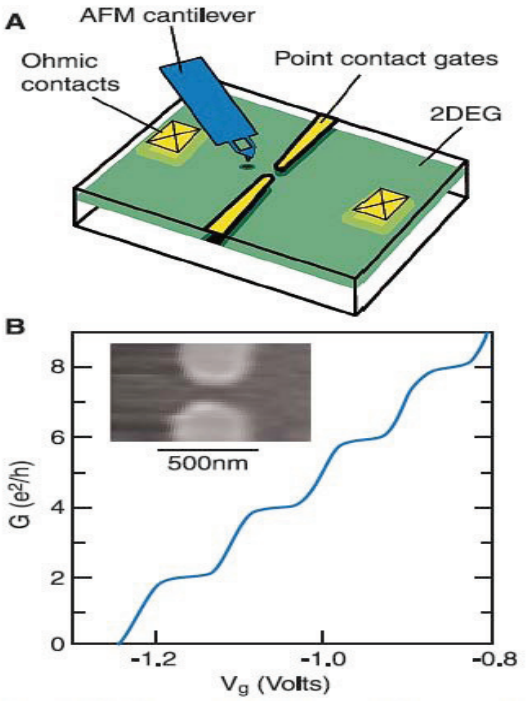


Fig. 1. (A) Schematic diagram of the experimental setup. QPC conductance is measured as a function of AFM tip position. **(B)** Point contact conductance G versus gate voltage V_g with no tip present at temperature $T = 1.7$ K. Plateaus at integer multiples of 2 e^2/h are clearly seen. The inset shows a topographic image of the point contact device.

where $\xi(x) = V_b$ describes the tunneling barrier according to Eq. (328).

To derive Eq. (350), we consider the WKB approximate solution of Eq. (327), with the following functional form:

$$\psi(x) = \psi_0 e^{i\int_0^x k(x')dx'}, \tag{351}$$

where $k(x) = \sqrt{2m[E - V(x)]/\hbar^2}$. Note that when $V(x)$ is constant, $\psi(x)$ corresponds to a particle moving to the right with constant momentum k. Substituting $\psi(x)$ as defined in Eq. (351), into Eq. (327), we obtain:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x) - \Delta, \tag{352}$$

with $\Delta = ik'(x)\frac{\hbar^2}{2m}\psi(x)$. Therefore, the WKB solution is a good approximation when $|k'(x)| << k(x)^2$.

According to the WKB solution, the probability density $|\psi(x)|^2$ remains constant on the left of the tunneling barrier, when $E > V_l$, since $\psi(x) = \psi(-\infty)e^{-i\int_{-\infty}^{x} dx' k_l}$ for $x < 0$. Inside the barrier, however, the probability density decays exponentially:

$$\psi(x) = \psi(0)e^{-\int_0^x dx'\sqrt{2m|E-\xi(x')|/\hbar^2}}, \tag{353}$$

since $E < \xi(x)$. In particular, at $x = a$, the probability density is

$$|\psi(x)|^2 = |\psi(0)|^2 e^{-2\int_0^a dx' |k(x')|}. \tag{354}$$

In the region with $x > a$, the probability density remains constant again since $\psi(x) = \psi(a)e^{-i\int_a^x dx' k_r}$ and $|\psi(x)|^2 = |\psi(a)|^2$. Therefore, estimating the transmission coefficient as the ratio of the probability densities to the right and to the left of the barrier, we obtain

$$\begin{aligned} T(E) &= \frac{|\psi(a)|^2}{|\psi(0)|^2}, \\ &= e^{-2\int_0^a dx \sqrt{2m|E-\xi(x)|/\hbar^2}}. \end{aligned} \tag{355}$$

47 Solutions to Computational Assignments

47.1 Problem 1

Computational Problem 1: Write a computer program to represent the wave-packet, introduced by Eq. (22) on a grid of equally spaced coordinates $x_j = x_{min} + (j-1)\Delta$ with finite resolution $\Delta = (x_{max} - x_{min})/(n-1)$ and visualize the output. Choose $x_0 = 0$ and $p_0 = 0$, in the range x=(-20,20), with $\alpha = \omega m$, where $m = 1$ and $\omega = 1$.

To visualize the output of this program, cut the source code attached below save it in a file named Problem1.f, compile it by typing

```
gfortran Problem1.f -o Problem1
```

run it by typing

```
./Problem1
```

Visualize the output as follows: type

```
gnuplot
```

then type

```
plot ``arch.0000''
```

That will show the representation of the Gaussian state, introduced in Eq. (6) in terms of an array of numbers associated with a grid in coordinate space. To exit, type

```
quit
```

Download from (http://ursula.chem.yale.edu/~batista/classes/summer/P1/Problem1.f) ,

```
      PROGRAM Problem_1
      call Initialize()
      CALL SAVEWF(0)
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE Initialize()
c
c     Wave Packet Initialization: Gaussian centered at xk, with momentum pk
c
      IMPLICIT NONE
      INTEGER nptx,npts,kk
      COMPLEX chi,EYE
      REAL omega,xmin,xmax,dx,pi,mass,xk,pk,x,alpha
      PARAMETER(npts=10,nptx=2**npts)
      COMMON / wfunc/ chi(nptx)
      common /xy/  xmin,xmax
      common /packet/mass,xk,pk
      xmin=-20.
      xmax=20.
      EYE=(0.0,1.0)
      pi= acos(-1.0)
      omega=1.
      dx=(xmax-xmin)/real(nptx)
      pk=0.0
      xk=0.0
      mass=1.0
      alpha=mass*omega
      do kk=1,nptx
         x=xmin+kk*dx
         chi(kk)=((alpha/pi)**0.25)
     1        *exp(-alpha/2.*(x-xk)**2+EYE*pk*(x-xk))
      end do
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE SAVEWF(j)
c
c     Save Wave-packet in coordinate space
c
      IMPLICIT NONE
      INTEGER nptx,npts,kk,j
      COMPLEX chi,EYE
      REAL RV,omega,xmin,xmax,dx,pi,mass,xk,pk,x,alpha,Vpot,RKE
      character*9 B
      PARAMETER(npts=10,nptx=2**npts)
      COMMON / wfunc/ chi(nptx)
      common /xy/  xmin,xmax
      common /packet/mass,xk,pk
      write(B, '(A,i4.4)') 'arch.', j
```

```
      OPEN(1,FILE=B)
      dx=(xmax-xmin)/real(nptx)
      do kk=1,nptx
         x=xmin+kk*dx
         WRITE(1,22) x,chi(kk)
      end do
      CLOSE(1)
 22   FORMAT(6(e13.6,2x))
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
```

47.2 Problem 2

Computational Problem 2: Write a computer program to represent the initial state, introduced by Eq. (22), in the momentum space by applying the FFT algorithm to the grid-based representation generated in Problem 1 and visualize the output. Represent the wave-packet amplitudes and phases in the range p=(-4,4) and compare your output with the corresponding values obtained from the analytic Fourier transform obtained by using:

$$\int dx \exp(-a_2 x^2 + a_1 x + a_0) = \sqrt{\pi/a_2} \exp(a_0 + a_1^2/(4a_2)).$$

In order to visualize the output of this program, cut the source code attached below save it in a file named Problem2.f, compile it by typing

```
gfortran Problem2.f -o Problem2
```

run it by typing

```
./Problem2
```

Visualize the output as follows: type

```
gnuplot
```

then type

```
plot ``nume.0000''
```

That will show the representation of the amplitude of the Fourier transform of the Gaussian state, introduced in Eq. (6), in terms of an array of numbers associated with a grid in momentum space. In order to visualize the analytic results on top of the numerical values type

```
replot ``anal.0000''
```

In order to visualize the numerically computed phases as a function of p type

```
plot ``nume.0000 u 1:3''
```

and to visualize the analytic results on top of the numerical values type

```
replot ``anal.0000''
```

To exit, type

```
quit
```

Download from (http://ursula.chem.yale.edu/~batista/classes/summer/P2/Problem2.f) ,

```
      PROGRAM Problem2
      call Initialize()
      CALL SAVEFT()
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE Initialize()
c
c     Wave Packet Initialization: Gaussian centered at xk, with momentum pk
c
      IMPLICIT NONE
      INTEGER nptx,npts,kk
      COMPLEX chi,EYE
      REAL omega,xmin,xmax,dx,pi,rmass,xk,pk,x,alpha
      PARAMETER(npts=10,nptx=2**npts)
      COMMON / wfunc/ chi(nptx)
      common /xy/  xmin,xmax
      common /packet/rmass,xk,pk
      xmin=-20.
      xmax=20.
      EYE=(0.0,1.0)
      pi= acos(-1.0)
      omega=1.
      dx=(xmax-xmin)/real(nptx)
      pk=0.0
      xk=5.0
      rmass=1.0
      alpha=rmass*omega
      do kk=1,nptx
         x=xmin+kk*dx
         chi(kk)=((alpha/pi)**0.25)
     1        *exp(-alpha/2.*(x-xk)**2+EYE*pk*(x-xk))
      end do
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine SAVEFT()
c
c     Save wave-packet in momentum space
c
      IMPLICIT NONE
      INTEGER nptx,kx,nx,npts,j
      REAL theta,wm,p,xmin,xmax,rmass,xk,pi,alenx,pk,rm,re,ri
      COMPLEX eye,chi,Psip
      character*9 B1,B2
      parameter(npts=10,nptx=2**npts)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
      COMMON / wfunc/ chi(nptx)
      j=0
```

```
      write(B1, '(A,i4.4)') 'anal.', j
      OPEN(1,FILE=B1)
      write(B2, '(A,i4.4)') 'nume.', j
      OPEN(2,FILE=B2)
      CALL fourn(chi,nptx,1,-1)
      pi = acos(-1.0)
      alenx=xmax-xmin
      do kx=1,nptx
         if(kx.le.(nptx/2+1)) then
            nx=kx-1
         else
            nx=kx-1-nptx
         end if
         p=0.
         if(nx.ne.0) p = real(nx)*2.*pi/alenx
c     Numerical Solution
         chi(kx)=chi(kx)*alenx/sqrt(2.0*pi)/nptx
         re=chi(kx)
         ri=imag(chi(kx))
         IF(re.NE.0) theta=atan(ri/re)
         rm=abs(chi(kx))
         IF(abs(p).LE.(4.)) WRITE(2,22) p,rm,theta
         IF(nx.EQ.(nptx/2)) WRITE(2,22)
c     Analytic Solution
         CALL FT_analy(Psip,p)
         re=Psip
         ri=imag(Psip)
         IF(re.NE.0) theta=atan(ri/re)
         rm=abs(Psip)
         IF(abs(p).LE.(4.)) WRITE(1,22) p,rm,theta
         IF(nx.EQ.(nptx/2)) WRITE(1,22)
      end do
      CALL fourn(chi,nptx,1,1)
 22   FORMAT(6(e13.6,2x))
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine FT_analy(Psip,p)
c
c     Analytic Fourier Transform of the initial Gaussian wave-packet
c
      IMPLICIT NONE
      REAL p,pi,alpha,rmass,xk,pk,omega
      COMPLEX Psip,c0,c1,c2,eye
      common /packet/  rmass,xk,pk
      eye=(0.0,1.0)
      omega=1.
      alpha = rmass*omega
      pi=acos(-1.0)
      c2=alpha/2.
      c1=alpha*xk+eye*(pk-p)
```

```
      c0=-alpha/2.*xk**2-eye*pk*xk
      Psip=sqrt(pi/c2)/sqrt(2.0*pi)*(alpha/pi)**0.25
     1     *exp(c1**2/(4.0*c2))*exp(c0)
      return
      end
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c     Subroutines from Numerical Recipes
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE FOURN(DATA,NN,NDIM,ISIGN)
      REAL*8 WR,WI,WPR,WPI,WTEMP,THETA
      DIMENSION NN(NDIM),DATA(*)
      NTOT=1
      DO 11 IDIM=1,NDIM
         NTOT=NTOT*NN(IDIM)
 11   CONTINUE
      NPREV=1
      DO 18 IDIM=1,NDIM
         N=NN(IDIM)
         NREM=NTOT/(N*NPREV)
         IP1=2*NPREV
         IP2=IP1*N
         IP3=IP2*NREM
         I2REV=1
         DO 14 I2=1,IP2,IP1
            IF(I2.LT.I2REV)THEN
               DO 13 I1=I2,I2+IP1-2,2
                  DO 12 I3=I1,IP3,IP2
                     I3REV=I2REV+I3-I2
                     TEMPR=DATA(I3)
                     TEMPI=DATA(I3+1)
                     DATA(I3)=DATA(I3REV)
                     DATA(I3+1)=DATA(I3REV+1)
                     DATA(I3REV)=TEMPR
                     DATA(I3REV+1)=TEMPI
 12               CONTINUE
 13            CONTINUE
            ENDIF
            IBIT=IP2/2
 1          IF ((IBIT.GE.IP1).AND.(I2REV.GT.IBIT)) THEN
               I2REV=I2REV-IBIT
               IBIT=IBIT/2
               GO TO 1
            ENDIF
            I2REV=I2REV+IBIT
 14      CONTINUE
         IFP1=IP1
 2       IF(IFP1.LT.IP2)THEN
            IFP2=2*IFP1
            THETA=ISIGN*6.28318530717959D0/(IFP2/IP1)
            WPR=-2.D0*DSIN(0.5D0*THETA)**2
            WPI=DSIN(THETA)
```

```
            WR=1.D0
            WI=0.D0
            DO 17 I3=1,IFP1,IP1
               DO 16 I1=I3,I3+IP1-2,2
                  DO 15 I2=I1,IP3,IFP2
                     K1=I2
                     K2=K1+IFP1
                     TEMPR=SNGL(WR)*DATA(K2)-SNGL(WI)*DATA(K2+1)
                     TEMPI=SNGL(WR)*DATA(K2+1)+SNGL(WI)*DATA(K2)
                     DATA(K2)=DATA(K1)-TEMPR
                     DATA(K2+1)=DATA(K1+1)-TEMPI
                     DATA(K1)=DATA(K1)+TEMPR
                     DATA(K1+1)=DATA(K1+1)+TEMPI
 15               CONTINUE
 16            CONTINUE
               WTEMP=WR
               WR=WR*WPR-WI*WPI+WR
               WI=WI*WPR+WTEMP*WPI+WI
 17         CONTINUE
            IFP1=IFP2
            GO TO 2
         ENDIF
         NPREV=N*NPREV
 18   CONTINUE
      RETURN
      END
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
```

47.3 Problem 3

Computational Problem 3: Write a computer program to compute the expectation values of the position $x(0) = \langle\Psi_0|\hat{x}|\Psi_0\rangle$ and the potential energy $V = \langle\Psi_0|V(\hat{x})|\Psi_0\rangle$, where $V(x)$ is defined according to Eq. (28) for the initial wave-packet, introduced by Eq. (22), with various possible values of x_0 and p_0, with $\alpha = \omega m$, where $m = 1$ and $\omega = 1$.

In order to visualize the output of this program, cut the source code attached below save it in a file named Problem3.f, compile it by typing

```
gfortran Problem3.f -o Problem3
```

run it by typing

```
./Problem3
```

The printout on the screen includes the numerically expectation values $\langle\Psi_t|\hat{V}|\Psi_t\rangle$ and $\langle\Psi_t|\hat{x}|\Psi_t\rangle$.

Download from (http://ursula.chem.yale.edu/~batista/classes/summer/P3/Problem3.f) ,

```
      PROGRAM Problem3
      IMPLICIT NONE
      REAL x,VENERGY
      CALL Initialize()
      CALL PE(VENERGY)
      CALL Px(x)
      PRINT *, "<Psi|V|Psi>=",VENERGY
      PRINT *, "<Psi|x|Psi>=",x
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE Initialize()
c
c     Wave Packet Initialization: Gaussian centered at xk, with momentum pk
c
      IMPLICIT NONE
      INTEGER nptx,npts,kk
      COMPLEX chi,EYE
      REAL omega,xmin,xmax,dx,pi,mass,xk,pk,x,alpha
      PARAMETER(npts=10,nptx=2**npts)
      COMMON / wfunc/ chi(nptx)
      common /xy/  xmin,xmax
      common /packet/mass,xk,pk
      xmin=-20.
      xmax=20.
      EYE=(0.0,1.0)
      pi= acos(-1.0)
      omega=1.
      dx=(xmax-xmin)/real(nptx)
      pk=0.0
      xk=0.0
      mass=1.0
      alpha=mass*omega
      do kk=1,nptx
         x=xmin+kk*dx
         chi(kk)=((alpha/pi)**0.25)
     1        *exp(-alpha/2.*(x-xk)**2+EYE*pk*(x-xk))
      end do
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE PE(RV)
c
c     Expectation Value of the Potential Enegy
c
      IMPLICIT NONE
      INTEGER nptx,npts,k
      COMPLEX chi
      REAL Vpot,RV,xmin,xmax,dx,x
      PARAMETER(npts=10,nptx=2**npts)
```

```
      COMMON / wfunc/ chi(nptx)
      common /xy/  xmin,xmax
      dx=(xmax-xmin)/real(nptx)
      RV=0.0
      do k=1,nptx
         x=xmin+k*dx
         CALL VA(Vpot,x)
         RV=RV+chi(k)*Vpot*conjg(chi(k))*dx
      end do
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE Px(RV)
c
c     Expectation Value of the position
c
      IMPLICIT NONE
      INTEGER nptx,npts,k
      COMPLEX chi
      REAL RV,xmin,xmax,dx,x
      PARAMETER(npts=10,nptx=2**npts)
      COMMON / wfunc/ chi(nptx)
      common /xy/  xmin,xmax
      dx=(xmax-xmin)/real(nptx)
      RV=0.0
      do k=1,nptx
         x=xmin+k*dx
         RV=RV+chi(k)*x*conjg(chi(k))*dx
      end do
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE VA(V,x)
c
c     Potential Energy Surface: Harmonic Oscillator
c
      IMPLICIT NONE
      REAL V,x,mass,xk,pk,rk,omega
      common /packet/ mass,xk,pk
      omega=1.0
      rk=mass*omega**2
      V=0.5*rk*x*x
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
```

47.4 Problem 4

Computational Problem 4: Write a computer program to compute the expectation values of the initial momentum $p(0) = \langle\Psi_0|\hat{p}|\Psi_0\rangle$ and the kinetic energy $T = \langle\Psi_0|\hat{p}^2/(2m)|\Psi_0\rangle$ by using the Fourier transform procedure, where Ψ_0 is the initial wave-packet introduced by Eq. (22), with $x_0 = 0$, $p_0 = 0$, and $\alpha = \omega m$, where $m = 1$ and $\omega = 1$. Compute the expectation value of the energy $E = \langle\Psi_0|\hat{H}|\Psi_0\rangle$, where $\hat{H} = \hat{p}^2/(2m) + V(\hat{x})$, with $V(x)$ defined according to Eq. (28) and compare your result with the zero-point energy $E_0 = \omega/2$.

In order to visualize the output of this program, cut the source code attached below save it in a file named Problem4.f, compile it by typing

```
gfortran Problem4.f -o Problem4
```

run it by typing

```
./Problem4
```

The printout on the screen includes the numerically expectation values $\langle\Psi_t|\hat{p}|\Psi_t\rangle$, $\langle\Psi_t|\hat{T}|\Psi_t\rangle$ and $\langle\Psi_t|\hat{H}|\Psi_t\rangle$. Note that the analytic value of $\langle\Psi_t|\hat{T}|\Psi_t\rangle$ is $\hbar\omega/2 = 0.5$ in agreement with the numerical solution.

Download from (http://ursula.chem.yale.edu/~batista/classes/summer/P4/Problem4.f),

```
      PROGRAM Problem4
      CALL Initialize()
      CALL Pp(p)
      PRINT *, "<Psi|p|Psi>=",p
      CALL KE(RKE)
      PRINT *, "<Psi|T|Psi>=",RKE
      CALL PE(RV)
      PRINT *, "<Psi|H|Psi>=",RKE+RV
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE Initialize()
c
c     Wave Packet Initialization: Gaussian centered at xk, with momentum pk
c
      IMPLICIT NONE
      INTEGER nptx,npts,kk
      COMPLEX chi,EYE
      REAL omega,xmin,xmax,dx,pi,mass,xk,pk,x,alpha
      PARAMETER(npts=10,nptx=2**npts)
      COMMON / wfunc/ chi(nptx)
      common /xy/  xmin,xmax
      common /packet/mass,xk,pk
      xmin=-20.
      xmax=20.
      EYE=(0.0,1.0)
      pi= acos(-1.0)
      omega=1.
      dx=(xmax-xmin)/real(nptx)
      pk=0.0
      xk=0.0
      mass=1.0
      alpha=mass*omega
      do kk=1,nptx
         x=xmin+kk*dx
         chi(kk)=((alpha/pi)**0.25)
     1        *exp(-alpha/2.*(x-xk)**2+EYE*pk*(x-xk))
      end do
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE PE(RV)
c
c     Expectation Value of the Potential Enegy
c
      IMPLICIT NONE
      INTEGER nptx,npts,k
      COMPLEX chi
      REAL Vpot,RV,xmin,xmax,dx,x
      PARAMETER(npts=10,nptx=2**npts)
```

```
      COMMON / wfunc/ chi(nptx)
      common /xy/  xmin,xmax
      dx=(xmax-xmin)/real(nptx)
      RV=0.0
      do k=1,nptx
         x=xmin+k*dx
         CALL VA(Vpot,x)
         RV=RV+chi(k)*Vpot*conjg(chi(k))*dx
      end do
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE KE(RKE)
c
c     Expectation value of the kinetic energy
c
      IMPLICIT NONE
      INTEGER kk,nptx,kx,nx,npts
      REAL dp,RKE,p,xmin,xmax,pi,alenx,dx,mass,xk,pk
      COMPLEX eye,chi,Psip,chic
      parameter(npts=10,nptx=2**npts)
      DIMENSION chic(nptx)
      common /xy/  xmin,xmax
      common /packet/mass,xk,pk
      COMMON / wfunc/ chi(nptx)
      RKE=0.0
      pi = acos(-1.0)
      dx=(xmax-xmin)/nptx
      dp=2.*pi/(xmax-xmin)
      do kk=1,nptx
         chic(kk)=chi(kk)
      end do
      CALL fourn(chic,nptx,1,1)
      do kx=1,nptx
         if(kx.le.(nptx/2+1)) then
            nx=kx-1
         else
            nx=kx-1-nptx
         end if
         p=0.
         if(nx.ne.0) p = real(nx)*dp
         chic(kx)=p**2/(2.0*mass)*chic(kx)/nptx
      end do
      CALL fourn(chic,nptx,1,-1)
      do kk=1,nptx
         RKE=RKE+conjg(chi(kk))*chic(kk)*dx
      end do
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE Pp(pe)
```

```
c
c     Expectation value of the momentum
c
      IMPLICIT NONE
      INTEGER kk,nptx,kx,nx,npts
      REAL dp,pe,p,xmin,xmax,pi,alenx,dx,mass,xk,pk
      COMPLEX eye,chi,Psip,chic
      parameter(npts=10,nptx=2**npts)
      DIMENSION chic(nptx)
      common /xy/  xmin,xmax
      common /packet/mass,xk,pk
      COMMON / wfunc/ chi(nptx)
      pe=0.0
      pi = acos(-1.0)
      dx=(xmax-xmin)/nptx
      dp=2.*pi/(xmax-xmin)
      do kk=1,nptx
         chic(kk)=chi(kk)
      end do
      CALL fourn(chic,nptx,1,1)
      do kx=1,nptx
         if(kx.le.(nptx/2+1)) then
            nx=kx-1
         else
            nx=kx-1-nptx
         end if
         p=0.
         if(nx.ne.0) p = real(nx)*dp
         chic(kx)=p*chic(kx)/nptx
      end do
      CALL fourn(chic,nptx,1,-1)
      do kk=1,nptx
         pe=pe+conjg(chi(kk))*chic(kk)*dx
      end do
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE VA(V,x)
c
c     Potential Energy Surface: Harmonic Oscillator
c
      implicit none
      REAL V,x,mass,xk,pk,rk,omega
      common /packet/ mass,xk,pk
      omega=1.0
      rk=mass*omega**2
      V=0.5*rk*x*x
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c     Subroutines from Numerical Recipes
```

```
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE FOURN(DATA,NN,NDIM,ISIGN)
      REAL*8 WR,WI,WPR,WPI,WTEMP,THETA
      DIMENSION NN(NDIM),DATA(*)
      NTOT=1
      DO 11 IDIM=1,NDIM
         NTOT=NTOT*NN(IDIM)
 11   CONTINUE
      NPREV=1
      DO 18 IDIM=1,NDIM
         N=NN(IDIM)
         NREM=NTOT/(N*NPREV)
         IP1=2*NPREV
         IP2=IP1*N
         IP3=IP2*NREM
         I2REV=1
         DO 14 I2=1,IP2,IP1
            IF(I2.LT.I2REV)THEN
               DO 13 I1=I2,I2+IP1-2,2
                  DO 12 I3=I1,IP3,IP2
                     I3REV=I2REV+I3-I2
                     TEMPR=DATA(I3)
                     TEMPI=DATA(I3+1)
                     DATA(I3)=DATA(I3REV)
                     DATA(I3+1)=DATA(I3REV+1)
                     DATA(I3REV)=TEMPR
                     DATA(I3REV+1)=TEMPI
 12               CONTINUE
 13            CONTINUE
            ENDIF
            IBIT=IP2/2
 1          IF ((IBIT.GE.IP1).AND.(I2REV.GT.IBIT)) THEN
               I2REV=I2REV-IBIT
               IBIT=IBIT/2
               GO TO 1
            ENDIF
            I2REV=I2REV+IBIT
 14      CONTINUE
         IFP1=IP1
 2       IF(IFP1.LT.IP2)THEN
            IFP2=2*IFP1
            THETA=ISIGN*6.28318530717959D0/(IFP2/IP1)
            WPR=-2.D0*DSIN(0.5D0*THETA)**2
            WPI=DSIN(THETA)
            WR=1.D0
            WI=0.D0
            DO 17 I3=1,IFP1,IP1
               DO 16 I1=I3,I3+IP1-2,2
                  DO 15 I2=I1,IP3,IFP2
                     K1=I2
                     K2=K1+IFP1
```

```
                      TEMPR=SNGL(WR)*DATA(K2)-SNGL(WI)*DATA(K2+1)
                      TEMPI=SNGL(WR)*DATA(K2+1)+SNGL(WI)*DATA(K2)
                      DATA(K2)=DATA(K1)-TEMPR
                      DATA(K2+1)=DATA(K1+1)-TEMPI
                      DATA(K1)=DATA(K1)+TEMPR
                      DATA(K1+1)=DATA(K1+1)+TEMPI
 15                CONTINUE
 16             CONTINUE
                WTEMP=WR
                WR=WR*WPR-WI*WPI+WR
                WI=WI*WPR+WTEMP*WPI+WI
 17          CONTINUE
             IFP1=IFP2
             GO TO 2
          ENDIF
          NPREV=N*NPREV
 18    CONTINUE
       RETURN
       END
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
```

47.5 Problem 5

Computational Problem 5: Expand the exponential operators in both sides of Eq. (87) and show that the Trotter expansion is accurate to second order in powers of τ.

Expanding the left-hand-side (l.h.s.) of Eq. (87) from the lecture notes gives:

$$e^{-i\hat{H}\tau} = 1 - i\hat{H}\tau - \frac{1}{2}\hat{H}^2\tau^2 + O(\tau^3), \tag{356}$$

where $\hat{H} = \hat{p}^2/(2m) + \hat{V}$. Therefore,

$$e^{-i\hat{H}\tau} = 1 - i\hat{H}\tau - \frac{1}{2}\frac{\hat{p}^4}{4m^2}\tau^2 - \frac{1}{2}\hat{V}^2\tau^2 - \frac{1}{2}\frac{\hat{p}^2}{2m}\hat{V}\tau^2 - \frac{1}{2}\hat{V}\frac{\hat{p}^2}{2m}\tau^2 + O(\tau^3), \tag{357}$$

In order to show that the Trotter expansion, introduced by Eq. (87), is accurate to second order in τ, we must expand the right-hand-side (r.h.s.) of Eq. (87) and show that such an expansion equals the r.h.s. of Eq. (357).

Expanding the right-hand-side (r.h.s.) of Eq. (18) gives,

$$\begin{aligned} e^{-iV(\hat{x})\tau/2}e^{-i\hat{p}^2\tau/(2m)}e^{-iV(\hat{x})\tau/2} = &\left(1 - i\hat{V}\tau/2 - \frac{1}{2}\hat{V}^2\tau^2/4 + O(\tau^3)\right)\left(1 - i\frac{\hat{p}^2}{2m}\tau - \frac{1}{2}\frac{\hat{p}^4}{4m^2}\tau^2 + O(\tau^3)\right) \\ &\times \left(1 - i\hat{V}\tau/2 - \frac{1}{2}\hat{V}^2\tau^2/4 + O(\tau^3)\right), \end{aligned} \tag{358}$$

$$\begin{aligned} e^{-iV(\hat{x})\tau/2}e^{-i\hat{p}^2\tau/(2m)}e^{-iV(\hat{x})\tau/2} = &\left(1 - i\hat{V}\tau/2 - \frac{1}{2}\hat{V}^2\tau^2/4 - i\frac{\hat{p}^2}{2m}\tau - \hat{V}\frac{\hat{p}^2}{2m}\tau^2/2 - \frac{1}{2}\frac{\hat{p}^4}{4m^2}\tau^2 + O(\tau^3)\right) \\ &\times \left(1 - i\hat{V}\tau/2 - \frac{1}{2}\hat{V}^2\tau^2/4 + O(\tau^3)\right), \end{aligned} \tag{359}$$

$$\begin{aligned} e^{-iV(\hat{x})\tau/2}e^{-i\hat{p}^2\tau/(2m)}e^{-iV(\hat{x})\tau/2} = &1 - i\hat{V}\tau/2 - \frac{1}{2}\hat{V}^2\tau^2/4 - i\frac{\hat{p}^2}{2m}\tau - \hat{V}\frac{\hat{p}^2}{2m}\tau^2/2 - \frac{1}{2}\frac{\hat{p}^4}{4m^2}\tau^2 \\ &- i\hat{V}\tau/2 - \hat{V}^2\tau^2/4 - \frac{\hat{p}^2}{2m}\hat{V}\tau^2/2 - \frac{1}{2}\hat{V}^2\tau^2/4 + O(\tau^3), \end{aligned} \tag{360}$$

$$\begin{aligned} e^{-iV(\hat{x})\tau/2}e^{-i\hat{p}^2\tau/(2m)}e^{-iV(\hat{x})\tau/2} = &1 - i\hat{V}\tau - i\frac{\hat{p}^2}{2m}\tau - \frac{1}{2}\hat{V}^2\tau^2 - \hat{V}\frac{\hat{p}^2}{2m}\tau^2/2 - \frac{1}{2}\frac{\hat{p}^4}{4m^2}\tau^2 \\ &- \frac{\hat{p}^2}{2m}\hat{V}\tau^2/2 + O(\tau^3). \end{aligned} \tag{361}$$

Note that the r.h.s. of Eq. (361) is identical to the r.h.s. of E. (357), completing the proof that the Trotter expansion, introduced by Eq. (18), is accurate to second order in τ.

47.6 Problem 6

Computational Problem 6: Write a computer program that propagates the initial state $\Psi_0(x)$ for a single time increment ($\tau = 0.1$ a.u.). Use $x_0 = -2.5$, $p_0 = 0$, and $\alpha = \omega m$, where $m = 1$ and $\omega = 1$. Implement the SOFT method for the Hamiltonian $\hat{H} = \hat{p}^2/(2m) + V(\hat{x})$, where $V(x)$ is defined according to Eq. (28). Compare the resulting propagated state with the analytic solution obtained by substituting Eq. (35) into Eq. (34).

In order to visualize the output of this program, cut the source code attached below save it in a file named Problem6.f, compile it by typing

```
gfortran Problem6.f -o Problem6
```

run it by typing

```
./Problem6
```

and visualize the output as follows: type

```
gnuplot
```

then type

```
set dat sty line
```

then type

```
set yrange[0:6]
```

and the type

```
plot ``arch.0002''
```

That will show the numerical propagation after one step with $\tau = 0.1$. In order to visualize the analytic result on top of the numerical propagation, type

```
replot ``arch.0002'' u 1:3
```

To exit, type

```
quit
```

Download from (http://ursula.chem.yale.edu/~batista/classes/summer/P6/Problem6.f),

```
      PROGRAM Problem6
c
c     1-D wave packet propagation
c
      IMPLICIT NONE
      INTEGER NN,npts,nptx,ndump
      INTEGER istep,nstep
      REAL dt,xc,pc
      COMPLEX vprop,tprop,x_mean,p_mean
      PARAMETER(npts=9,nptx=2**npts,NN=1)
      DIMENSION vprop(nptx,NN,NN),tprop(nptx)
      DIMENSION x_mean(NN),p_mean(NN)
      COMMON /class/ xc,pc
c
      CALL ReadParam(nstep,ndump,dt)
      call Initialize()
      CALL SetKinProp(dt,tprop)
      CALL SetPotProp(dt,vprop)
      DO istep=1,nstep+1
         IF(mod(istep-1,10).EQ.0)
     1        PRINT *, "Step=", istep-1,", Final step=", nstep
         IF(istep.GE.1) CALL PROPAGATE(vprop,tprop)
         IF(mod((istep-1),ndump).EQ.0) THEN
            CALL SAVEWF(istep,ndump,dt)
         END IF
      END DO
 22   FORMAT(6(e13.6,2x))
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine ReadParam(nstep,ndump,dt)
c
c     Parameters defining the grid (xmin, xmax), integration time step (dt),
c     mass (rmass), initial position (xk), initial momentum (pk),
c     number of propagation steps (nstep), and how often to save a pic (ndump)
c
      IMPLICIT NONE
      INTEGER ntype,nstep,nrpt,ireport,ndump,nlit
      REAL xmin,xmax,pk,rmass,xk,dt
      common /packet/  rmass,xk,pk
      common /xy/  xmin,xmax
c
      xmin=-10.0
      xmax= 10.0
      dt=0.1
      rmass=1.0
      xk=-2.5
      pk=1.0
      nstep=1
      ndump=1
```

```
c
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE Initialize()

      IMPLICIT NONE
      INTEGER NN,nptx,npts,kk
      COMPLEX chi0,chi,EYE,CRV
      REAL xc,pc,omega,xk2,xmin,xmax,dx,pi,rmass,xk,pk,x,alpha,alpha2
      PARAMETER(npts=9,nptx=2**npts,NN=1)
      DIMENSION CRV(NN,NN)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
      COMMON / wfunc/ chi(nptx,NN)
      COMMON / iwfunc/ chi0(nptx,NN)
      COMMON /class/ xc,pc

      EYE=(0.0,1.0)
      pi= acos(-1.0)
      omega=1.
      dx=(xmax-xmin)/real(nptx)
      xc=kk
      pc=pk
c
c     Wave Packet Initialization: Gaussian centered at xk, with momentum pk
c
      alpha=rmass*omega
      do kk=1,nptx
         x=xmin+kk*dx
         chi(kk,1)=((alpha/pi)**0.25)
     1        *exp(-alpha/2.*(x-xk)**2+EYE*pk*(x-xk))
         chi0(kk,1)=chi(kk,1)
      end do
c
c     Hamiltonian Matrix CRV
c
      do kk=1,nptx
         x=xmin+kk*dx
         CALL HAMIL(CRV,x)
         WRITE(11,22) x,real(CRV(1,1))
      END DO
 22   FORMAT(6(e13.6,2x))
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE HAMIL(CRV,x)
c
c     Hamiltonian Matrix
c
      IMPLICIT NONE
```

```
      INTEGER NN
      REAL x,VPOT1
      COMPLEX CRV
      PARAMETER(NN=1)
      DIMENSION CRV(NN,NN)
c
      CALL VA(VPOT1,x)
      CRV(1,1)=VPOT1
c
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE VA(V,x)
c
c     Potential Energy Surface: Harmonic Oscillator
c
      implicit none
      REAL V,x,rmass,xk,pk,rk,omega
      common /packet/ rmass,xk,pk
      omega=1.0
      rk=rmass*omega**2
      V=0.5*rk*x*x
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine SetKinProp(dt,tprop)
c
c     Kinetic Energy part of the Trotter Expansion: exp(-i p^2 dt/(2 m))
c
      IMPLICIT NONE
      INTEGER nptx,kx,nx,npts
      REAL xsc,xmin,xmax,propfacx,rmass,xk,pi,alenx,dt,pk
      COMPLEX tprop,eye
      parameter(npts=9,nptx=2**npts)
      DIMENSION tprop(nptx)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
c
      eye=(0.,1.)
      pi = acos(-1.0)
      alenx=xmax-xmin
      propfacx=-dt/2./rmass*(2.*pi)**2
      do kx=1,nptx
         if(kx.le.(nptx/2+1)) then
            nx=kx-1
         else
            nx=kx-1-nptx
         end if
         xsc=0.
         if(nx.ne.0) xsc=real(nx)/alenx
         tprop(kx)=exp(eye*(propfacx*xsc**2))
```

```
       end do
c
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine SetPotProp(dt,vprop)
c
c     Potential Energy part of the Trotter Expansion: exp(-i V dt/2)
c
      IMPLICIT NONE
      INTEGER NN,ii,nptx,npts
      REAL xmin,xmax,dx,dt,x,VPOT
      COMPLEX vprop,eye
      parameter(npts=9,nptx=2**npts,NN=1)
      DIMENSION vprop(nptx,NN,NN)
      common /xy/  xmin,xmax
      eye=(0.,1.)
      dx=(xmax-xmin)/real(nptx)
c
      do ii=1,nptx
         x=xmin+ii*dx
         CALL VA(VPOT,x)
         vprop(ii,1,1)=exp(-eye*0.5*dt*VPOT)/sqrt(nptx*1.0)
      END DO
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE energies(energy)
      IMPLICIT NONE
      INTEGER j,NN
      COMPLEX energy,RV,RKE
      PARAMETER (NN=1)
      DIMENSION RV(NN),RKE(NN),energy(NN)
      CALL PE(RV)
      CALL KE(RKE)
      DO j=1,NN
         energy(j)=RV(j)+RKE(j)
      END DO
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      FUNCTION Psia(x,istep,dt)
c
c     Analytic wave-packet <x|Psia(istep)> obtained by applying the
c     harmonic propagator to the initial state,
c     <x'|Psi(0)> = (alpha/pi)**.25*exp(-alpha/2*(x'-xk)**2+eye*pk*(x'-xk)),
c     where the propagator is
c     <x|exp(-beta H)|x'> = A exp(-rgamma*(x**2+x'**2)+rgammap*x*x'), with
c     A = sqrt(m*omega/(pi*(exp(beta*omega)-exp(-beta*omega)))), beta = i*t,
c     rgamma = 0.5*m*omega*cosh(beta*omega)/sinh(beta*omega) and
c     rgammap = m*omega/sinh(beta*omega).
```

```
c
      IMPLICIT NONE
      INTEGER istep
      REAL pk,rmass,xk,dt,x,t,omega,pi,alpha
      COMPLEX eye,Psia,beta,A,rgamma,rgammap,c0,c1,c2
      common /packet/  rmass,xk,pk
      eye=(0.0,1.0)
      omega=1.0
      alpha = omega*rmass
      pi=acos(-1.0)
      beta = eye*dt*istep
      IF(abs(beta).EQ.0) beta = eye*1.0E-7
      A = sqrt(rmass*omega/(pi*(exp(beta*omega)-exp(-beta*omega))))
      rgamma=0.5*rmass*omega*(exp(beta*omega)+exp(-beta*omega))
     1     /(exp(beta*omega)-exp(-beta*omega))
      rgammap=2.*rmass*omega/(exp(beta*omega)-exp(-beta*omega))
      c0=-eye*pk*xk-alpha/2.*xk**2
      c1=rgammap*x+alpha*xk+eye*pk
      c2=rgamma+alpha/2.
c
      Psia = A*(alpha/pi)**.25*sqrt(pi/c2)*
     1     exp(-rgamma*x**2)*exp(c0+c1**2/(4.0*c2))
c
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE SAVEWF(je2,ndump,dt)
c
c     Dump Time Evolved Wave packet
c
      IMPLICIT NONE
      INTEGER je2,nptx,npts,kk,NN,ncount,ndump,jj
      COMPLEX chi,CRV,energy,psi,Psia
      character*9 B
      REAL V,x1,c1,c2,c1a,x,xmin,xmax,dx,EVALUES,dt
      PARAMETER(npts=9,nptx=2**npts,NN=1)
      DIMENSION CRV(NN,NN),energy(NN),EVALUES(NN)
      DIMENSION psi(NN,NN)
      common /xy/  xmin,xmax
      COMMON / wfunc/ chi(nptx,NN)
c
      CALL energies(energy)
      jj=je2/ndump
      write(B, '(A,i4.4)') 'arch.', jj
      OPEN(1,FILE=B)
      dx=(xmax-xmin)/real(nptx)
      ncount=(je2-1)/ndump
c
c     Save Wave-packet components
c
      do kk=1,nptx
```

```
         x=xmin+kk*dx
         c1=chi(kk,1)*conjg(chi(kk,1))
         c1a=Psia(x,je2,dt)*conjg(Psia(x,je2,dt))
         write(1,33) x,sqrt(c1)+real(energy(1))
     1        ,sqrt(c1a)+real(energy(1))
       end do
       write(1,33)
       do kk=1,nptx
         x=xmin+kk*dx
         write(1,33) x
     1        ,real(chi(kk,1))+real(energy(1))
     1        ,real(Psia(x,je2,dt))+real(energy(1))
       end do
       write(1,33)
c
c      Save Adiabatic states
c
       do kk=1,nptx
         x=xmin+kk*dx
         CALL HAMIL(CRV,x)
         write(1,33) x,CRV(1,1)
       end do
       CLOSE(1)
 33    format(6(e13.6,2x))
       RETURN
       END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
       SUBROUTINE PE(RV)
c
c      Expectation Value of the Potential Enegy
c
       IMPLICIT NONE
       INTEGER nptx,npts,kk,NN,j
       COMPLEX chi,EYE,RV
       REAL Vpot,omega,xmin,xmax,dx,pi,rmass,xk,pk,x,alpha
       PARAMETER(npts=9,nptx=2**npts,NN=1)
       DIMENSION RV(NN)
       COMMON / wfunc/ chi(nptx,NN)
       common /xy/  xmin,xmax
       common /packet/rmass,xk,pk

       dx=(xmax-xmin)/real(nptx)
       DO j=1,NN
         RV(j)=0.0
         do kk=1,nptx
           x=xmin+kk*dx
           IF(j.EQ.1) CALL VA(Vpot,x)
           RV(j)=RV(j)+chi(kk,j)*Vpot*conjg(chi(kk,j))*dx
         end do
       END DO
       RETURN
```

```
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine KE(RKE)
c
c     Expectation value of the kinetic energy
c
      IMPLICIT NONE
      INTEGER NN,kk,nptx,kx,nx,npts,j
      REAL dp,theta,wm,p,xmin,xmax,rmass,xk,pi,alenx,pk,rm,re,ri,dx
      COMPLEX eye,chi,Psip,chic,RKE
      parameter(npts=9,nptx=2**npts,NN=1)
      DIMENSION chic(nptx),RKE(NN)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
      COMMON / wfunc/ chi(nptx,NN)
c
      pi = acos(-1.0)
      dx=(xmax-xmin)/nptx
      dp=2.*pi/(xmax-xmin)
c
      DO j=1,NN
         RKE(j)=0.0
         do kk=1,nptx
            chic(kk)=chi(kk,j)
         end do
         CALL fourn(chic,nptx,1,-1)
         do kx=1,nptx
            if(kx.le.(nptx/2+1)) then
               nx=kx-1
            else
               nx=kx-1-nptx
            end if
            p=0.
            if(nx.ne.0) p = real(nx)*dp
            chic(kx)=p**2/(2.0*rmass)*chic(kx)/nptx
         end do
         CALL fourn(chic,nptx,1,1)
         do kk=1,nptx
            RKE(j)=RKE(j)+conjg(chi(kk,j))*chic(kk)*dx
         end do
      END DO
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE PROPAGATE(vprop,tprop)
c
c     Split Operator Fourier Transform Propagation Method
c     J. Comput. Phys. 47, 412 (1982); J. Chem. Phys. 78, 301 (1983)
c
      IMPLICIT NONE
      INTEGER i,j,NN,ii,nptx,npts
```

```
      COMPLEX chi,vprop,chin1,chin2,tprop
      PARAMETER(npts=9,nptx=2**npts,NN=1)
      DIMENSION chin1(nptx),chin2(nptx)
      DIMENSION tprop(nptx),vprop(nptx,NN,NN)
      COMMON / wfunc/ chi(nptx,NN)
c
c     Apply potential energy part of the Trotter Expansion
c
      DO i=1,nptx
         chin1(i)=0.0
         DO j=1,NN
            chin1(i)=chin1(i)+vprop(i,1,j)*chi(i,j)
         END DO
      END DO
c
c     Fourier Transform wave-packet to the momentum representation
c
      CALL fourn(chin1,nptx,1,-1)
c
c     Apply kinetic energy part of the Trotter Expansion
c
      DO i=1,nptx
         chin1(i)=tprop(i)*chin1(i)
      END DO
c
c     Inverse Fourier Transform wave-packet to the coordinate representation
c
      CALL fourn(chin1,nptx,1,1)
c
c     Apply potential energy part of the Trotter Expansion
c
      DO i=1,nptx
         DO j=1,NN
            chi(i,j)=vprop(i,j,1)*chin1(i)
         END DO
      END DO
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c     Subroutine for FFT from Numerical Recipes
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE FOURN(DATA,NN,NDIM,ISIGN)
      REAL*8 WR,WI,WPR,WPI,WTEMP,THETA
      DIMENSION NN(NDIM),DATA(*)
      NTOT=1
      DO 11 IDIM=1,NDIM
         NTOT=NTOT*NN(IDIM)
 11   CONTINUE
      NPREV=1
      DO 18 IDIM=1,NDIM
         N=NN(IDIM)
         NREM=NTOT/(N*NPREV)
```

```
      IP1=2*NPREV
      IP2=IP1*N
      IP3=IP2*NREM
      I2REV=1
      DO 14 I2=1,IP2,IP1
         IF(I2.LT.I2REV)THEN
            DO 13 I1=I2,I2+IP1-2,2
               DO 12 I3=I1,IP3,IP2
                  I3REV=I2REV+I3-I2
                  TEMPR=DATA(I3)
                  TEMPI=DATA(I3+1)
                  DATA(I3)=DATA(I3REV)
                  DATA(I3+1)=DATA(I3REV+1)
                  DATA(I3REV)=TEMPR
                  DATA(I3REV+1)=TEMPI
12             CONTINUE
13          CONTINUE
         ENDIF
         IBIT=IP2/2
1        IF ((IBIT.GE.IP1).AND.(I2REV.GT.IBIT)) THEN
            I2REV=I2REV-IBIT
            IBIT=IBIT/2
            GO TO 1
         ENDIF
         I2REV=I2REV+IBIT
14    CONTINUE
      IFP1=IP1
2     IF(IFP1.LT.IP2)THEN
         IFP2=2*IFP1
         THETA=ISIGN*6.28318530717959D0/(IFP2/IP1)
         WPR=-2.D0*DSIN(0.5D0*THETA)**2
         WPI=DSIN(THETA)
         WR=1.D0
         WI=0.D0
         DO 17 I3=1,IFP1,IP1
            DO 16 I1=I3,I3+IP1-2,2
               DO 15 I2=I1,IP3,IFP2
                  K1=I2
                  K2=K1+IFP1
                  TEMPR=SNGL(WR)*DATA(K2)-SNGL(WI)*DATA(K2+1)
                  TEMPI=SNGL(WR)*DATA(K2+1)+SNGL(WI)*DATA(K2)
                  DATA(K2)=DATA(K1)-TEMPR
                  DATA(K2+1)=DATA(K1+1)-TEMPI
                  DATA(K1)=DATA(K1)+TEMPR
                  DATA(K1+1)=DATA(K1+1)+TEMPI
15             CONTINUE
16          CONTINUE
            WTEMP=WR
            WR=WR*WPR-WI*WPI+WR
            WI=WI*WPR+WTEMP*WPI+WI
17       CONTINUE
```

```
            IFP1=IFP2
            GO TO 2
         ENDIF
         NPREV=N*NPREV
 18   CONTINUE
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
```

47.7 Problem 7

Computational Problem 7: Loop the computer program developed in Problem 5 with $x_0 = -2.5$ and $p_0 = 0$ for 100 steps with $\tau = 0.1$ a.u. For each step compute the expectation values of coordinates $x(t)$ and momenta $p(t)$ as done in Problems 3 and 4, respectively. Compare your calculations with the analytic solutions obtained by substituting Eq. (35) into Eq. (34). Verify that these correspond to the classical trajectories $x(t) = \bar{x} + (x_0 - \bar{x})\cos(\omega t)$ and $p(t) = p_0 - (x_0 - \bar{x})\omega m \sin(\omega t)$, which can be computed according to the Velocity-Verlet algorithm:

$$\begin{aligned} p_{j+1} &= p_j + (F(x_j) + F(x_{j+1}))\tau/2 \\ x_{j+1} &= x_j + p_j\tau/m + F(x_j)\tau^2/(2m). \end{aligned} \tag{362}$$

In order to visualize the output of this program, cut the source code attached below, compile it by typing

```
gfortran Problem7.f -o Problem7
```

run it by typing

```
./Problem7
```

Visualize the output of time dependent expectation values as compared to classical trajectories as follows: type

```
gnuplot
```

then type

```
set dat sty line
```

then type

```
plot ``traj.0000''
```

That will show the numerical computation of the expectation value $< \Psi_t|\hat{x}|\Psi_t >$ as a function of time. In order to visualize the classical result on top of the quantum mechanical expectation value, type

```
replot ``traj.0000'' u 1:4
```

In order to visualize the output of $< \Psi_t|\hat{p}|\Psi_t >$ as a function of time, type

```
plot ``traj.0000'' u 1:3
```

and to visualize the classical result on top of the quantum mechanical expectation value, type

```
replot ``traj.0000'' u 1:5
```

The plot of $< \Psi_t|\hat{p}|\Psi_t >$ vs. $< \Psi_t|\hat{x}|\Psi_t >$ can be obtained by typing

```
plot ``traj.0000'' u 3:2
```

, and the corresponding classical results $p(t)$ vs. $x(t)$

```
plot ``traj.0000'' u 5:4
```

To exit, type

```
quit
```

The snapshots of the time-dependent wave-packet can be visualized as a movie by typing

```
gnuplot<pp_7
```

where the file named

```
pp_7
```

has the following lines:

Download from (http://ursula.chem.yale.edu/∼batista/classes/summer/P7/pp_7)

```
set yrange[0:6]
set xrange[-10:10]
set dat sty l
plot "arch.0001" u 1:2 lw 3
pause .1
plot "arch.0002" u 1:2 lw 3
pause .1
plot "arch.0003" u 1:2 lw 3
pause .1
plot "arch.0004" u 1:2 lw 3
pause .1
plot "arch.0005" u 1:2 lw 3
pause .1
plot "arch.0006" u 1:2 lw 3
pause .1
plot "arch.0007" u 1:2 lw 3
pause .1
plot "arch.0008" u 1:2 lw 3
pause .1
plot "arch.0009" u 1:2 lw 3
pause .1
plot "arch.0010" u 1:2 lw 3
pause .1
plot "arch.0011" u 1:2 lw 3
pause .1
plot "arch.0012" u 1:2 lw 3
pause .1
plot "arch.0013" u 1:2 lw 3
pause .1
plot "arch.0014" u 1:2 lw 3
```

```
pause .1
plot "arch.0015" u 1:2 lw 3
pause .1
plot "arch.0016" u 1:2 lw 3
pause .1
plot "arch.0017" u 1:2 lw 3
pause .1
plot "arch.0018" u 1:2 lw 3
pause .1
plot "arch.0019" u 1:2 lw 3
pause .1
plot "arch.0020" u 1:2 lw 3
pause .1
plot "arch.0021" u 1:2 lw 3
pause .1
plot "arch.0022" u 1:2 lw 3
pause .1
plot "arch.0023" u 1:2 lw 3
pause .1
plot "arch.0024" u 1:2 lw 3
pause .1
plot "arch.0025" u 1:2 lw 3
pause .1
plot "arch.0026" u 1:2 lw 3
pause .1
plot "arch.0027" u 1:2 lw 3
pause .1
plot "arch.0028" u 1:2 lw 3
pause .1
plot "arch.0029" u 1:2 lw 3
pause .1
plot "arch.0030" u 1:2 lw 3
pause .1
plot "arch.0031" u 1:2 lw 3
pause .1
plot "arch.0032" u 1:2 lw 3
pause .1
plot "arch.0033" u 1:2 lw 3
pause .1
plot "arch.0034" u 1:2 lw 3
pause .1
plot "arch.0035" u 1:2 lw 3
pause .1
plot "arch.0036" u 1:2 lw 3
pause .1
plot "arch.0037" u 1:2 lw 3
pause .1
plot "arch.0038" u 1:2 lw 3
pause .1
plot "arch.0039" u 1:2 lw 3
pause .1
```

```
plot  "arch.0040" u 1:2 lw 3
pause .1
plot "arch.0041" u 1:2 lw 3
pause .1
plot "arch.0042" u 1:2 lw 3
pause .1
plot "arch.0043" u 1:2 lw 3
pause .1
plot "arch.0044" u 1:2 lw 3
pause .1
plot "arch.0045" u 1:2 lw 3
pause .1
plot "arch.0046" u 1:2 lw 3
pause .1
plot "arch.0047" u 1:2 lw 3
pause .1
plot "arch.0048" u 1:2 lw 3
pause .1
plot "arch.0049" u 1:2 lw 3
pause .1
plot "arch.0050" u 1:2 lw 3
pause .1
plot "arch.0051" u 1:2 lw 3
pause .1
plot "arch.0052" u 1:2 lw 3
pause .1
plot "arch.0053" u 1:2 lw 3
pause .1
plot "arch.0054" u 1:2 lw 3
pause .1
plot "arch.0055" u 1:2 lw 3
pause .1
plot "arch.0056" u 1:2 lw 3
pause .1
plot "arch.0057" u 1:2 lw 3
pause .1
plot "arch.0058" u 1:2 lw 3
pause .1
plot "arch.0059" u 1:2 lw 3
pause .1
plot "arch.0060" u 1:2 lw 3
pause .1
plot "arch.0061" u 1:2 lw 3
pause .1
plot "arch.0062" u 1:2 lw 3
pause .1
plot "arch.0063" u 1:2 lw 3
pause .1
plot "arch.0064" u 1:2 lw 3
pause .1
plot "arch.0065" u 1:2 lw 3
```

```
pause .1
plot "arch.0066" u 1:2 lw 3
pause .1
plot "arch.0067" u 1:2 lw 3
pause .1
plot "arch.0068" u 1:2 lw 3
pause .1
plot "arch.0069" u 1:2 lw 3
pause .1
plot "arch.0070" u 1:2 lw 3
pause .1
plot "arch.0071" u 1:2 lw 3
pause .1
plot "arch.0072" u 1:2 lw 3
pause .1
plot "arch.0073" u 1:2 lw 3
pause .1
plot "arch.0074" u 1:2 lw 3
pause .1
plot "arch.0075" u 1:2 lw 3
pause .1
plot "arch.0076" u 1:2 lw 3
pause .1
plot "arch.0077" u 1:2 lw 3
pause .1
plot "arch.0078" u 1:2 lw 3
pause .1
plot "arch.0079" u 1:2 lw 3
pause .1
plot  "arch.0080" u 1:2 lw 3
pause .1
plot "arch.0081" u 1:2 lw 3
pause .1
plot "arch.0082" u 1:2 lw 3
pause .1
plot "arch.0083" u 1:2 lw 3
pause .1
plot "arch.0084" u 1:2 lw 3
pause .1
plot "arch.0085" u 1:2 lw 3
pause .1
plot "arch.0086" u 1:2 lw 3
pause .1
plot "arch.0087" u 1:2 lw 3
pause .1
plot "arch.0088" u 1:2 lw 3
pause .1
plot "arch.0089" u 1:2 lw 3
pause .1
plot  "arch.0090" u 1:2 lw 3
pause .1
```

```
plot "arch.0091" u 1:2 lw 3
pause .1
plot "arch.0092" u 1:2 lw 3
pause .1
plot "arch.0093" u 1:2 lw 3
pause .1
plot "arch.0094" u 1:2 lw 3
pause .1
plot "arch.0095" u 1:2 lw 3
pause .1
plot "arch.0096" u 1:2 lw 3
pause .1
plot "arch.0097" u 1:2 lw 3
pause .1
plot "arch.0098" u 1:2 lw 3
pause .1
plot "arch.0099" u 1:2 lw 3
pause .1
```

Download from (http://ursula.chem.yale.edu/~batista/classes/summer/P7/Problem7.f)

```
      PROGRAM Problem7
c
c     1-D wave packet propagation and Velocity-Verlet propagation
c     on a Harmonic potential energy surface
c
      IMPLICIT NONE
      INTEGER NN,npts,nptx,ndump
      INTEGER istep,nstep,jj
      REAL dt,xc,pc
      COMPLEX vprop,tprop,x_mean,p_mean
      character*9 Bfile
      PARAMETER(npts=9,nptx=2**npts,NN=1)
      DIMENSION vprop(nptx,NN,NN),tprop(nptx)
      DIMENSION x_mean(NN),p_mean(NN)
      COMMON /class/ xc,pc
c
      jj=0
      write(Bfile, '(A,i4.4)') 'traj.', jj
      OPEN(10,FILE=Bfile)
      CALL ReadParam(nstep,ndump,dt)
      call Initialize()
      CALL SetKinProp(dt,tprop)
      CALL SetPotProp(dt,vprop)
      DO istep=1,nstep+1
         IF(mod(istep-1,10).EQ.0)
     1        PRINT *, "Step=", istep-1,", Final step=", nstep
         IF(istep.GE.1) CALL PROPAGATE(vprop,tprop)
         IF(mod((istep-1),ndump).EQ.0) THEN
            CALL SAVEWF(istep,ndump,dt)
            CALL XM(x_mean)
            CALL PM(p_mean)
            CALL VV(dt)
            WRITE(10,22) (istep-1.)*dt
     1           ,real(x_mean(1)),real(p_mean(1)),xc,pc
         END IF
      END DO
      CLOSE(10)
 22   FORMAT(6(e13.6,2x))
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine ReadParam(nstep,ndump,dt)
c
c     Parameters defining the grid (xmin, xmax), integration time step (dt),
c     rmass (rmass), initial position (xk), initial momentum (pk),
c     number of propagation steps (nstep), and how often to save a pic (ndump)
c
      IMPLICIT NONE
      INTEGER ntype,nstep,nrpt,ireport,ndump,nlit
      REAL xmin,xmax,pk,rmass,xk,dt
```

```
      common /packet/  rmass,xk,pk
      common /xy/  xmin,xmax
c
      xmin=-10.0
      xmax= 10.0
      dt=0.1
      rmass=1.0
      xk=-2.5
      pk=0.0
      nstep=100
      ndump=1
c
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE VV(dt)
c
c     Velocity Verlet Algorithm J. Chem. Phys. 76, 637 (1982)
c
      IMPLICIT NONE
      REAL v,dx,dt,xc,pc,rmass,xk,pk,acc,xt,VPOT1,VPOT2,F
      COMMON /class/ xc,pc
      common /packet/  rmass,xk,pk
c
c     Compute Force
c
      dx=0.01
      xt=xc+dx
      CALL VA(VPOT1,xt)
      xt=xc-dx
      CALL VA(VPOT2,xt)
      F=-(VPOT1-VPOT2)/(2.0*dx)
      v=pc/rmass
c
c     Advance momenta half a step
c
      pc=pc+0.5*F*dt
c
c     Advance coordinates a step
c
      xc=xc+v*dt+0.5*dt**2*F/rmass
c
c     Compute Force
c
      dx=0.01
      xt=xc+dx
      CALL VA(VPOT1,xt)
      xt=xc-dx
      CALL VA(VPOT2,xt)
      F=-(VPOT1-VPOT2)/(2.0*dx)
c
```

```
c     Advance momenta half a step
c
      pc=pc+0.5*F*dt
c
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE Initialize()

      IMPLICIT NONE
      INTEGER NN,nptx,npts,kk
      COMPLEX chi0,chi,EYE,CRV
      REAL xc,pc,omega,xk2,xmin,xmax,dx,pi,rmass,xk,pk,x,alpha,alpha2
      PARAMETER(npts=9,nptx=2**npts,NN=1)
      DIMENSION CRV(NN,NN)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
      COMMON / wfunc/ chi(nptx,NN)
      COMMON / iwfunc/ chi0(nptx,NN)
      COMMON /class/ xc,pc

      EYE=(0.0,1.0)
      pi= acos(-1.0)
      omega=1.
      dx=(xmax-xmin)/real(nptx)
      xc=xk
      pc=pk
c
c     Wave Packet Initialization: Gaussian centered at xk, with momentum pk
c
      alpha=rmass*omega
      do kk=1,nptx
         x=xmin+kk*dx
         chi(kk,1)=((alpha/pi)**0.25)
     1        *exp(-alpha/2.*(x-xk)**2+EYE*pk*(x-xk))
         chi0(kk,1)=chi(kk,1)
      end do
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE HAMIL(CRV,x)
c
c     Hamiltonian Matrix
c
      IMPLICIT NONE
      INTEGER NN
      REAL x,VPOT1
      COMPLEX CRV
      PARAMETER(NN=1)
      DIMENSION CRV(NN,NN)
c
```

```
      CALL VA(VPOT1,x)
      CRV(1,1)=VPOT1
c
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE VA(V,x)
c
c     Potential Energy Surface: Harmonic Oscillator
c
      implicit none
      REAL V,x,rmass,xk,pk,rk,omega
      common /packet/ rmass,xk,pk
      omega=1.0
      rk=rmass*omega**2
      V=0.5*rk*x*x
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine SetKinProp(dt,tprop)
c
c     Kinetic Energy part of the Trotter Expansion: exp(-i p^2 dt/(2 m))
c
      IMPLICIT NONE
      INTEGER nptx,kx,nx,npts
      REAL xsc,xmin,xmax,propfacx,rmass,xk,pi,alenx,dt,pk
      COMPLEX tprop,eye
      parameter(npts=9,nptx=2**npts)
      DIMENSION tprop(nptx)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
c
      eye=(0.,1.)
      pi = acos(-1.0)
      alenx=xmax-xmin
      propfacx=-dt/2./rmass*(2.*pi)**2
      do kx=1,nptx
         if(kx.le.(nptx/2+1)) then
            nx=kx-1
         else
            nx=kx-1-nptx
         end if
         xsc=0.
         if(nx.ne.0) xsc=real(nx)/alenx
         tprop(kx)=exp(eye*(propfacx*xsc**2))
       end do
c
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine SetPotProp(dt,vprop)
```

```
c
c     Potential Energy part of the Trotter Expansion: exp(-i V dt/2)
c
      IMPLICIT NONE
      INTEGER NN,ii,nptx,npts
      REAL xmin,xmax,dx,dt,x,VPOT
      COMPLEX vprop,eye
      parameter(npts=9,nptx=2**npts,NN=1)
      DIMENSION vprop(nptx,NN,NN)
      common /xy/  xmin,xmax
      eye=(0.,1.)
      dx=(xmax-xmin)/real(nptx)
c
      do ii=1,nptx
         x=xmin+ii*dx
         CALL VA(VPOT,x)
         vprop(ii,1,1)=exp(-eye*0.5*dt*VPOT)/sqrt(nptx*1.0)
      END DO
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE energies(energy)
      IMPLICIT NONE
      INTEGER j,NN
      COMPLEX energy,RV,RKE
      PARAMETER (NN=1)
      DIMENSION RV(NN),RKE(NN),energy(NN)
      CALL PE(RV)
      CALL KE(RKE)
      DO j=1,NN
         energy(j)=RV(j)+RKE(j)
      END DO
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      FUNCTION Psia(x,istep,dt)
c
c     Analytic wave-packet <x|Psia(istep)> obtained by applying the
c     harmonic propagator to the initial state,
c     <x'|Psi(0)> = (alpha/pi)**.25*exp(-alpha/2*(x'-xk)**2+eye*pk*(x'-xk)),
c     where the propagator is
c     <x|exp(-beta H)|x'> = A exp(-rgamma*(x**2+x'**2)+rgammap*x*x'), with
c     A = sqrt(m*omega/(pi*(exp(beta*omega)-exp(-beta*omega)))), beta = i*t,
c     rgamma = 0.5*m*omega*cosh(beta*omega)/sinh(beta*omega) and
c     rgammap = m*omega/sinh(beta*omega).
c
      IMPLICIT NONE
      INTEGER istep
      REAL pk,rmass,xk,dt,x,t,omega,pi,alpha
      COMPLEX eye,Psia,beta,A,rgamma,rgammap,c0,c1,c2
      common /packet/  rmass,xk,pk
```

```
      eye=(0.0,1.0)
      omega=1.0
      alpha = omega*rmass
      pi=acos(-1.0)
      beta = eye*dt*istep
      IF(abs(beta).EQ.0) beta = eye*1.0E-7
      A = sqrt(rmass*omega/(pi*(exp(beta*omega)-exp(-beta*omega))))
      rgamma=0.5*rmass*omega*(exp(beta*omega)+exp(-beta*omega))
     1     /(exp(beta*omega)-exp(-beta*omega))
      rgammap=2.*rmass*omega/(exp(beta*omega)-exp(-beta*omega))
      c0=-eye*pk*xk-alpha/2.*xk**2
      c1=rgammap*x+alpha*xk+eye*pk
      c2=rgamma+alpha/2.
c
      Psia = A*(alpha/pi)**.25*sqrt(pi/c2)*
     1     exp(-rgamma*x**2)*exp(c0+c1**2/(4.0*c2))
c
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE SAVEWF(je2,ndump,dt)
c
c     Dump Time Evolved Wave packet
c
      IMPLICIT NONE
      INTEGER je2,nptx,npts,kk,NN,ncount,ndump,jj
      COMPLEX chi,CRV,energy,psi,Psia
      character*9 B
      REAL V,x1,c1,c2,c1a,x,xmin,xmax,dx,EVALUES,dt
      PARAMETER(npts=9,nptx=2**npts,NN=1)
      DIMENSION CRV(NN,NN),energy(NN),EVALUES(NN)
      DIMENSION psi(NN,NN)
      common /xy/  xmin,xmax
      COMMON / wfunc/ chi(nptx,NN)
c
      CALL energies(energy)
      jj=je2/ndump
      write(B, '(A,i4.4)') 'arch.', jj
      OPEN(1,FILE=B)
      dx=(xmax-xmin)/real(nptx)
      ncount=(je2-1)/ndump
c
c     Save Wave-packet components
c
      do kk=1,nptx
         x=xmin+kk*dx
         c1=chi(kk,1)*conjg(chi(kk,1))
         c1a=Psia(x,je2,dt)*conjg(Psia(x,je2,dt))
         write(1,33) x,sqrt(c1)+real(energy(1))
     1        ,sqrt(c1a)+real(energy(1))
      end do
```

```
      write(1,33)
      do kk=1,nptx
         x=xmin+kk*dx
         write(1,33) x
     1        ,real(chi(kk,1))+real(energy(1))
     1        ,real(Psia(x,je2,dt))+real(energy(1))
      end do
      write(1,33)
c
c     Save Adiabatic states
c
      do kk=1,nptx
         x=xmin+kk*dx
         CALL HAMIL(CRV,x)
         write(1,33) x,CRV(1,1)
      end do
      CLOSE(1)
 33   format(6(e13.6,2x))
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE XM(RV)
c
c     Expectation Value of the Position
c
      IMPLICIT NONE
      INTEGER nptx,npts,kk,NN,j
      COMPLEX chi,EYE,RV
      REAL Vpot,omega,xmin,xmax,dx,pi,rmass,xk,pk,x,alpha
      PARAMETER(npts=9,nptx=2**npts,NN=1)
      DIMENSION RV(NN)
      COMMON / wfunc/ chi(nptx,NN)
      common /xy/  xmin,xmax
      common /packet/rmass,xk,pk

      dx=(xmax-xmin)/real(nptx)
      DO j=1,NN
         RV(j)=0.0
         do kk=1,nptx
            x=xmin+kk*dx
            IF(j.EQ.1) CALL VA(Vpot,x)
            RV(j)=RV(j)+chi(kk,j)*x*conjg(chi(kk,j))*dx
         end do
      END DO
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE PE(RV)
c
c     Expectation Value of the Potential Enegy
c
```

```
      IMPLICIT NONE
      INTEGER nptx,npts,kk,NN,j
      COMPLEX chi,EYE,RV
      REAL Vpot,omega,xmin,xmax,dx,pi,rmass,xk,pk,x,alpha
      PARAMETER(npts=9,nptx=2**npts,NN=1)
      DIMENSION RV(NN)
      COMMON / wfunc/ chi(nptx,NN)
      common /xy/  xmin,xmax
      common /packet/rmass,xk,pk

      dx=(xmax-xmin)/real(nptx)
      DO j=1,NN
         RV(j)=0.0
         do kk=1,nptx
            x=xmin+kk*dx
            IF(j.EQ.1) CALL VA(Vpot,x)
            RV(j)=RV(j)+chi(kk,j)*Vpot*conjg(chi(kk,j))*dx
         end do
      END DO
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine KE(RKE)
c
c     Expectation value of the kinetic energy
c
      IMPLICIT NONE
      INTEGER NN,kk,nptx,kx,nx,npts,j
      REAL dp,theta,wm,p,xmin,xmax,rmass,xk,pi,alenx,pk,rm,re,ri,dx
      COMPLEX eye,chi,Psip,chic,RKE
      parameter(npts=9,nptx=2**npts,NN=1)
      DIMENSION chic(nptx),RKE(NN)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
      COMMON / wfunc/ chi(nptx,NN)
c
      pi = acos(-1.0)
      dx=(xmax-xmin)/nptx
      dp=2.*pi/(xmax-xmin)
c
      DO j=1,NN
         RKE(j)=0.0
         do kk=1,nptx
            chic(kk)=chi(kk,j)
         end do
         CALL fourn(chic,nptx,1,-1)
         do kx=1,nptx
            if(kx.le.(nptx/2+1)) then
               nx=kx-1
            else
               nx=kx-1-nptx
```

```
            end if
            p=0.
            if(nx.ne.0) p = real(nx)*dp
            chic(kx)=p**2/(2.0*rmass)*chic(kx)/nptx
         end do
         CALL fourn(chic,nptx,1,1)
         do kk=1,nptx
            RKE(j)=RKE(j)+conjg(chi(kk,j))*chic(kk)*dx
         end do
      END DO
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine PM(RKE)
c
c     Expectation value of the kinetic energy
c
      IMPLICIT NONE
      INTEGER NN,kk,nptx,kx,nx,npts,j
      REAL dp,theta,wm,p,xmin,xmax,rmass,xk,pi,alenx,pk,rm,re,ri,dx
      COMPLEX eye,chi,Psip,chic,RKE
      parameter(npts=9,nptx=2**npts,NN=1)
      DIMENSION chic(nptx),RKE(NN)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
      COMMON / wfunc/ chi(nptx,NN)
c
      pi = acos(-1.0)
      dx=(xmax-xmin)/nptx
      dp=2.*pi/(xmax-xmin)
c
      DO j=1,NN
         RKE(j)=0.0
         do kk=1,nptx
            chic(kk)=chi(kk,j)
         end do
         CALL fourn(chic,nptx,1,-1)
         do kx=1,nptx
            if(kx.le.(nptx/2+1)) then
               nx=kx-1
            else
               nx=kx-1-nptx
            end if
            p=0.
            if(nx.ne.0) p = real(nx)*dp
            chic(kx)=p*chic(kx)/nptx
         end do
         CALL fourn(chic,nptx,1,1)
         do kk=1,nptx
            RKE(j)=RKE(j)+conjg(chi(kk,j))*chic(kk)*dx
         end do
```

```
      END DO
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE PROPAGATE(vprop,tprop)
c
c     Split Operator Fourier Transform Propagation Method
c     J. Comput. Phys. 47, 412 (1982); J. Chem. Phys. 78, 301 (1983)
c
      IMPLICIT NONE
      INTEGER i,j,NN,ii,nptx,npts
      COMPLEX chi,vprop,chin1,chin2,tprop
      PARAMETER(npts=9,nptx=2**npts,NN=1)
      DIMENSION chin1(nptx),chin2(nptx)
      DIMENSION tprop(nptx),vprop(nptx,NN,NN)
      COMMON / wfunc/ chi(nptx,NN)
c
c     Apply potential energy part of the Trotter Expansion
c
      DO i=1,nptx
         chin1(i)=0.0
         DO j=1,NN
            chin1(i)=chin1(i)+vprop(i,1,j)*chi(i,j)
         END DO
      END DO
c
c     Fourier Transform wave-packet to the momentum representation
c
      CALL fourn(chin1,nptx,1,-1)
c
c     Apply kinetic energy part of the Trotter Expansion
c
      DO i=1,nptx
         chin1(i)=tprop(i)*chin1(i)
      END DO
c
c     Inverse Fourier Transform wave-packet to the coordinate representation
c
      CALL fourn(chin1,nptx,1,1)
c
c     Apply potential energy part of the Trotter Expansion
c
      DO i=1,nptx
         DO j=1,NN
            chi(i,j)=vprop(i,j,1)*chin1(i)
         END DO
      END DO
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c     Subroutine for FFT from Numerical Recipes
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
```

```
      SUBROUTINE FOURN(DATA,NN,NDIM,ISIGN)
      REAL*8 WR,WI,WPR,WPI,WTEMP,THETA
      DIMENSION NN(NDIM),DATA(*)
      NTOT=1
      DO 11 IDIM=1,NDIM
         NTOT=NTOT*NN(IDIM)
11    CONTINUE
      NPREV=1
      DO 18 IDIM=1,NDIM
         N=NN(IDIM)
         NREM=NTOT/(N*NPREV)
         IP1=2*NPREV
         IP2=IP1*N
         IP3=IP2*NREM
         I2REV=1
         DO 14 I2=1,IP2,IP1
            IF(I2.LT.I2REV)THEN
               DO 13 I1=I2,I2+IP1-2,2
                  DO 12 I3=I1,IP3,IP2
                     I3REV=I2REV+I3-I2
                     TEMPR=DATA(I3)
                     TEMPI=DATA(I3+1)
                     DATA(I3)=DATA(I3REV)
                     DATA(I3+1)=DATA(I3REV+1)
                     DATA(I3REV)=TEMPR
                     DATA(I3REV+1)=TEMPI
12                CONTINUE
13             CONTINUE
            ENDIF
            IBIT=IP2/2
1           IF ((IBIT.GE.IP1).AND.(I2REV.GT.IBIT)) THEN
               I2REV=I2REV-IBIT
               IBIT=IBIT/2
               GO TO 1
            ENDIF
            I2REV=I2REV+IBIT
14       CONTINUE
         IFP1=IP1
2        IF(IFP1.LT.IP2)THEN
            IFP2=2*IFP1
            THETA=ISIGN*6.28318530717959D0/(IFP2/IP1)
            WPR=-2.D0*DSIN(0.5D0*THETA)**2
            WPI=DSIN(THETA)
            WR=1.D0
            WI=0.D0
            DO 17 I3=1,IFP1,IP1
               DO 16 I1=I3,I3+IP1-2,2
                  DO 15 I2=I1,IP3,IFP2
                     K1=I2
                     K2=K1+IFP1
                     TEMPR=SNGL(WR)*DATA(K2)-SNGL(WI)*DATA(K2+1)
```

```
                    TEMPI=SNGL(WR)*DATA(K2+1)+SNGL(WI)*DATA(K2)
                    DATA(K2)=DATA(K1)-TEMPR
                    DATA(K2+1)=DATA(K1+1)-TEMPI
                    DATA(K1)=DATA(K1)+TEMPR
                    DATA(K1+1)=DATA(K1+1)+TEMPI
 15              CONTINUE
 16           CONTINUE
              WTEMP=WR
              WR=WR*WPR-WI*WPI+WR
              WI=WI*WPR+WTEMP*WPI+WI
 17        CONTINUE
           IFP1=IFP2
           GO TO 2
        ENDIF
        NPREV=N*NPREV
 18   CONTINUE
      RETURN
      END
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
```

47.8 Problem 8

Computational Problem 8: Change the potential to that of a Morse oscillator $V(\hat{x}) = De(1 - \exp(-a(\hat{x} - x_e)))^2$, with $x_e = 0$, $De = 8$, and $a = \sqrt{k/(2D_e)}$, where $k = m\omega^2$. Recompute the wave-packet propagation with $x_0 = -0.5$ and $p_0 = 0$ for 100 steps with $\tau = 0.1$ a.u., and compare the expectation values $x(t)$ and $p(t)$ with the corresponding classical trajectories obtained by recursively applying the Velocity-Verlet algorithm.

The output of this program is analogous to Problem 6 but for a Morse potential. Cut the source code attached below, save it in a file named Problem8.f, compile it by typing

```
gfortran Problem8.f -o Problem8
```

run it by typing

```
./Problem8
```

Visualize the output of the time dependent expectation values as compared to classical trajectories as follows: type

```
gnuplot
```

then type

```
set dat sty line
```

then type

```
plot ''traj.0000''
```

That will show the numerical computation of the expectation value $< \Psi_t|\hat{x}|\Psi_t >$ as a function of time. In order to visualize the classical result on top of the quantum mechanical expectation value, type

```
replot ''traj.0000'' u 1:4
```

In order to visualize the output of $< \Psi_t|\hat{p}|\Psi_t >$ as a function of time, type

```
plot ''traj.0000'' u 1:3
```

and to visualize the classical result on top of the quantum mechanical expectation value, type

```
replot ''traj.0000'' u 1:5
```

The plot of $< \Psi_t|\hat{p}|\Psi_t >$ vs. $< \Psi_t|\hat{x}|\Psi_t >$ can be obtained by typing

```
plot ''traj.0000'' u 3:2
```

and the corresponding classical results $p(t)$ vs. $x(t)$

```
plot ''traj.0000'' u 5:4
```

To exit, type

```
quit
```

The snapshots of the time-dependent wave-packet can be visualized as a movie by typing

```
gnuplot<pp_8
```

where the file named

```
pp_8
```

has the following lines:

Download from (http://ursula.chem.yale.edu/~batista/classes/summer/P8/pp_8)

```
set yrange[0:9]
set xrange[-5:25]
set dat sty l
plot "arch.0001" u 1:2 lw 3
pause .1
plot "arch.0002" u 1:2 lw 3
pause .1
plot "arch.0003" u 1:2 lw 3
pause .1
plot "arch.0004" u 1:2 lw 3
pause .1
plot "arch.0005" u 1:2 lw 3
pause .1
plot "arch.0006" u 1:2 lw 3
pause .1
plot "arch.0007" u 1:2 lw 3
pause .1
plot "arch.0008" u 1:2 lw 3
pause .1
plot "arch.0009" u 1:2 lw 3
pause .1
plot "arch.0010" u 1:2 lw 3
pause .1
plot "arch.0011" u 1:2 lw 3
pause .1
plot "arch.0012" u 1:2 lw 3
pause .1
plot "arch.0013" u 1:2 lw 3
pause .1
plot "arch.0014" u 1:2 lw 3
pause .1
plot "arch.0015" u 1:2 lw 3
pause .1
plot "arch.0016" u 1:2 lw 3
pause .1
plot "arch.0017" u 1:2 lw 3
```

```
pause .1
plot "arch.0018" u 1:2 lw 3
pause .1
plot "arch.0019" u 1:2 lw 3
pause .1
plot "arch.0020" u 1:2 lw 3
pause .1
plot "arch.0021" u 1:2 lw 3
pause .1
plot "arch.0022" u 1:2 lw 3
pause .1
plot "arch.0023" u 1:2 lw 3
pause .1
plot "arch.0024" u 1:2 lw 3
pause .1
plot "arch.0025" u 1:2 lw 3
pause .1
plot "arch.0026" u 1:2 lw 3
pause .1
plot "arch.0027" u 1:2 lw 3
pause .1
plot "arch.0028" u 1:2 lw 3
pause .1
plot "arch.0029" u 1:2 lw 3
pause .1
plot "arch.0030" u 1:2 lw 3
pause .1
plot "arch.0031" u 1:2 lw 3
pause .1
plot "arch.0032" u 1:2 lw 3
pause .1
plot "arch.0033" u 1:2 lw 3
pause .1
plot "arch.0034" u 1:2 lw 3
pause .1
plot "arch.0035" u 1:2 lw 3
pause .1
plot "arch.0036" u 1:2 lw 3
pause .1
plot "arch.0037" u 1:2 lw 3
pause .1
plot "arch.0038" u 1:2 lw 3
pause .1
plot "arch.0039" u 1:2 lw 3
pause .1
plot  "arch.0040" u 1:2 lw 3
pause .1
plot "arch.0041" u 1:2 lw 3
pause .1
plot "arch.0042" u 1:2 lw 3
pause .1
```

```
plot "arch.0043" u 1:2 lw 3
pause .1
plot "arch.0044" u 1:2 lw 3
pause .1
plot "arch.0045" u 1:2 lw 3
pause .1
plot "arch.0046" u 1:2 lw 3
pause .1
plot "arch.0047" u 1:2 lw 3
pause .1
plot "arch.0048" u 1:2 lw 3
pause .1
plot "arch.0049" u 1:2 lw 3
pause .1
plot "arch.0050" u 1:2 lw 3
pause .1
plot "arch.0051" u 1:2 lw 3
pause .1
plot "arch.0052" u 1:2 lw 3
pause .1
plot "arch.0053" u 1:2 lw 3
pause .1
plot "arch.0054" u 1:2 lw 3
pause .1
plot "arch.0055" u 1:2 lw 3
pause .1
plot "arch.0056" u 1:2 lw 3
pause .1
plot "arch.0057" u 1:2 lw 3
pause .1
plot "arch.0058" u 1:2 lw 3
pause .1
plot "arch.0059" u 1:2 lw 3
pause .1
plot "arch.0060" u 1:2 lw 3
pause .1
plot "arch.0061" u 1:2 lw 3
pause .1
plot "arch.0062" u 1:2 lw 3
pause .1
plot "arch.0063" u 1:2 lw 3
pause .1
plot "arch.0064" u 1:2 lw 3
pause .1
plot "arch.0065" u 1:2 lw 3
pause .1
plot "arch.0066" u 1:2 lw 3
pause .1
plot "arch.0067" u 1:2 lw 3
pause .1
plot "arch.0068" u 1:2 lw 3
```

```
pause .1
plot "arch.0069" u 1:2 lw 3
pause .1
plot "arch.0070" u 1:2 lw 3
pause .1
plot "arch.0071" u 1:2 lw 3
pause .1
plot "arch.0072" u 1:2 lw 3
pause .1
plot "arch.0073" u 1:2 lw 3
pause .1
plot "arch.0074" u 1:2 lw 3
pause .1
plot "arch.0075" u 1:2 lw 3
pause .1
plot "arch.0076" u 1:2 lw 3
pause .1
plot "arch.0077" u 1:2 lw 3
pause .1
plot "arch.0078" u 1:2 lw 3
pause .1
plot "arch.0079" u 1:2 lw 3
pause .1
plot  "arch.0080" u 1:2 lw 3
pause .1
plot "arch.0081" u 1:2 lw 3
pause .1
plot "arch.0082" u 1:2 lw 3
pause .1
plot "arch.0083" u 1:2 lw 3
pause .1
plot "arch.0084" u 1:2 lw 3
pause .1
plot "arch.0085" u 1:2 lw 3
pause .1
plot "arch.0086" u 1:2 lw 3
pause .1
plot "arch.0087" u 1:2 lw 3
pause .1
plot "arch.0088" u 1:2 lw 3
pause .1
plot "arch.0089" u 1:2 lw 3
pause .1
plot  "arch.0090" u 1:2 lw 3
pause .1
plot "arch.0091" u 1:2 lw 3
pause .1
plot "arch.0092" u 1:2 lw 3
pause .1
plot "arch.0093" u 1:2 lw 3
pause .1
```

```
plot "arch.0094" u 1:2 lw 3
pause .1
plot "arch.0095" u 1:2 lw 3
pause .1
plot "arch.0096" u 1:2 lw 3
pause .1
plot "arch.0097" u 1:2 lw 3
pause .1
plot "arch.0098" u 1:2 lw 3
pause .1
plot "arch.0099" u 1:2 lw 3
pause .1
```

Download from (http://ursula.chem.yale.edu/~batista/classes/summer/P8/Problem8.f)

```
      PROGRAM Problem8
c
c     1-D wave packet propagation and Velocity-Verlet propagation
c     on a Morse potential energy surface
c
      IMPLICIT NONE
      INTEGER NN,npts,nptx,ndump
      INTEGER istep,nstep,jj
      REAL dt,xc,pc
      COMPLEX vprop,tprop,x_mean,p_mean
      character*9 Bfile
      PARAMETER(npts=10,nptx=2**npts,NN=1)
      DIMENSION vprop(nptx,NN,NN),tprop(nptx)
      DIMENSION x_mean(NN),p_mean(NN)
      COMMON /class/ xc,pc
c     xo
      jj=0
      write(Bfile, '(A,i4.4)') 'traj.', jj
      OPEN(10,FILE=Bfile)
      CALL ReadParam(nstep,ndump,dt)
      call Initialize()
      CALL SetKinProp(dt,tprop)
      CALL SetPotProp(dt,vprop)
      DO istep=1,nstep+1
         IF(mod(istep-1,10).EQ.0)
     1        PRINT *, "Step=", istep-1,", Final step=", nstep
         IF(istep.GE.1) CALL PROPAGATE(vprop,tprop)
         IF(mod((istep-1),ndump).EQ.0) THEN
            CALL SAVEWF(istep,ndump,dt)
            CALL XM(x_mean)
            CALL PM(p_mean)
            CALL VV(dt)
            WRITE(10,22) (istep-1.)*dt
     1           ,real(x_mean(1)),real(p_mean(1)),xc,pc
         END IF
      END DO
      CLOSE(10)
 22   FORMAT(6(e13.6,2x))
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine ReadParam(nstep,ndump,dt)
c
c     Parameters defining the grid (xmin, xmax), integration time step (dt),
c     rmass (rmass), initial position (xk), initial momentum (pk),
c     number of propagation steps (nstep), and how often to save a pic (ndump)
c
      IMPLICIT NONE
      INTEGER ntype,nstep,nrpt,ireport,ndump,nlit
      REAL xmin,xmax,pk,rmass,xk,dt
```

```
      common /packet/  rmass,xk,pk
      common /xy/  xmin,xmax
c
      xmin=-5.0
      xmax=25.0
      dt=0.2
      rmass=1.0
      xk=-.5
      pk=0.0
      nstep=100
      ndump=1
c
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE VV(dt)
c
c     Velocity Verlet Algorithm J. Chem. Phys. 76, 637 (1982)
c
      IMPLICIT NONE
      REAL v,dx,dt,xc,pc,rmass,xk,pk,acc,xt,VPOT1,VPOT2,F
      COMMON /class/ xc,pc
      common /packet/  rmass,xk,pk
c
c     Compute Force
c
      dx=0.01
      xt=xc+dx
      CALL VA(VPOT1,xt)
      xt=xc-dx
      CALL VA(VPOT2,xt)
      F=-(VPOT1-VPOT2)/(2.0*dx)
      v=pc/rmass
c
c     Advance momenta half a step
c
      pc=pc+0.5*F*dt
c
c     Advance coordinates a step
c
      xc=xc+v*dt+0.5*dt**2*F/rmass
c
c     Compute Force
c
      dx=0.01
      xt=xc+dx
      CALL VA(VPOT1,xt)
      xt=xc-dx
      CALL VA(VPOT2,xt)
      F=-(VPOT1-VPOT2)/(2.0*dx)
c
```

```
c     Advance momenta half a step
c
      pc=pc+0.5*F*dt
c
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE Initialize()

      IMPLICIT NONE
      INTEGER NN,nptx,npts,kk
      COMPLEX chi0,chi,EYE,CRV
      REAL xc,pc,omega,xk2,xmin,xmax,dx,pi,rmass,xk,pk,x,alpha,alpha2
      PARAMETER(npts=10,nptx=2**npts,NN=1)
      DIMENSION CRV(NN,NN)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
      COMMON / wfunc/ chi(nptx,NN)
      COMMON / iwfunc/ chi0(nptx,NN)
      COMMON /class/ xc,pc

      EYE=(0.0,1.0)
      pi= acos(-1.0)
      omega=1.
      dx=(xmax-xmin)/real(nptx)
      xc=xk
      pc=pk
c
c     Wave Packet Initialization: Gaussian centered at xk, with momentum pk
c
      alpha=rmass*omega
      do kk=1,nptx
         x=xmin+kk*dx
         chi(kk,1)=((alpha/pi)**0.25)
     1        *exp(-alpha/2.*(x-xk)**2+EYE*pk*(x-xk))
         chi0(kk,1)=chi(kk,1)
      end do
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE HAMIL(CRV,x)
c
c     Hamiltonian Matrix
c
      IMPLICIT NONE
      INTEGER NN
      REAL x,VPOT1
      COMPLEX CRV
      PARAMETER(NN=1)
      DIMENSION CRV(NN,NN)
c
```

```
      CALL VA(VPOT1,x)
      CRV(1,1)=VPOT1
c
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE VA(V,x)
c
c     Potential Energy Surface: Morse Potential [Phys. Rev. (1929) 34:57]
c
      implicit none
      REAL V,x,rmass,xk,pk,rk,omega,De,xeq,a
      common /packet/ rmass,xk,pk
      xeq=0.0
      omega=1.0
      De=8.0
      rk=rmass*omega**2
      a=sqrt(rk/(2.0*De))
      V=De*(1.0-exp(-a*(x-xeq)))**2
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine SetKinProp(dt,tprop)
c
c     Kinetic Energy part of the Trotter Expansion: exp(-i p^2 dt/(2 m))
c
      IMPLICIT NONE
      INTEGER nptx,kx,nx,npts
      REAL xsc,xmin,xmax,propfacx,rmass,xk,pi,alenx,dt,pk
      COMPLEX tprop,eye
      parameter(npts=10,nptx=2**npts)
      DIMENSION tprop(nptx)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
c
      eye=(0.,1.)
      pi = acos(-1.0)
      alenx=xmax-xmin
      propfacx=-dt/2./rmass*(2.*pi)**2
      do kx=1,nptx
         if(kx.le.(nptx/2+1)) then
            nx=kx-1
         else
            nx=kx-1-nptx
         end if
         xsc=0.
         if(nx.ne.0) xsc=real(nx)/alenx
         tprop(kx)=exp(eye*(propfacx*xsc**2))
       end do
c
      return
```

```
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine SetPotProp(dt,vprop)
c
c     Potential Energy part of the Trotter Expansion: exp(-i V dt/2)
c
      IMPLICIT NONE
      INTEGER NN,ii,nptx,npts
      REAL xmin,xmax,dx,dt,x,VPOT
      COMPLEX vprop,eye
      parameter(npts=10,nptx=2**npts,NN=1)
      DIMENSION vprop(nptx,NN,NN)
      common /xy/  xmin,xmax
      eye=(0.,1.)
      dx=(xmax-xmin)/real(nptx)
c
      do ii=1,nptx
         x=xmin+ii*dx
         CALL VA(VPOT,x)
         vprop(ii,1,1)=exp(-eye*0.5*dt*VPOT)/sqrt(nptx*1.0)
      END DO
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE energies(energy)
      IMPLICIT NONE
      INTEGER j,NN
      COMPLEX energy,RV,RKE
      PARAMETER (NN=1)
      DIMENSION RV(NN),RKE(NN),energy(NN)
      CALL PE(RV)
      CALL KE(RKE)
      DO j=1,NN
         energy(j)=RV(j)+RKE(j)
      END DO
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE SAVEWF(je2,ndump,dt)
c
c     Dump Time Evolved Wave packet
c
      IMPLICIT NONE
      INTEGER je2,nptx,npts,kk,NN,ncount,ndump,jj
      COMPLEX chi,CRV,energy,psi,Psia
      character*9 B
      REAL V,x1,c1,c2,c1a,x,xmin,xmax,dx,EVALUES,dt
      PARAMETER(npts=10,nptx=2**npts,NN=1)
      DIMENSION CRV(NN,NN),EVALUES(NN)
      DIMENSION psi(NN,NN)
      common /xy/  xmin,xmax
```

```
      COMMON / wfunc/ chi(nptx,NN)
      COMMON /ENER/ energy(NN)
c
      IF(je2.EQ.1) CALL energies(energy)
      jj=je2/ndump
      write(B, '(A,i4.4)') 'arch.', jj
      OPEN(1,FILE=B)
      dx=(xmax-xmin)/real(nptx)
      ncount=(je2-1)/ndump
c
c     Save Wave-packet components
c
      do kk=1,nptx
         x=xmin+kk*dx
         c1=chi(kk,1)*conjg(chi(kk,1))
         write(1,33) x,sqrt(c1)+real(energy(1))
      end do
      write(1,33)
      do kk=1,nptx
         x=xmin+kk*dx
         write(1,33) x,real(energy(1))
      end do
      write(1,33)
c
c     Save Adiabatic states
c
      do kk=1,nptx
         x=xmin+kk*dx
         CALL HAMIL(CRV,x)
         write(1,33) x,CRV(1,1)
      end do
      CLOSE(1)
 33   format(6(e13.6,2x))
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE XM(RV)
c
c     Expectation Value of the Position
c
      IMPLICIT NONE
      INTEGER nptx,npts,kk,NN,j
      COMPLEX chi,EYE,RV
      REAL Vpot,omega,xmin,xmax,dx,pi,rmass,xk,pk,x,alpha
      PARAMETER(npts=10,nptx=2**npts,NN=1)
      DIMENSION RV(NN)
      COMMON / wfunc/ chi(nptx,NN)
      common /xy/  xmin,xmax
      common /packet/rmass,xk,pk

      dx=(xmax-xmin)/real(nptx)
```

```
      DO j=1,NN
         RV(j)=0.0
         do kk=1,nptx
            x=xmin+kk*dx
            IF(j.EQ.1) CALL VA(Vpot,x)
            RV(j)=RV(j)+chi(kk,j)*x*conjg(chi(kk,j))*dx
         end do
      END DO
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE PE(RV)
c
c     Expectation Value of the Potential Enegy
c
      IMPLICIT NONE
      INTEGER nptx,npts,kk,NN,j
      COMPLEX chi,EYE,RV
      REAL Vpot,omega,xmin,xmax,dx,pi,rmass,xk,pk,x,alpha
      PARAMETER(npts=10,nptx=2**npts,NN=1)
      DIMENSION RV(NN)
      COMMON / wfunc/ chi(nptx,NN)
      common /xy/  xmin,xmax
      common /packet/rmass,xk,pk

      dx=(xmax-xmin)/real(nptx)
      DO j=1,NN
         RV(j)=0.0
         do kk=1,nptx
            x=xmin+kk*dx
            IF(j.EQ.1) CALL VA(Vpot,x)
            RV(j)=RV(j)+chi(kk,j)*Vpot*conjg(chi(kk,j))*dx
         end do
      END DO
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine KE(RKE)
c
c     Expectation value of the kinetic energy
c
      IMPLICIT NONE
      INTEGER NN,kk,nptx,kx,nx,npts,j
      REAL dp,theta,wm,p,xmin,xmax,rmass,xk,pi,alenx,pk,rm,re,ri,dx
      COMPLEX eye,chi,Psip,chic,RKE
      parameter(npts=10,nptx=2**npts,NN=1)
      DIMENSION chic(nptx),RKE(NN)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
      COMMON / wfunc/ chi(nptx,NN)
c
```

```
      pi = acos(-1.0)
      dx=(xmax-xmin)/nptx
      dp=2.*pi/(xmax-xmin)
c
      DO j=1,NN
         RKE(j)=0.0
         do kk=1,nptx
            chic(kk)=chi(kk,j)
         end do
         CALL fourn(chic,nptx,1,-1)
         do kx=1,nptx
            if(kx.le.(nptx/2+1)) then
               nx=kx-1
            else
               nx=kx-1-nptx
            end if
            p=0.
            if(nx.ne.0) p = real(nx)*dp
            chic(kx)=p**2/(2.0*rmass)*chic(kx)/nptx
         end do
         CALL fourn(chic,nptx,1,1)
         do kk=1,nptx
            RKE(j)=RKE(j)+conjg(chi(kk,j))*chic(kk)*dx
         end do
      END DO
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine PM(RKE)
c
c     Expectation value of the kinetic energy
c
      IMPLICIT NONE
      INTEGER NN,kk,nptx,kx,nx,npts,j
      REAL dp,theta,wm,p,xmin,xmax,rmass,xk,pi,alenx,pk,rm,re,ri,dx
      COMPLEX eye,chi,Psip,chic,RKE
      parameter(npts=10,nptx=2**npts,NN=1)
      DIMENSION chic(nptx),RKE(NN)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
      COMMON / wfunc/ chi(nptx,NN)
c
      pi = acos(-1.0)
      dx=(xmax-xmin)/nptx
      dp=2.*pi/(xmax-xmin)
c
      DO j=1,NN
         RKE(j)=0.0
         do kk=1,nptx
            chic(kk)=chi(kk,j)
         end do
```

```
         CALL fourn(chic,nptx,1,-1)
         do kx=1,nptx
            if(kx.le.(nptx/2+1)) then
               nx=kx-1
            else
               nx=kx-1-nptx
            end if
            p=0.
            if(nx.ne.0) p = real(nx)*dp
            chic(kx)=p*chic(kx)/nptx
         end do
         CALL fourn(chic,nptx,1,1)
         do kk=1,nptx
            RKE(j)=RKE(j)+conjg(chi(kk,j))*chic(kk)*dx
         end do
      END DO
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE PROPAGATE(vprop,tprop)
c
c     Split Operator Fourier Transform Propagation Method
c     J. Comput. Phys. 47, 412 (1982); J. Chem. Phys. 78, 301 (1983)
c
      IMPLICIT NONE
      INTEGER i,j,NN,ii,nptx,npts
      COMPLEX chi,vprop,chin1,chin2,tprop
      PARAMETER(npts=10,nptx=2**npts,NN=1)
      DIMENSION chin1(nptx),chin2(nptx)
      DIMENSION tprop(nptx),vprop(nptx,NN,NN)
      COMMON / wfunc/ chi(nptx,NN)
c
c     Apply potential energy part of the Trotter Expansion
c
      DO i=1,nptx
         chin1(i)=0.0
         DO j=1,NN
            chin1(i)=chin1(i)+vprop(i,1,j)*chi(i,j)
         END DO
      END DO
c
c     Fourier Transform wave-packet to the momentum representation
c
      CALL fourn(chin1,nptx,1,-1)
c
c     Apply kinetic energy part of the Trotter Expansion
c
      DO i=1,nptx
         chin1(i)=tprop(i)*chin1(i)
      END DO
c
```

```
c     Inverse Fourier Transform wave-packet to the coordinate representation
c
      CALL fourn(chin1,nptx,1,1)
c
c     Apply potential energy part of the Trotter Expansion
c
      DO i=1,nptx
         DO j=1,NN
            chi(i,j)=vprop(i,j,1)*chin1(i)
         END DO
      END DO
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c     Subroutine for FFT from Numerical Recipes
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE FOURN(DATA,NN,NDIM,ISIGN)
      REAL*8 WR,WI,WPR,WPI,WTEMP,THETA
      DIMENSION NN(NDIM),DATA(*)
      NTOT=1
      DO 11 IDIM=1,NDIM
         NTOT=NTOT*NN(IDIM)
 11   CONTINUE
      NPREV=1
      DO 18 IDIM=1,NDIM
         N=NN(IDIM)
         NREM=NTOT/(N*NPREV)
         IP1=2*NPREV
         IP2=IP1*N
         IP3=IP2*NREM
         I2REV=1
         DO 14 I2=1,IP2,IP1
            IF(I2.LT.I2REV)THEN
               DO 13 I1=I2,I2+IP1-2,2
                  DO 12 I3=I1,IP3,IP2
                     I3REV=I2REV+I3-I2
                     TEMPR=DATA(I3)
                     TEMPI=DATA(I3+1)
                     DATA(I3)=DATA(I3REV)
                     DATA(I3+1)=DATA(I3REV+1)
                     DATA(I3REV)=TEMPR
                     DATA(I3REV+1)=TEMPI
 12               CONTINUE
 13            CONTINUE
            ENDIF
            IBIT=IP2/2
 1          IF ((IBIT.GE.IP1).AND.(I2REV.GT.IBIT)) THEN
               I2REV=I2REV-IBIT
               IBIT=IBIT/2
               GO TO 1
            ENDIF
            I2REV=I2REV+IBIT
```

```
 14       CONTINUE
          IFP1=IP1
 2        IF(IFP1.LT.IP2)THEN
             IFP2=2*IFP1
             THETA=ISIGN*6.28318530717959D0/(IFP2/IP1)
             WPR=-2.D0*DSIN(0.5D0*THETA)**2
             WPI=DSIN(THETA)
             WR=1.D0
             WI=0.D0
             DO 17 I3=1,IFP1,IP1
                DO 16 I1=I3,I3+IP1-2,2
                   DO 15 I2=I1,IP3,IFP2
                      K1=I2
                      K2=K1+IFP1
                      TEMPR=SNGL(WR)*DATA(K2)-SNGL(WI)*DATA(K2+1)
                      TEMPI=SNGL(WR)*DATA(K2+1)+SNGL(WI)*DATA(K2)
                      DATA(K2)=DATA(K1)-TEMPR
                      DATA(K2+1)=DATA(K1+1)-TEMPI
                      DATA(K1)=DATA(K1)+TEMPR
                      DATA(K1+1)=DATA(K1+1)+TEMPI
 15                CONTINUE
 16             CONTINUE
                WTEMP=WR
                WR=WR*WPR-WI*WPI+WR
                WI=WI*WPR+WTEMP*WPI+WI
 17          CONTINUE
             IFP1=IFP2
             GO TO 2
          ENDIF
          NPREV=N*NPREV
 18    CONTINUE
       RETURN
       END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
```

47.9 Problem 9

Computational Problem 9: Simulate the propagation of a wave-packet with $x_0 = -5.5$ and initial momentum $p_0 = 2$ colliding with a barrier potential $V(x) = 3$, if abs$(x) < 0.5$, and $V(x) = 0$, otherwise. Hint: In order to avoid artificial recurrences you might need to add an absorbing imaginary potential $V_a(x) = i(\text{abs}(x) - 10)^4$, if abs$(x) > 10$, and $V_a(x) = 0$, otherwise.

The output of this program can be generated and visualized as follows. Cut the source code attached below, save it in a file named Problem9.f, compile it by typing

```
gfortran Problem9.f -o Problem9
```

run it by typing

```
./Problem9
```

The snapshots of the time-dependent wave-packet can be visualized as a movie by typing

```
gnuplot<pp_9
```

where the file named

```
pp_9
```

has the following lines:

Download from (http://ursula.chem.yale.edu/∼batista/classes/summer/P9/pp_9)

```
set yrange[0:4]
set xrange[-10:10]
set dat sty l
plot "arch.0001" u 1:2 lw 3
pause .1
plot "arch.0002" u 1:2 lw 3
pause .1
plot "arch.0003" u 1:2 lw 3
pause .1
plot "arch.0004" u 1:2 lw 3
pause .1
plot "arch.0005" u 1:2 lw 3
pause .1
plot "arch.0006" u 1:2 lw 3
pause .1
plot "arch.0007" u 1:2 lw 3
pause .1
plot "arch.0008" u 1:2 lw 3
pause .1
plot "arch.0009" u 1:2 lw 3
pause .1
plot "arch.0010" u 1:2 lw 3
pause .1
plot "arch.0011" u 1:2 lw 3
```

```
pause .1
plot "arch.0012" u 1:2 lw 3
pause .1
plot "arch.0013" u 1:2 lw 3
pause .1
plot "arch.0014" u 1:2 lw 3
pause .1
plot "arch.0015" u 1:2 lw 3
pause .1
plot "arch.0016" u 1:2 lw 3
pause .1
plot "arch.0017" u 1:2 lw 3
pause .1
plot "arch.0018" u 1:2 lw 3
pause .1
plot "arch.0019" u 1:2 lw 3
pause .1
plot "arch.0020" u 1:2 lw 3
pause .1
plot "arch.0021" u 1:2 lw 3
pause .1
plot "arch.0022" u 1:2 lw 3
pause .1
plot "arch.0023" u 1:2 lw 3
pause .1
plot "arch.0024" u 1:2 lw 3
pause .1
plot "arch.0025" u 1:2 lw 3
pause .1
plot "arch.0026" u 1:2 lw 3
pause .1
plot "arch.0027" u 1:2 lw 3
pause .1
plot "arch.0028" u 1:2 lw 3
pause .1
plot "arch.0029" u 1:2 lw 3
pause .1
plot "arch.0030" u 1:2 lw 3
pause .1
plot "arch.0031" u 1:2 lw 3
pause .1
plot "arch.0032" u 1:2 lw 3
pause .1
plot "arch.0033" u 1:2 lw 3
pause .1
plot "arch.0034" u 1:2 lw 3
pause .1
plot "arch.0035" u 1:2 lw 3
pause .1
plot "arch.0036" u 1:2 lw 3
pause .1
```

```
plot "arch.0037" u 1:2 lw 3
pause .1
plot "arch.0038" u 1:2 lw 3
pause .1
plot "arch.0039" u 1:2 lw 3
pause .1
plot  "arch.0040" u 1:2 lw 3
pause .1
plot "arch.0041" u 1:2 lw 3
pause .1
plot "arch.0042" u 1:2 lw 3
pause .1
plot "arch.0043" u 1:2 lw 3
pause .1
plot "arch.0044" u 1:2 lw 3
pause .1
plot "arch.0045" u 1:2 lw 3
pause .1
plot "arch.0046" u 1:2 lw 3
pause .1
plot "arch.0047" u 1:2 lw 3
pause .1
plot "arch.0048" u 1:2 lw 3
pause .1
plot "arch.0049" u 1:2 lw 3
pause .1
plot "arch.0050" u 1:2 lw 3
pause .1
plot "arch.0051" u 1:2 lw 3
pause .1
plot "arch.0052" u 1:2 lw 3
pause .1
plot "arch.0053" u 1:2 lw 3
pause .1
plot "arch.0054" u 1:2 lw 3
pause .1
plot "arch.0055" u 1:2 lw 3
pause .1
plot "arch.0056" u 1:2 lw 3
pause .1
plot "arch.0057" u 1:2 lw 3
pause .1
plot "arch.0058" u 1:2 lw 3
pause .1
plot "arch.0059" u 1:2 lw 3
pause .1
plot "arch.0060" u 1:2 lw 3
pause .1
plot "arch.0061" u 1:2 lw 3
pause .1
plot "arch.0062" u 1:2 lw 3
```

```
pause .1
plot "arch.0063" u 1:2 lw 3
pause .1
plot "arch.0064" u 1:2 lw 3
pause .1
plot "arch.0065" u 1:2 lw 3
pause .1
plot "arch.0066" u 1:2 lw 3
pause .1
plot "arch.0067" u 1:2 lw 3
pause .1
plot "arch.0068" u 1:2 lw 3
pause .1
plot "arch.0069" u 1:2 lw 3
pause .1
plot "arch.0070" u 1:2 lw 3
pause .1
plot "arch.0071" u 1:2 lw 3
pause .1
plot "arch.0072" u 1:2 lw 3
pause .1
plot "arch.0073" u 1:2 lw 3
pause .1
plot "arch.0074" u 1:2 lw 3
pause .1
plot "arch.0075" u 1:2 lw 3
pause .1
plot "arch.0076" u 1:2 lw 3
pause .1
plot "arch.0077" u 1:2 lw 3
pause .1
plot "arch.0078" u 1:2 lw 3
pause .1
plot "arch.0079" u 1:2 lw 3
pause .1
plot  "arch.0080" u 1:2 lw 3
pause .1
plot "arch.0081" u 1:2 lw 3
pause .1
plot "arch.0082" u 1:2 lw 3
pause .1
plot "arch.0083" u 1:2 lw 3
pause .1
plot "arch.0084" u 1:2 lw 3
pause .1
plot "arch.0085" u 1:2 lw 3
pause .1
plot "arch.0086" u 1:2 lw 3
pause .1
plot "arch.0087" u 1:2 lw 3
pause .1
```

```
plot "arch.0088" u 1:2 lw 3
pause .1
plot "arch.0089" u 1:2 lw 3
pause .1
plot  "arch.0090" u 1:2 lw 3
pause .1
plot "arch.0091" u 1:2 lw 3
pause .1
plot "arch.0092" u 1:2 lw 3
pause .1
plot "arch.0093" u 1:2 lw 3
pause .1
plot "arch.0094" u 1:2 lw 3
pause .1
plot "arch.0095" u 1:2 lw 3
pause .1
plot "arch.0096" u 1:2 lw 3
pause .1
plot "arch.0097" u 1:2 lw 3
pause .1
plot "arch.0098" u 1:2 lw 3
pause .1
plot "arch.0099" u 1:2 lw 3
pause .1
```

Download from (http://ursula.chem.yale.edu/~batista/classes/summer/P9/Problem9.f)

```
      PROGRAM Problem9
c
c     1-D wave packet propagation of tunneling through a barrier
c
      IMPLICIT NONE
      INTEGER NN,npts,nptx,ndump
      INTEGER istep,nstep,jj
      REAL dt,xc,pc
      COMPLEX vprop,tprop,x_mean,p_mean
      PARAMETER(npts=10,nptx=2**npts,NN=1)
      DIMENSION vprop(nptx,NN,NN),tprop(nptx)
      DIMENSION x_mean(NN),p_mean(NN)
      COMMON /class/ xc,pc
c
      CALL ReadParam(nstep,ndump,dt)
      call Initialize()
      CALL SetKinProp(dt,tprop)
      CALL SetPotProp(dt,vprop)
      DO istep=1,nstep+1
         IF(mod(istep-1,10).EQ.0)
     1        PRINT *, "Step=", istep-1,", Final step=", nstep
         IF(istep.GE.1) CALL PROPAGATE(vprop,tprop)
         IF(mod((istep-1),ndump).EQ.0) THEN
            CALL SAVEWF(istep,ndump,dt)
         END IF
      END DO
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine ReadParam(nstep,ndump,dt)
c
c     Parameters defining the grid (xmin, xmax), integration time step (dt),
c     rmass (rmass), initial position (xk), initial momentum (pk),
c     number of propagation steps (nstep), and how often to save a pic (ndump)
c
      IMPLICIT NONE
      INTEGER ntype,nstep,nrpt,ireport,ndump,nlit
      REAL xmin,xmax,pk,rmass,xk,dt
      common /packet/  rmass,xk,pk
      common /xy/  xmin,xmax
c
      xmin=-13.0
      xmax=13.0
      dt=0.1
      rmass=1.0
      xk=-4.5
      pk=1.
      nstep=100
      ndump=1
c
```

```
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE Initialize()

      IMPLICIT NONE
      INTEGER NN,nptx,npts,kk
      COMPLEX chi0,chi,EYE,CRV
      REAL xc,pc,omega,xk2,xmin,xmax,dx,pi,rmass,xk,pk,x,alpha,alpha2
      PARAMETER(npts=10,nptx=2**npts,NN=1)
      DIMENSION CRV(NN,NN)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
      COMMON / wfunc/ chi(nptx,NN)
      COMMON / iwfunc/ chi0(nptx,NN)
      COMMON /class/ xc,pc

      EYE=(0.0,1.0)
      pi= acos(-1.0)
      omega=1.
      dx=(xmax-xmin)/real(nptx)
      xc=xk
      pc=pk
c
c     Wave Packet Initialization: Gaussian centered at xk, with momentum pk
c
      alpha=rmass*omega
      do kk=1,nptx
         x=xmin+kk*dx
         chi(kk,1)=((alpha/pi)**0.25)
     1        *exp(-alpha/2.*(x-xk)**2+EYE*pk*(x-xk))
         chi0(kk,1)=chi(kk,1)
      end do
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE HAMIL(CRV,x)
c
c     Hamiltonian Matrix
c
      IMPLICIT NONE
      INTEGER NN
      REAL x,VPOT1
      COMPLEX CRV
      PARAMETER(NN=1)
      DIMENSION CRV(NN,NN)
c
      CALL VA(VPOT1,x)
      CRV(1,1)=VPOT1
c
      RETURN
```

```
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE VA(V,x)
c
c     Potential Energy Surface: Barrier
c
      implicit none
      REAL V,x,rmass,xk,pk,rk,omega
      common /packet/ rmass,xk,pk
      V=0.0
      IF(abs(x).LE.(.5)) V=3.
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine SetKinProp(dt,tprop)
c
c     Kinetic Energy part of the Trotter Expansion: exp(-i p^2 dt/(2 m))
c
      IMPLICIT NONE
      INTEGER nptx,kx,nx,npts
      REAL xsc,xmin,xmax,propfacx,rmass,xk,pi,alenx,dt,pk
      COMPLEX tprop,eye
      parameter(npts=10,nptx=2**npts)
      DIMENSION tprop(nptx)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
c
      eye=(0.,1.)
      pi = acos(-1.0)
      alenx=xmax-xmin
      propfacx=-dt/2./rmass*(2.*pi)**2
      do kx=1,nptx
         if(kx.le.(nptx/2+1)) then
            nx=kx-1
         else
            nx=kx-1-nptx
         end if
         xsc=0.
         if(nx.ne.0) xsc=real(nx)/alenx
         tprop(kx)=exp(eye*(propfacx*xsc**2))
       end do
c
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine SetPotProp(dt,vprop)
c
c     Potential Energy part of the Trotter Expansion: exp(-i V dt/2)
c
      IMPLICIT NONE
      INTEGER NN,ii,nptx,npts
```

```
      REAL xmin,xmax,dx,dt,x,VPOT,xa
      COMPLEX vprop,eye
      parameter(npts=10,nptx=2**npts,NN=1,xa=10.)
      DIMENSION vprop(nptx,NN,NN)
      common /xy/  xmin,xmax
      eye=(0.,1.)
      dx=(xmax-xmin)/real(nptx)
c
      do ii=1,nptx
         x=xmin+ii*dx
         CALL VA(VPOT,x)
         vprop(ii,1,1)=exp(-eye*0.5*dt*VPOT)/sqrt(nptx*1.0)
         IF(abs(x).GT.(xa))
     1        vprop(ii,1,1)=vprop(ii,1,1)*exp(-(abs(x)-xa)**4)
      END DO
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE energies(energy)
      IMPLICIT NONE
      INTEGER j,NN
      COMPLEX energy,RV,RKE
      PARAMETER (NN=1)
      DIMENSION RV(NN),RKE(NN),energy(NN)
      CALL PE(RV)
      CALL KE(RKE)
      DO j=1,NN
         energy(j)=RV(j)+RKE(j)
      END DO
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE SAVEWF(je2,ndump,dt)
c
c     Dump Time Evolved Wave packet
c
      IMPLICIT NONE
      INTEGER je2,nptx,npts,kk,NN,ncount,ndump,jj
      COMPLEX chi,CRV,energy,psi,Psia
      character*9 B
      REAL V,x1,c1,c2,c1a,x,xmin,xmax,dx,EVALUES,dt
      PARAMETER(npts=10,nptx=2**npts,NN=1)
      DIMENSION CRV(NN,NN),EVALUES(NN)
      DIMENSION psi(NN,NN)
      common /xy/  xmin,xmax
      COMMON / wfunc/ chi(nptx,NN)
      COMMON /ENER/ energy(NN)
c
      IF(je2.EQ.1) CALL energies(energy)
      jj=je2/ndump
      write(B, '(A,i4.4)') 'arch.', jj
```

```
      OPEN(1,FILE=B)
      dx=(xmax-xmin)/real(nptx)
      ncount=(je2-1)/ndump
c
c     Save Wave-packet components
c
      do kk=1,nptx
         x=xmin+kk*dx
         c1=chi(kk,1)*conjg(chi(kk,1))
         write(1,33) x,sqrt(c1)+real(energy(1))
      end do
      write(1,33)
      do kk=1,nptx
         x=xmin+kk*dx
         write(1,33) x
     1        ,real(chi(kk,1))+real(energy(1))
      end do
      write(1,33)
c
c     Save Adiabatic states
c
      do kk=1,nptx
         x=xmin+kk*dx
         CALL HAMIL(CRV,x)
         write(1,33) x,CRV(1,1)
      end do
      CLOSE(1)
 33   format(6(e13.6,2x))
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE PE(RV)
c
c     Expectation Value of the Potential Enegy
c
      IMPLICIT NONE
      INTEGER nptx,npts,kk,NN,j
      COMPLEX chi,EYE,RV
      REAL Vpot,omega,xmin,xmax,dx,pi,rmass,xk,pk,x,alpha
      PARAMETER(npts=10,nptx=2**npts,NN=1)
      DIMENSION RV(NN)
      COMMON / wfunc/ chi(nptx,NN)
      common /xy/  xmin,xmax
      common /packet/rmass,xk,pk

      dx=(xmax-xmin)/real(nptx)
      DO j=1,NN
         RV(j)=0.0
         do kk=1,nptx
            x=xmin+kk*dx
            IF(j.EQ.1) CALL VA(Vpot,x)
```

```
            RV(j)=RV(j)+chi(kk,j)*Vpot*conjg(chi(kk,j))*dx
         end do
      END DO
      RETURN
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      subroutine KE(RKE)
c
c     Expectation value of the kinetic energy
c
      IMPLICIT NONE
      INTEGER NN,kk,nptx,kx,nx,npts,j
      REAL dp,theta,wm,p,xmin,xmax,rmass,xk,pi,alenx,pk,rm,re,ri,dx
      COMPLEX eye,chi,Psip,chic,RKE
      parameter(npts=10,nptx=2**npts,NN=1)
      DIMENSION chic(nptx),RKE(NN)
      common /xy/  xmin,xmax
      common /packet/  rmass,xk,pk
      COMMON / wfunc/ chi(nptx,NN)
c
      pi = acos(-1.0)
      dx=(xmax-xmin)/nptx
      dp=2.*pi/(xmax-xmin)
c
      DO j=1,NN
         RKE(j)=0.0
         do kk=1,nptx
            chic(kk)=chi(kk,j)
         end do
         CALL fourn(chic,nptx,1,-1)
         do kx=1,nptx
            if(kx.le.(nptx/2+1)) then
               nx=kx-1
            else
               nx=kx-1-nptx
            end if
            p=0.
            if(nx.ne.0) p = real(nx)*dp
            chic(kx)=p**2/(2.0*rmass)*chic(kx)/nptx
         end do
         CALL fourn(chic,nptx,1,1)
         do kk=1,nptx
            RKE(j)=RKE(j)+conjg(chi(kk,j))*chic(kk)*dx
         end do
      END DO
      return
      end
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE PROPAGATE(vprop,tprop)
c
c     Split Operator Fourier Transform Propagation Method
```

```
c     J. Comput. Phys. 47, 412 (1982); J. Chem. Phys. 78, 301 (1983)
c
      IMPLICIT NONE
      INTEGER i,j,NN,ii,nptx,npts
      COMPLEX chi,vprop,chin1,chin2,tprop
      PARAMETER(npts=10,nptx=2**npts,NN=1)
      DIMENSION chin1(nptx),chin2(nptx)
      DIMENSION tprop(nptx),vprop(nptx,NN,NN)
      COMMON / wfunc/ chi(nptx,NN)
c
c     Apply potential energy part of the Trotter Expansion
c
      DO i=1,nptx
         chin1(i)=0.0
         DO j=1,NN
            chin1(i)=chin1(i)+vprop(i,1,j)*chi(i,j)
         END DO
      END DO
c
c     Fourier Transform wave-packet to the momentum representation
c
      CALL fourn(chin1,nptx,1,-1)
c
c     Apply kinetic energy part of the Trotter Expansion
c
      DO i=1,nptx
         chin1(i)=tprop(i)*chin1(i)
      END DO
c
c     Inverse Fourier Transform wave-packet to the coordinate representation
c
      CALL fourn(chin1,nptx,1,1)
c
c     Apply potential energy part of the Trotter Expansion
c
      DO i=1,nptx
         DO j=1,NN
            chi(i,j)=vprop(i,j,1)*chin1(i)
         END DO
      END DO
      END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c     Subroutine for FFT from Numerical Recipes
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE FOURN(DATA,NN,NDIM,ISIGN)
      REAL*8 WR,WI,WPR,WPI,WTEMP,THETA
      DIMENSION NN(NDIM),DATA(*)
      NTOT=1
      DO 11 IDIM=1,NDIM
         NTOT=NTOT*NN(IDIM)
 11   CONTINUE
```

```
      NPREV=1
      DO 18 IDIM=1,NDIM
         N=NN(IDIM)
         NREM=NTOT/(N*NPREV)
         IP1=2*NPREV
         IP2=IP1*N
         IP3=IP2*NREM
         I2REV=1
         DO 14 I2=1,IP2,IP1
            IF(I2.LT.I2REV)THEN
               DO 13 I1=I2,I2+IP1-2,2
                  DO 12 I3=I1,IP3,IP2
                     I3REV=I2REV+I3-I2
                     TEMPR=DATA(I3)
                     TEMPI=DATA(I3+1)
                     DATA(I3)=DATA(I3REV)
                     DATA(I3+1)=DATA(I3REV+1)
                     DATA(I3REV)=TEMPR
                     DATA(I3REV+1)=TEMPI
12                CONTINUE
13             CONTINUE
            ENDIF
            IBIT=IP2/2
1           IF ((IBIT.GE.IP1).AND.(I2REV.GT.IBIT)) THEN
               I2REV=I2REV-IBIT
               IBIT=IBIT/2
               GO TO 1
            ENDIF
            I2REV=I2REV+IBIT
14       CONTINUE
         IFP1=IP1
2        IF(IFP1.LT.IP2)THEN
            IFP2=2*IFP1
            THETA=ISIGN*6.28318530717959D0/(IFP2/IP1)
            WPR=-2.D0*DSIN(0.5D0*THETA)**2
            WPI=DSIN(THETA)
            WR=1.D0
            WI=0.D0
            DO 17 I3=1,IFP1,IP1
               DO 16 I1=I3,I3+IP1-2,2
                  DO 15 I2=I1,IP3,IFP2
                     K1=I2
                     K2=K1+IFP1
                     TEMPR=SNGL(WR)*DATA(K2)-SNGL(WI)*DATA(K2+1)
                     TEMPI=SNGL(WR)*DATA(K2+1)+SNGL(WI)*DATA(K2)
                     DATA(K2)=DATA(K1)-TEMPR
                     DATA(K2+1)=DATA(K1+1)-TEMPI
                     DATA(K1)=DATA(K1)+TEMPR
                     DATA(K1+1)=DATA(K1+1)+TEMPI
15                CONTINUE
16             CONTINUE
```

```
               WTEMP=WR
               WR=WR*WPR-WI*WPI+WR
               WI=WI*WPR+WTEMP*WPI+WI
 17          CONTINUE
             IFP1=IFP2
             GO TO 2
           ENDIF
           NPREV=N*NPREV
 18    CONTINUE
       RETURN
       END
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
```