

PHY 308 Problem Set: Spring 2018

Stony Brook University
Instructor: Prof. Thomas K. Allison

1 Wave Function Push-ups (18 points)

Consider a particle confined to one dimension and positive x with the wave function

$$\psi(x) = \begin{cases} Nxe^{-\alpha x}, & x \geq 0 \\ 0, & x < 0 \end{cases} \quad (1.1)$$

where N is a real normalization constant and α is a real positive constant with units of $(\text{length})^{-1}$. For the following, express your answers in terms of α :

- Find the normalization constant N . What are the units of your result and do they make sense?
- What is the most probable location to find the particle, or more precisely, at what x is the probability density maximum?
- Calculate the expectation value $\langle \hat{x} \rangle$.
- Calculate the expectation value $\langle \hat{x}^2 \rangle$.
- Use your results from c) and d) to calculate the variance in the position, σ_x^2 .
- Calculate the expectation value of the momentum, $\langle \hat{p} \rangle$ via the canonical expression

$$\langle \hat{p} \rangle = \int_{-\infty}^{\infty} dx \psi^*(x) \left(-i\hbar \frac{d}{dx} \right) \psi(x) \quad (1.2)$$

- Calculate the expectation value of $\langle \hat{p}^2 \rangle$ via the canonical expression

$$\langle \hat{p}^2 \rangle = \int_{-\infty}^{\infty} dx \psi^*(x) \left(-i\hbar \frac{d}{dx} \right)^2 \psi(x) \quad (1.3)$$

- Use your results for $\langle \hat{p} \rangle$ and $\langle \hat{p}^2 \rangle$ to calculate the variance in momentum, σ_p^2 .
- Calculate the uncertainty product $\sigma_x \sigma_p$. Is your result consistent with the Heisenberg uncertainty principle?

2 Momentum Space (10 points)

Usually, we think of a wave function as a complex-valued function existing in real-space defined by position coordinates, such as the cartesian coordinate (x, y, z) , or the spherical coordinates (r, θ, ϕ) . But one can think of the state vector of the system $|\psi\rangle$ in a more abstract way that is basis independent. Indeed, tying the formulation of quantum mechanics to coordinates fails spectacularly when one starts thinking about spin angular momentum, because you can't write down a function of coordinates to represent the spin of a particle. From this more general and abstract "state vector" perspective, the function we call the "wave function" is just a projection of the state vector $|\psi\rangle$ onto the position basis, viz.

$$\psi(x) = \langle x | \psi \rangle \quad (2.1)$$

We will explore these ideas in more detail later in the course when we look at Quantum Mechanics from a linear algebra perspective. The first chapter of Sakurai's book, *Modern Quantum Mechanics*, has a beautifully clear exposition on the subject.

One can project the wave function onto bases other than position. For example, one could work in momentum space. In 1D, the momentum space wave function $\Phi(p)$ is related to the position space wave function $\psi(x)$ via a simple Fourier transform pair:

$$\phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx e^{-ipx/\hbar} \psi(x) \quad (2.2)$$

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp e^{ipx/\hbar} \phi(p) \quad (2.3)$$

Let's look at how this works for the wave function we worked with in problem 1, equation (1.1). Starting with this wave function,

a) Calculate the momentum space wave function.

b) Verify that the momentum space wave function is normalized such that.

$$\int_{-\infty}^{\infty} dp |\phi(p)|^2 = 1 \quad (2.4)$$

c) Use the momentum space wave function to calculate the expectation value $\langle \hat{p} \rangle$ via

$$\langle p \rangle = \int_{-\infty}^{\infty} dp \phi^*(p) p \phi(p) \quad (2.5)$$

You should get the same expression as in problem 1f).

3 Complex Absorbing Potentials (10 points)

A normalized wave function would not be of much use if it did not stay normalized. Indeed, it can be shown that time evolution of the wave function via the Schrödinger equation does not change the norm of the wave function:

$$\frac{d}{dt} \int_{-\infty}^{\infty} dx |\Psi(x, t)|^2 = 0 \quad (3.1)$$

So that the total probability density is a constant of the motion. However, there are cases where this fact is computationally inconvenient, and one would like to introduce a mechanism for the wave function to decay (or leave a region of interest) without rigorously including all of the physics required to do this. As you will show below for a simple case, one can do this by letting the potential function become *complex*. Some examples where complex absorbing potentials are used are spontaneous emission, particle decay, and problems solved numerically on a finite sized grid where one would like the particle to leave the grid without reflection from its boundaries. For the latter case, the complex absorbing potential is sometimes called a “Gobbler”, since it is placed at the edge of the boundary to eat the wave function when it gets to the boundary.

Consider a particle governed by the 1D time dependent Schrödinger equation, except now with a complex constant added to the potential, viz.

$$V = V_0(x) - i\Gamma \quad (3.2)$$

where Γ is a real positive constant.

a) Show that instead of equation (3.1), you now get

$$\frac{dP}{dt} = -\frac{2\Gamma}{\hbar} P \quad (3.3)$$

where $P \equiv \int_{-\infty}^{\infty} dx |\Psi(x, t)|^2$

b) Solve for $P(t)$ and find the lifetime of the particle in terms of Γ .

4 Normalization and Orthogonality (5 points)

(a) The wave functions $f(x)$ and $g(x)$ are normalized and orthogonal. This means that the wave functions $f(x)$ and $g(x)$ satisfy:

$$\langle f|f \rangle = \int_{-\infty}^{\infty} dx f(x)^* f(x) = 1, \quad \langle g|g \rangle = \int_{-\infty}^{\infty} dx g(x)^* g(x) = 1 \quad (4.1)$$

and

$$\langle f|g \rangle = \int_{-\infty}^{\infty} dx f(x)^* g(x) = 0 = \int_{-\infty}^{\infty} dx g(x)^* f(x) = \langle g|f \rangle \quad (4.2)$$

Find the normalization constant N for the wave function that is a superposition of these $\phi(x) = af(x) + bg(x)$ where a and b are complex valued constants.

(b) Now find the normalization for the superposition $\phi(x) = af(x) + bg(x)$, but take the functions f and g to be normalized but *not* orthogonal with their overlap integral given by

$$\int_{-\infty}^{\infty} dx f(x)^* g(x) = S \quad (4.3)$$

5 Quantum Cascade Lasers (5 points)

There are currently few solid state lasers that emit light in the mid-infrared (i.e. $\lambda > 3 \mu\text{m}$). Researchers in the mid 1990's demonstrated such a laser based on transitions between adjacent energy levels in a semiconductor "quantum well", which consists of a thin layer of material sandwiched between layers of another material resulting in confinement of the electron. The most commonly used structure is a layer of GaAs sandwiched between layers of AlGaAs.

(a) By modeling the states of the electron as those of an infinite square well of width a , calculate the energy of the emitted photon when an electron makes a transition from the $n + 1$ state to the n state. Since the electron is in the periodic potential of the bulk semiconductor, it has an effective reduced mass of $0.07m_e$.

(b) How thick should the layer be if $10 \mu\text{m}$ is the desired wavelength of the $n = 2$ to $n = 1$ transitions?

The quantum cascade laser, first demonstrated in 1994, is based on this type of transition. Crystal growth techniques can now produce layers thinner than 1 nm .

6 Particle Moving in a box (10 points)

A "wave-packet" can be formed by a coherent superposition of stationary states. Unlike stationary states, wave packets move. Consider the superposition of particle in the box eigenstates.

$$\Psi(x, t = 0) = \frac{1}{\sqrt{2}}\psi_1(x) + \frac{1}{\sqrt{2}}\psi_2(x) = \left(\frac{1}{L}\right)^{1/2} \left[\sin\left(\frac{\pi x}{L}\right) + \sin\left(\frac{2\pi x}{L}\right) \right] \quad (6.1)$$

for $0 < x < L$ and $\Psi = 0$ outside of this interval.

a) Write out $\Psi(x, t)$.

b) Make plots of the probability density $|\Psi(x, t)|^2$ for the different times $t = 0, \frac{\hbar\pi}{2\Delta E}$, and $\frac{\hbar\pi}{\Delta E}$. Where $\Delta E = E_2 - E_1$ is the difference between the first two energy levels this particle in a box system. The point is to see the shape $|\Psi|^2$, so for the purpose of making these plots, set $\hbar = m = L = 1$.

c) What is the expectation value of the system's total energy $\langle \hat{H} \rangle$? Does this change with time?

(d) Derive an expression for the time dependent expectation value of $\langle x \rangle(t)$. *Hint: Utilize the symmetry of the wavefunctions around $x = L/2$.*

7 Free Particles, Wave Packets, and Quantum Diffusion (15 points)

The Schrödinger equation is often called a wave equation and has "wave-like" solutions. On the other hand, it also looks very similar to the diffusion equation. The equations below are the Schrödinger equation with $V = 0$ (i.e. The Schrödinger equation for a free particle), diffusion equation, and classical wave equation (e.g. for a wave on a guitar string).

$$\frac{\partial \Psi}{\partial t} = D \frac{\partial^2 \Psi}{\partial x^2} \quad \text{1D Diffusion Equation} \quad (7.1)$$

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} \quad \text{1D Schrödinger Equation} \quad (7.2)$$

$$\frac{\partial^2 \Psi}{\partial t^2} = c^2 \frac{\partial^2 \Psi}{\partial x^2} \quad \text{1D Wave Equation} \quad (7.3)$$

In these equations D is the diffusion coefficient and c is the wave's phase velocity. One way to view the free particle Schrödinger equation is as a diffusion equation in imaginary time.

(a) Show that the plane wave given by

$$\Psi(x, t) = Ae^{i(k_0 x - \omega t)} \quad (7.4)$$

satisfies the time dependent 1D Schrödinger equation with $V = 0$. Find the resulting expression for ω and the energy E as functions of k_0 . What is the speed of the wave? Express your answer in terms k_0 , \hbar , and m . *Hint: rewrite this as a function of $x - vt$ and find v .*

(b) Show that this plane wave solution also satisfies the wave equation. Find the resulting expression for ω as functions of k . What is the speed of the wave?

(c) Show that the function

$$\Psi(x, t) = \sqrt{\frac{t_0}{t}} \exp\left(\frac{-x^2}{4Dt}\right) \quad (7.5)$$

satisfies the diffusion equation, where t_0 is a constant such that $Dt_0 = x_0^2$. How does the width of the function depend on time?

(d) Show that the function

$$\Psi(x, t) = \sqrt{\frac{\pi}{\alpha + i\beta t}} e^{i(k_0 x - \omega_0 t)} \exp\left(\frac{-(x - v_g t)^2}{4(\alpha + i\beta t)}\right) \quad (7.6)$$

satisfies the time dependent Schrödinger equation. Find the resulting relations for v_g and β in terms of k_0 and fundamental constants. Use your previous result for the relation between ω_0 and k_0 .

(e) The function described by equation (7.6) is called a wave packet and can be used to describe the unbound motion of quantum mechanical systems. A good example might be the wave-packet produced in the photodissociation of a molecule by an ultrashort laser pulse. What is the speed with which this wave packet moves with (a.k.a. the *group velocity*)? Or to ask more precisely, what is the speed that the center of the wave packet moves with? Express your answer in terms k_0 , \hbar , and m .

(f) How does the width of $|\Psi|^2$ of the wave packet depend on time for $\beta t \gg \alpha$? Compare this “quantum diffusion” to your result from (c).

(g) In part (a), you calculated a speed for the plane wave solution to the Schrödinger equation, and in part (e), you calculated the speed of the wave packet? Considering that the momentum of a wave is $\hbar k$ (the de Broglie relation), which solution do you think makes more physical sense? *Hint: Consulting David J. Griffiths' "Introduction to Quantum Mechanics" will be insightful.*

Understanding the difference between the *phase velocity* and the *group velocity* is invaluable for understanding wave phenomena, whether in quantum mechanics, optics, or water waves (e.g. a Tsunami).

8 Image Potential States (10 points)

Consider an electron at the surface of a metal. If the electron tries go away from the metal with surface at $x = 0$, it will experience an attractive force from its “image charge” in the metal. For $x > 0$, the electron then experiences an attractive Coloumb potential $\propto -1/x$. However, if the electron tries to go into the metal it must have an energy compatible with one of the allowed (and unoccupied) states of the metal. An electron with an energy within the solid's band gap thus experiences an effective repulsive potential at the surface. The combination of these two effects creates a potential well at the metal's surface which can support bound states at the metal's surface commonly called “image potential states”.

In this problem we will use a model potential to get a feel for the problem. Consider a particle governed by the 1D Schrodinger equation with the following potential $V(x)$,

$$V(x) = \begin{cases} -\frac{1}{4\pi\epsilon_0} \frac{e^2}{4x}, & x > 0 \\ \infty, & x \leq 0 \end{cases} \quad (8.1)$$

- a) What are the boundary conditions that $\psi(x)$ must obey?
- b) Verify that the wave function you already experimented with in problems 1 and 2, equation (1.1), can be a solution to the Schrödinger equation with appropriate choices for α and E . What are the resulting values of α and E , in terms of fundamental constants.
- c) Does wave function (1.1) also satisfy the necessary boundary conditions? Why or why not?
- d) Use your results from problem 1 to calculate the expectation value $\langle x \rangle$ in units of ångströms.

It turns out that wave function (1.1) describes the ground state of this system. There are excited states as well, described reasonably well by a Rydberg series with $E_n \propto -1/n^2$. Indeed, the Schrödinger equation with this model potential is of the same functional form as the radial equation for the Hydrogen atom. This simple model potential was first applied to image potential states by Cole and Cohen in 1969 (*Phys. Rev. Lett.* **23**, 1238 (1969)). If a superposition of image potential states is formed, the electron can be made to oscillate at the surface. For a beautiful experimental observation of this, see U. Höfer *et al.*, *Science* **277**, 1480 (1997).

9 Resonant Tunneling Diodes (15 points)

Resonant tunneling diodes (RTD), formed by sandwiched layers of different semiconductors, are high-speed electronic components that make use of quantum-mechanical tunneling. In this problem, we will explore some of the essential features of these devices using a simple model. While typical high-performance digital clock speeds are in the GHz range, the fastest RTDs can switch at speeds over 1 THz!

Consider an electron with kinetic energy $E = 0.1$ eV incident from the left ($x < 0$) on the potential shown in figure 1. For the sake of simplicity, take the effective mass of the electron to be its regular mass $m_e = 9.1 \times 10^{-31}$ kg (In silicon it can be close to this). It may be convenient to use the fact that $\hbar^2/2m_e = 3.81$ eV-Å².

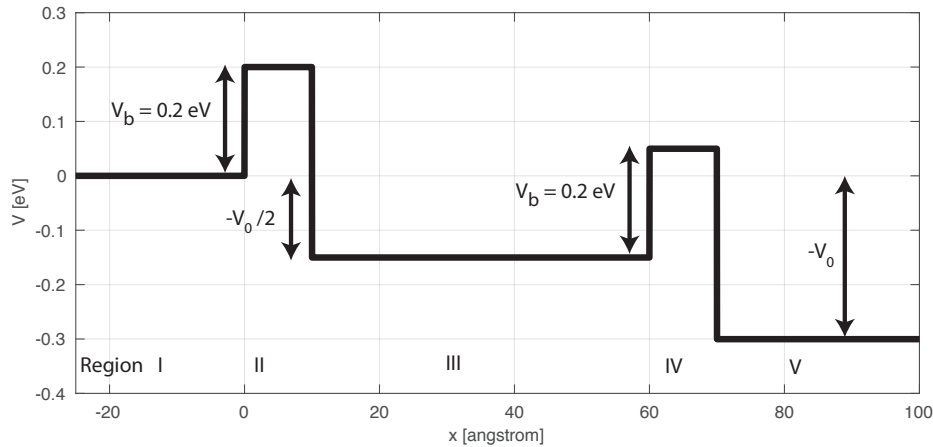


Figure 1: Scattering potential for problem 9. A 0.1 eV electron is incident from the left. You will calculate the transmission as a function of the bias potential in the range $V_0 = 0$ -2 eV. The barriers are 0.2 eV high and 10 Å thick. The spacing between the barriers is 50 Å. The wave function has a different form in each labeled region.

- a) Write down the general form of the wavefunction in each region of the potential in terms of plane waves or exponential decays. For example, in region I, we have $E > V$, so we can write the wave function as a sum of leftward (incident) and rightward (reflected) going plane waves $\psi(x) = Ae^{ikx} + Be^{-ikx}$.
- b) Apply the boundary conditions to calculate the reflection coefficient, R , for the particle as a function of the bias potential V_0 over the range $V_0 = 0$ -2 eV and make a plot of this. Use $R + T = 1$ to calculate the

transmission coefficient, T . The plot of the transmission versus bias voltage is akin to the current-voltage (I-V curve) of the device. *Hint 2: this involves at least 8 linear equations for 8 unknowns, so you should use a computer to do the algebra. If you write the problem in terms of matrices, it is very easy to use MATLAB or other such softwares to invert matrices.*

c) Why do you get the wrong answer for the transmission coefficient in this problem (and $R + T \neq 1$) if you simply use the square modulus of the amplitude of the wave function in region V to calculate T ?

d) Why do you observe resonances in the transmission curve? At what energies do you observe them?

e) Why can there not be bound states trapped in the well formed by the two potential barriers?

f) At the lowest bias potential that shows a resonance, make a representative plot of the total wave function overlaid on top of the potential. Your wave function is likely complex, so plot the real and imaginary components separately.

g) If you increase the height of the two barrier regions, V_b , do you expect the resonances to get sharper or broader? *Hint: think about a Fabry-Pérot interferometer.*

10 Scattering Phases and Wigner Delay (15 points)

Consider a free particle of mass m and energy E incident from the left on the scattering potential confined to the region $-a < x < 0$:

$$V(x) = \begin{cases} 0, & x < -a \\ V_0, & -a \leq x < 0 \\ \infty, & x \geq 0 \end{cases} \quad (10.1)$$

The incident free particle can be described in the region $x < -a$ by a plane wave $\psi = Ae^{ikx}$ with $k = \sqrt{2mE}/\hbar$. Since the potential barrier is infinite, the reflected wave in the region $x < -a$, Be^{-ikx} , must have the same amplitude as the incident wave, so we must have $|B| = |A|$. However, the reflected wave can acquire a phase shift, and by convention we define the scattering phase δ via

$$B \equiv -Ae^{i2\delta} \quad (10.2)$$

The scattering problem then reduces to determining this phase shift. Many other scattering problems are also formulated in terms of phase shifts. In a seminal 1955 paper (E.P. Wigner *Phys. Rev.* **98**, 145 (1955)) explored the connections between the scattering phase shift and time delays in the scattering process. The so-called Wigner delay is calculated from the scattering phase shift via

$$\tau_W = \hbar \frac{d\delta}{dE} \quad (10.3)$$

Wigner showed that the scattering phase shift is thus constrained by causality. A particle, described by a wave packet, cannot emerge from the scattering region (in this problem $-a < x < 0$) before it arrives. In this problem, you will explore the scattering phase shift and its connections to time delays for this simple 1D problem.

a) Show that for the scattering potential of equation (10.1) the amplitude of the reflected wave is given by

$$B = Ae^{-2ika} \left[\frac{k - ik' \cot(k'a)}{k + ik' \cot(k'a)} \right] \quad (10.4)$$

where $k' = \sqrt{2m(E - V_0)}/\hbar$ and \cot detones the cotangent. *Hint: These formulae hold for all E with k' becoming imaginary for $E < V_0$ and $\cot(ix) = -i \coth(x)$, but it is more natural derive for $E > V_0$, since then k' is real.*

b) Confirm that the reflected wave has the same amplitude as the incident wave $|B| = |A|$.

c) Use a computer to calculate and plot the phase shift δ over the range $0.1 < \frac{Ema^2}{\hbar^2} < 100$ for $V_0 = 30 \frac{\hbar^2}{ma^2}$. It is easiest to write your program in units with $\hbar = a = m = 1$, such that E ranges between 0.1 and 100 and $V_0 = 30$.

d) Numerically take the derivative of your data in c) to calculate the Wigner delay. Make a plot showing the Wigner delay vs. energy. Also on this graph, plot the quantity $-a/(\hbar k/m)$. Recall that in problem 7 you worked out that $\hbar k/m$ is the group velocity for a free particle with momentum $\hbar k$. Your Wigner delay should never be smaller than $-a/(\hbar k/m)$, but should approach it for $E \ll V_0$. Interpret this fact along with the Wigner delay at any resonances you observe.

11 Projection onto a basis (10 points)

We are unable to exactly solve the Schrödinger equation for all but the simplest quantum systems. However, we are able to approximately solve the Schrödinger equation for a great many systems. A key concept in all the approximate solution schemes is projection of the wave function onto a set of basis functions. A sum of basis functions then forms an approximate solution to the Schrödinger equation, which can be systematically improved to the desired accuracy. This is the essence of the field of Quantum Chemistry. In this problem we will see how this works with a very simple example. Consider the 1D function defined on the interval $x = 0$ to $x = L$

$$\psi(x) = \left(\frac{1}{L}\right)^{1/2} \left[\frac{1}{4} - \left(\frac{x}{L} - \frac{1}{2}\right)^2 \right] \quad (11.1)$$

and the set of basis functions $f_n(x)$

$$f_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \quad (11.2)$$

with $n = 1, 2, 3, \dots$. Perhaps you recognize these basis functions as the normalized eigenfunctions of the particle in the box. The set of basis functions f_n are *orthogonal*, *normalized*, and form a *complete basis*. We will discuss what this means more formally later in the course. From a practical perspective, this means the function $\psi(x)$ can be written as a sum of the basis functions with the appropriate coefficients c_n :

$$\psi(x) = \sum_{n=1}^{\infty} c_n f_n(x) \quad (11.3)$$

with the coefficients given by

$$c_n = \int_0^L dx f_n(x)^* \psi(x) \quad (11.4)$$

Now since equation (11.3) contains a sum of an infinite number of functions, it cannot actually be evaluated. However, in practice, truncating the sum at some finite number is usually acceptable.

- Rewrite equations (11.3) and (11.4) in Dirac bra-ket notation.
- Calculate the coefficients c_n for $n = 1, 2, 3$, and 4. *Hint: You may not actually have to evaluate some of these integrals if you think about the symmetry of the functions around $x = L/2$.*
- Make a plot showing three curves on the same graph on the interval $x = 0$ to $x = L$: (1) the original function $\psi(x)$, (2) the sum in equation (11.3) truncated at $n = 2$, and (3) the sum truncated at $n = 4$.

12 Commutator Push-ups (10 points)

Evaluate the following commutators:

- $[\frac{\hat{1}}{x}, \hat{p}_x]$
- $[V(x), \hat{p}_x]$, where $V(x)$ is any function of x .
- $[\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{y}\hat{p}_z - \hat{z}\hat{p}_y]$
- $[x^2 \frac{\partial^2}{\partial y^2}, y \frac{\partial}{\partial x}]$

13 Vector Spaces (5 points)

a) Does the set of all polynomials $f(x)$ (with complex coefficients) of degree $< N$ that satisfy $f(1) = 0$ constitute a vector space?

b) Show that the equation $[\hat{A}, \hat{B}] = \hat{I}$ cannot be satisfied by operators working on finite dimensional vector spaces, or equivalently that the matrix equation $[\mathbf{A}, \mathbf{B}] = \mathbf{I}$ cannot be satisfied by finite dimensional matrices. This was realized early in the history of Quantum Mechanics, soon after the discovery that $[\hat{x}, \hat{p}] = i\hbar$.

14 Commuting Observables and Quantum numbers (10 points)

Quantum chemists often use a lot of labels to describe a quantum mechanical state of a system. For example, the ground electronic state of the N_2 molecule is labeled $^1\Sigma_g^+$. Why so many labels? Sometimes one label just isn't enough, particularly when energy levels are degenerate. Consider a system with two energy levels, one of which is two-fold degenerate. Take the Hamiltonian \hat{H} for the system to be represented in the orthonormal basis $|\alpha\rangle, |\beta\rangle, |\gamma\rangle$, such that

$$\hat{H}|\alpha\rangle = E_1|\alpha\rangle \quad (14.1)$$

$$\hat{H}|\beta\rangle = E_2|\beta\rangle \quad (14.2)$$

$$\hat{H}|\gamma\rangle = E_2|\gamma\rangle \quad (14.3)$$

In some sense the system is ill defined, in that labeling the states by the energy eigenvalue is ambiguous. If I ask you to describe the E_2 state, you could answer with $|\beta\rangle, |\gamma\rangle$, or in fact any normalized linear combination of the two for an infinite number of possibilities (see part a) below)! This is not a very satisfactory situation. It implies that we need a second quantum number to label the states to remove the ambiguity.

Such a second quantum number can be found using another observable that commutes with the Hamiltonian. For a molecule, this might be a symmetry operator that leaves the molecule unchanged. This problem explores the linear algebra of commuting observables.

a) Show that any linear combination of $|\beta\rangle$ and $|\gamma\rangle$ is also an eigenvector of \hat{H} with eigenvalue E_2 .

b) Write down a matrix representation of \hat{H} in the $|\alpha\rangle, |\beta\rangle, |\gamma\rangle$ basis.

c) Consider the operator \hat{A} such that

$$\hat{A}|\alpha\rangle = a|\alpha\rangle \quad (14.4)$$

$$\hat{A}|\beta\rangle = b|\beta\rangle + ic|\gamma\rangle \quad (14.5)$$

$$\hat{A}|\gamma\rangle = -ic|\beta\rangle + b|\gamma\rangle \quad (14.6)$$

Write down a matrix representation in the $|\alpha\rangle, |\beta\rangle, |\gamma\rangle$ basis and use it to show that \hat{A} commutes with \hat{H} .

d) Using linear combinations of $|\alpha\rangle, |\beta\rangle$, and $|\gamma\rangle$ construct simultaneous eigenkets $|\lambda_H, \lambda_A\rangle$ of \hat{H} and \hat{A} . The labels λ_H and λ_A correspond to the eigenvalues of \hat{H} and \hat{A} , which you need to find as part of this problem.

15 Ehrenfest's Theorem (10 points)

Using the Schrödinger equation, show that for a system obeying the time-dependent Schrödinger equation in one dimension:

$$\frac{d\langle p \rangle}{dt} = \left\langle -\frac{dV}{dx} \right\rangle \quad (15.1)$$

This is a manifestation of Ehrenfest's theorem, and it tells us that expectation values obey Newton's second law of mechanics. This theorem is exploited in many semi-classical formulations of molecular dynamics (e.g. <http://link.aip.org/link/doi/10.1063/1.2008258>)

Hint: This problem can be solved by differentiating the integral expression for $\langle \Psi | \hat{p} | \Psi \rangle$ but is much easier if you use operator/commutator formalism. Consider the expectation value of the commutator $[\hat{H}, \hat{p}]$.

16 Time Evolution Operator (5 points)

When an operator is written in an exponent such as $e^{\hat{A}}$, it is understood that this means

$$e^{\hat{A}} = \sum_{n=0}^{\infty} \frac{1}{n!} \hat{A}^n \quad (16.1)$$

The time evolution operator is

$$\hat{U}(t, t_0) = \exp \left(-i \frac{\hat{H}}{\hbar} (t - t_0) \right) \quad (16.2)$$

a) Show that for a system with wave function $|\Psi(x, t_0)\rangle$ at $t = t_0$, the wave function at later times $|\Psi(x, t)\rangle$ is given by

$$|\Psi(x, t)\rangle = \hat{U}(t, t_0) |\Psi(x, t_0)\rangle \quad (16.3)$$

b) Show that the \hat{U} is a unitary operator, which means that $\hat{U}^\dagger = \hat{U}^{-1}$ or equivalently: $\hat{U}^\dagger \hat{U} = 1$.

17 The Classically Forbidden Region (10 points)

A dynamical system obeying the laws of classical mechanics must always have $T + V = E$, where T is the kinetic energy, V is the potential energy, and E is the total energy. A classical system can then never be found outside of the region where $V(\vec{r}) \leq E$ because this would require a negative kinetic energy. For example, if you release a pendulum at rest from a certain height y_0 , you will never find it later at greater height $y > y_0$. The region $y > y_0$ is the “forbidden region”.

Quantum mechanics has no such restriction. In this problem, we will examine the wave functions of the harmonic oscillator in the classically forbidden region.

a) Use a computer to calculate the probability of finding the displacement of a harmonic oscillator in the classically forbidden region for the states with quantum number $n = 0$ to 9. Remember that while your time is valuable, computers are mindless idiots good at repetitive tasks, so automate your code using for loops, etc. Plot and interpret your results.

b) The harmonic oscillator wave functions do not have any nodes in the classically forbidden region (this is unfortunately not so easy to prove, as it involves deriving bounds on the roots of the Hermite Polynomials). Why might you expect this to be the case? *Hint: Consider the form of the Schrödinger equation for $V > E$.*

18 Heisenberg Picture (5 points)

In this course, as in most modern treatments of quantum mechanics, we have been considering the operators (e.g. \hat{p}, \hat{x}) to be time independent and the state vector (e.g. $|\Psi(x, t)\rangle$) to be time dependent to account for time evolution. This is the so-called “Schrödinger picture”. In the “Heisenberg picture”, one accounts for time evolution by taking the state vectors to be stationary and letting the operators become time-dependent. The operators then obey Heisenberg equations of motion.

Solve the Heisenberg equations of motion

$$\frac{d\hat{a}(t)}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{a}(t)] \quad , \quad \frac{d\hat{a}^\dagger(t)}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{a}^\dagger(t)]$$

for the creation and destruction operators associated with a harmonic oscillator of natural angular frequency ω .

19 Quantum or Classical? A wave mechanics perspective (15 points).

It is usually much easier to treat the motion of a particle or (especially) a system of particles using classical mechanics than quantum mechanics. One can show that classical mechanics is the $\hbar \rightarrow 0$ limit of quantum mechanics, and thus classical mechanics describes systems well for which \hbar is an insignificant quantity, but how would you access whether it is significant or not?

One way to do this is to calculate the product of the length scale and momentum scale of the problem, $\sim \sqrt{\langle x^2 \rangle \langle p^2 \rangle}$ and compare this to \hbar . If the product xp is much much larger than \hbar , then it is likely safe to use classical mechanics. Viewed another way, since the de Broglie wavelength of a particle is given by $\lambda = h/p$, one can compare the size of the particle's characteristic de Broglie wavelength λ to the spatial dimensions x it is confined to. If $x \gg \lambda$ classical mechanics will do well, if λ is order x or larger, one had better use quantum mechanics.¹ Perhaps you've encountered a similar argument in optics regarding whether it is appropriate to use ray optics or solve Maxwell's equations for the propagation of light through optical systems.

For this problem estimate (order of magnitude is good enough) the quantity x/λ for the scenarios below.

- a) The moon orbiting the earth, with $x = 2\pi R$, where R is the average distance between the center of the moon and the center of the earth.
- b) An electron orbiting a hydrogen atom $x \approx 2\pi a_0$, where a_0 is the Bohr radius, with an average kinetic energy of 13.6 eV.
- c) An electron moving in a block of Aluminum at the Fermi energy (kinetic energy = 11.6 eV) and lattice spacing $x = 4 \text{ \AA}$.
- d) A 1 GeV electron from a particle accelerator slammed into a block of Aluminum with lattice spacing $x = 4 \text{ \AA}$.
- e) A neutron confined to an ^{56}Fe nucleus ($x \approx 7.5 \text{ fm}$) with a kinetic energy of 4 MeV.
- f) A proton moving in a beaker of acidic water, with average O-O distance $x \approx 2.3 \text{ \AA}$, with a thermal velocity of $v \sim \sqrt{kT/m_p}$ at room temperature.
- g) A hydrogen atom in a water molecule gently vibrating with an amplitude of 0.1 \AA at the natural frequency of $\sim 100 \text{ THz}$.
- h) A 40 kg test mass at the Laser Interferometric Gravitational Observatory (LIGO), suspended from 50 cm long fused silica fibers, executing an oscillation at the system's natural pendular frequency, with an amplitude of 10^{-19} m due to a passing gravitational wave.
- i) An atomic force microscope tip with a mass of 5 ng, oscillating with an amplitude of $x = 10 \text{ nm}$ at a frequency of 100 kHz.
- j) Your completed Quantum Mechanics problem set being enthusiastically shoved into the homework box ($x \approx 30 \text{ cm}$) with a velocity of 1 m/s!

20 Quantum or Classical? A density of states perspective. (15 points)

Another metric that is often useful in determining if classical mechanics can be applied to a problem is the degree to which the granularity of the quantum states is relevant. A handy example comes from our familiarity with U.S. dollars, which are currently still quantized in units of the penny \$0.01. If one has only 10¢, then the quantized nature of money is relevant, but if one has millions of dollars, then it is likely not so important.

Often an estimate can be made using thermodynamic arguments. In thermal equilibrium, a system in contact with a "bath" at temperature T will have significant (incoherent) population of states within approximately $k_B T$ of the ground state of the system, where k_B is Boltzmann's constant. When the number of states thermally populated is much larger than 1, then it is often reasonable to treat the system classically.² Thus, a quick metric for determining if a classical or quantum treatment is appropriate is the ratio of the energy level spacing ΔE to the available thermal energy $k_B T$. If $k_B T \gg \Delta E$, then often a classical description is appropriate.

For this problem, estimate (order of magnitude is good enough) the ratio $k_B T/\Delta E$ for the systems below:

¹In the intermediate regime between these two limits, clever people have developed an array of so-called *semiclassical* methods, which are easier to use than the Schrödinger equation, but capture some of the essential quantum features of the motion. The WKB method in the Griffiths book is an example of this.

²There is, in fact, a way to deal with such systems, and departures from (boring) thermal equilibrium that can occur upon exciting such systems, using the quantum formalism of density matrices - but this is beyond the scope of this course.

- a) The moon confined to a ring of radius R , where R is the average distance between the center of the moon and the center of the earth. The surface temperature of the moon varies widely depending on illumination, but the core temperature is steady at around 1700 K.
- b) A hydrogen atom at room temperature. Use the Rydberg formula for the energy levels of the hydrogen atom and take ΔE to be the energy difference between the ground state and the first excited state.
- c) An electron in aluminum experiencing thermal fluctuations around the Fermi energy (kinetic energy = 11.6 eV). *Hint: Look up the expression for the density of states per unit energy in a metal, and multiply the density of states times $k_B T$ to get a rough estimate for the number of states populated.*
- d) A 3.0 GeV electron, with 0.1% energy spread, confined to the NSLS-II storage ring with a circumference of 792 m. For this case use the beam's intrinsic energy spread instead of the thermal spread. *Hint: What is the energy level spacing for particles confined to the ring at 3 GeV and how does this compare to spread of energies in the electron beam.*
- e) A neutron confined to an ^{56}Fe nucleus ($x \approx 7.5$ fm) at room temperature. *Hint: model the nucleus as a "box" confining the neutron. What is the energy level spacing.*
- f) A proton vibrating in a beaker of acidic water at room temperature, with a characteristic vibrational frequency of ~ 80 THz.
- g) A hydrogen atom in a room temperature water molecule vibrating at its natural frequency of ~ 100 THz.
- h) A 40 kg test mass at the Laser Interferometric Gravitational Observatory (LIGO), suspended from 50 cm long fused silica fiber, at room temperature.
- i) An atomic force microscope tip with a resonant frequency of 100 kHz, held at a cryogenic temperature of 1 K.
- j) Your completed Quantum Mechanics problem set undergoing random thermal motions at room temperature in the homework box ($x \approx 30$ cm).

21 Angular Momentum Basics (10 points)

A certain state $|\Psi\rangle$ is an eigenstate of the total angular momentum \hat{L}^2 and z-component \hat{L}_z such that

$$\hat{L}_z |\Psi\rangle = \hbar l |\Psi\rangle \quad \text{and} \quad \hat{L}^2 |\Psi\rangle = \hbar^2 l(l+1) |\Psi\rangle$$

- a) Calculate the expectation value $\langle \hat{L}_z \rangle$ for this state.
- b) Show that for this state, one must have $\langle \hat{L}_x \rangle = \langle \hat{L}_y \rangle = 0$. *Hint: Consider what the ladder operators would do to this state.*
- c) Calculate the expectation value $\langle \hat{L}_x^2 \rangle$ for this state. *Hint: You can assume symmetry with respect to x and y such that $\langle \hat{L}_x^2 \rangle = \langle \hat{L}_y^2 \rangle$.*
- d) Calculate the uncertainties in the x and y components of the angular momentum for this state. Are your results consistent with the generalized uncertainty principle?

22 Photofragment angular distributions (10 points)

This problem will examine the photodissociation of molecules in the gas phase: $AB + h\nu \rightarrow A + B$. An important example of such a reaction is the dissociation of O_2 molecules by VUV radiation in the upper atmosphere, which leads to the formation of ozone, O_3 . In the lab, one can measure the angular distributions in photo fragmentation of molecules to learn about molecular structure and gain insight into molecular dynamics. In a typical experiment, one might cross a light beam with a molecular beam and use a detector positioned at different angles to measure the molecular fragments (e.g. A or B) emerging from the interaction region between the two beams.

Unfortunately, gas phase molecules are usually oriented randomly, so that the angular distribution that is measured in the lab frame is averaged over the random orientations of the molecules, blurring the picture.

One can prove quite generally that this blurring process produces a generic functional form for the angular distribution (see for example *Angular Momentum*, by Dick Zare). Specifically, when a beam of linearly polarized light intersects a gas of randomly oriented molecules, the angular distribution of fragments always obeys the simple equation:

$$I(\theta, \phi) \propto \frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos \theta)] \quad (22.1)$$

where θ is the angle between the light polarization (electric field vector of the light) and the momenta of the outgoing particles, P_2 is the second order Legendre polynomial, and β depends on the details of the dissociation reaction, such as the direction of the molecule's light-induced dipole moment and the dynamics of the fragmentation. β can take on values between 2 and -1. σ is the total cross section and $\frac{d\sigma}{d\Omega}$ is called a differential cross section. The differential cross section has a similar meaning to the probability densities you are used to by now: the probability of detecting a particle emerging from the interaction region in a differential solid angle $d\Omega$ is proportional to $\frac{d\sigma}{d\Omega} d\Omega$.

a) Show that if one collects all the particles emerging from all angles without determining the angular distribution, this total signal is independent of β .

b) It may be difficult to collect particles emerging from all angles as in a). Another trick for measuring the integrated cross section is to only collect particles emerging from at the so called "magic angle", where the signal is independent of β . Find the magic angle.

c) The β parameter for the photodissociation of O_2 into two oxygen atoms with VUV radiation has been measured to be very nearly 2 (see for example J. J. Lin *et al.*, J. Chem. Phys. **109**, 1758 (1998)). Based on this, do you think the light-induced dipole is parallel or perpendicular to the molecular axis? Why? *Hint: It is likely helpful to plot the distribution with respect to the laser polarization for $\beta = 2$*

23 Field-free alignment of molecules using laser pulses (15 points)

The results of problem 22 are quite general and apply whether one is talking about angular distributions of photoelectrons, ions, atoms, molecules, etc. This is quite limiting, because no matter how much detailed information there could be in the angular fragmentation of a molecule, averaging over the random orientations of molecules always produces the distribution (22.1), and all that can be extracted is β , (which is itself calculated from an average in the molecular frame).

In the last 15 years or so, researchers have found ways to align molecules in the lab frame using laser pulses (see for example H. Stapelfeldt and T. Seideman, Rev. Mod. Phys. **75**, 543 (2003)). In the impulsive, or non-adiabatic technique, a short laser pulse (much shorter than the rotational period) produces a torque on the molecule. Immediately after the laser pulse, the molecule is left in a coherent superposition of rotational states. Lets consider the simple case of a diatomic molecule, N_2 , modeled as a rigid rotor in the following state immediately after the laser pulse.

$$\Psi(\theta, \phi, t = 0) = \frac{1}{\sqrt{11}} \sum_{J=0}^{10} Y_J^{m=0}(\theta, \phi) e^{iJ\pi/4} \quad (23.1)$$

a) Show that the expectation value $\langle \cos^2 \theta \rangle$ for an isotropic ensemble of molecules or one molecule in it's (isotropic) rotational ground state ($J=0$) is $1/3$.

b) Using a computer, Calculate the time-dependent expectation value $\langle \cos^2 \theta \rangle(t)$ for an N_2 molecule prepared in the initial state given by (23.1). The rotational constant of N_2 is $B = 1.9896 \text{ cm}^{-1}$. Plot your results over the time interval 0 to 10 ps.

c) At what times does the wave function experience a revival and the molecule is "aligned" along $\theta = 0$? What is the approximate temporal width of these peaks?

For fun you can compare your results of this simple model to the experimental results of I.V. Litvinyuk *et al.*, Phys. Rev. Lett., **90**, 233033 (2003).

24 Scaling in Hydrogenic Atoms (10 points)

This problem explores how energy and length scales change when we change either the charge or mass in the two-body problem of the hydrogen atom.

- a) Taking the results for the hydrogen atom but now generalized to a nucleus of charge $+Ze$, estimate the binding energy of the 1s electron of 5 times ionized carbon (C^{5+} or C VI)? Compare your results to the “K edge” of neutral carbon (the x-ray energy required to remove the 1s electron), which you can find in the x-ray data book here (<http://xdb.lbl.gov>). Qualitatively explain why the 1s binding energy found in the data book is substantially less than your hydrogenic estimate.
- b) Again using your generalized hydrogen atom result, estimate the binding energy of the 1s electron for 91 times ionized Uranium (U^{91+} or U XCII).
- c) Compare your results from parts a) and b) to those found at the NIST atomic database (http://physics.nist.gov/PhysRefData/ASD/levels_form.html). Why is your estimate for carbon much closer to the tabulated value than that of Uranium? *Hint: Compare the average kinetic energy to the rest energy of the electron $m_e c^2 = 0.511$ MeV. Is the electron “moving” close to the speed of light?*
- d) The proton has a finite size of roughly 8.78×10^{-16} m. This makes a small, but easily measurable shift in the energy levels of Hydrogen. The 1s energy level is most affected, because it has $|\psi|^2 \neq 0$ at the origin. Using our (unperturbed) result for the 1s orbital of hydrogen, calculate the probability of finding the electron inside the proton.
- e) Now consider “muonic hydrogen”, where the electron is replaced by a muon which has charge $-e$ but mass m_μ about 207 times that of the electron. Repeat your calculation of part d), but now for muonic hydrogen. How much larger is the probability than in part d)? The answer to part e) is *not* strictly academic. Even though the lifetime of the muon is only about $2 \mu\text{s}$, recently spectroscopy on muonic hydrogen was performed with sufficient resolution to refine our knowledge of the size of the proton (R. Pohl *et al.*, *Nature* **466**, 213 (2010)).

25 Interaction of Light with Matter Basics (10 points)

In this problem we will use our understanding of the hydrogen atom to study some basic properties of the interaction of light with matter. Consider a hydrogen atom in an external electric field of the form.

$$\vec{E}(\vec{r}, t) = \hat{e}_z E_0 \cos(kx - \omega t) \quad (25.1)$$

with $k = 2\pi/\lambda$, E_0 a constant representing the amplitude of the electric field, \hat{e}_z the unit vector in the z-direction, and λ and ω the wavelength and frequency of the electromagnetic wave, respectively. The corresponding potential felt by an electron is $V(\vec{r}, t) = -\int d\vec{r}' \cdot \vec{F} = ezE_0 \cos(kx - \omega t)$.

- a) Estimate the phase accumulated by a visible light wave as it traverses a hydrogen atom. Would it be safe to neglect the propagation kx term in (25.1)?
- b) The intensity of bright sunlight at the earth's surface is approximately 1000 W/m^2 . Using your knowledge of electromagnetism, estimate the corresponding electric field strength of this radiation. Compare your result to the scale of electric fields felt by the electron in a hydrogen atom (e.g. the atomic unit for electric field).
- c) Laser light can be generated with many orders of magnitude higher intensity than sunlight. Calculate the electric field (and the corresponding light intensity needed) for “barrier suppression” of the hydrogen atom potential below the binding energy of the 1s electron of hydrogen? Express your answers E_0 and the intensity in the SI units V/m and W/m^2 , and also (for E_0) in atomic units. *Hint: Add the Coloumb potential of the hydrogen atom to the potential of the external field and find the local maximum of the “barrier” as a function of field strength. Find the field strength at which this barrier height is below the 1s binding energy. Sketching the superposition of Coloumb potential and laser potential along the z direction might be helpful.*

Your answers to part c) may seem ridiculously impractical considering we live in a world where we measure voltage in Volts and power in Watts, but are now readily attained in the laboratory using ultrashort laser pulses. In this regime, the light-matter interaction cannot be treated with perturbation theory, giving rise

to a host of fascinating phenomena (see for example T. Brabec and F. Krausz, *Rev. Mod. Phys.* **72**, 545 (2000)).

26 Atomic Dipoles (10 points)

Despite the apparent weak electric fields of conventional light sources, atoms and molecules can (and frequently do in nature) absorb and emit light, making a transition from one energy level to another. For light linearly polarized along the z direction, the transition rate for a system going from state $|\psi_i\rangle$ to state $|\psi_f\rangle$ is proportional to the square modulus of the dipole matrix element between those two states:

$$W_{f \leftarrow i} \propto |\langle \psi_f | e \hat{z} | \psi_i \rangle|^2 = |\langle \psi_f | e r \cos \theta | \psi_i \rangle|^2 \quad (26.1)$$

a) Calculate the dipole matrix element between the 1s and 2s states of hydrogen. Express your answer in terms of ea_0 , where e is the charge of the electron and a_0 is the Bohr radius.

b) Calculate the dipole matrix element between the 1s and all the 2p states of hydrogen (all the magnetic sub levels). Express your answer in terms of ea_0 .

c) Give a qualitative explanation of why an atom in the superposition state

$$|\Psi\rangle = \frac{1}{\sqrt{2}} e^{-iE_1 t/\hbar} |1s\rangle + \frac{1}{\sqrt{2}} e^{-iE_2 t/\hbar} |2p_z\rangle \quad (26.2)$$

radiates electromagnetic waves. *Hint: It may be helpful to revisit your results from problem 6 for insight.*

27 Spin Precession (10 points)

Consider a proton in a nuclear magnetic resonance spectrometer, immersed in a uniform magnetic field B_0 in the z direction. After a “ $\pi/2$ pulse” is applied, the initial state of the particle at time zero is

$$|\Psi(t=0)\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle) \quad (27.1)$$

a) Write down the Hamiltonian for this system in terms of the gyromagnetic ratio of the proton $\gamma \approx 2.7 \times 10^8$ rad/(T-s), and the nuclear spin angular momentum operators, \hat{I}_x , \hat{I}_y , and \hat{I}_z .

b) Write down an expression for the time dependent wave function, $|\Psi(t)\rangle$.

c) Draw the vector $\langle \vec{I} \rangle = \langle \hat{I}_x \rangle \hat{e}_x + \langle \hat{I}_y \rangle \hat{e}_y + \langle \hat{I}_z \rangle \hat{e}_z$ at times $t = 0$, $t = \frac{1}{2} \frac{\pi}{\gamma B_0}$, and $t = \frac{\pi}{\gamma B_0}$. *Hint: Use the Pauli matrix formalism to calculate the expectation values quickly!*

28 Nuclear Spin Statistics (15 points)

When two identical atoms join to make a molecule, the spins of their (identical) nuclei combine to form a total nuclear spin wave function. Since the magnetic moments of nuclei are small, the effect of including nuclear spin on the total energy is very small (but measurable). However, even though the energy shifts produced by nuclear spin are tiny, the symmetry requirements imposed can have profound effects.

Consider, for example, the oxygen molecule (O_2), the second most abundant molecule in the atmosphere. The ^{16}O nucleus has spin 0, and is thus a (composite) boson. The only spin angular momentum wave function you can get by combining two spin 0 particles is the totally symmetric $|0, 0\rangle$. Explicitly

$$|\psi^{(\text{nuc. spin})}\rangle_{O_2} = |I_1 = 0, m_{I_1} = 0\rangle |I_2 = 0, m_{I_2} = 0\rangle = |I = 0, m_I = 0\rangle \quad (28.1)$$

The symbol I is customarily used to denote nuclear spin. Now since the ^{16}O nuclei are bosons, the *total* wave function must be symmetric under interchange of the two nuclei. The total wave function for the molecule is given by

$$|\psi\rangle_{O_2} = |\psi^{(\text{electronic})}\rangle |\psi^{(\text{vibrational})}\rangle |\psi^{(\text{rotational})}\rangle |\psi^{(\text{nuc. spin})}\rangle \quad (28.2)$$

For O_2 , the electronic wave is antisymmetric under interchange of the two nuclei, and the vibrational component is always symmetric. This then means that the product of the nuclear spin wave function and the

rotational wave function must be antisymmetric. Since for O_2 , the only possible spin wave function is symmetric, this means that the rotational states *must* be antisymmetric. The spherical harmonics Y_J^m with odd J (molecular spectroscopists use the symbol J instead of l to denote the total rotational angular momentum quantum number) all pick up a minus sign upon a 180° rotation (C_2), equivalent to interchanging the nuclei, while the even J -states do not, so thus the oxygen molecule with two ^{16}O nuclei (more than 99.5% of naturally occurring oxygen molecules), has *only* odd rotational states. The even rotational states simply do not exist due only to the spin statistics theorem. Indeed, the ^{17}O isotope was discovered via the observation very weak lines observed in the UV spectrum of oxygen corresponding to these rotational states that are forbidden for the $^{16}O^{16}O$ molecule.

In this problem, you will examine the effect of nuclear spin statistics on the nitrogen molecule N_2 with two identical ^{14}N nuclei. The ^{14}N nucleus has spin 1, and the electronic wave function is symmetric under exchange of the two nuclei.

- Is the ^{14}N nucleus a boson or a fermion?
- When the spin angular momenta of the two spin-1 nuclei are added, what are the allowed values of the *total* spin angular momentum, I ? Neglecting any contribution of the nuclear spin to the energy what is the degeneracy of each I ? How many possible combined nuclear spin states are there in total?
- For each allowed value of the total nuclear spin, write down the allowed z components (magnetic sub-levels m_I). If you were unable to figure out the degeneracy in part b), you can do this by counting the number of magnetic sub-levels for each I .
- Use the Clebsch-Gordon coefficients to write out each $|I, m_I\rangle$ state in terms of the single nucleus spin states $|I_1, m_{I_1}\rangle, |I_2, m_{I_2}\rangle$.
- Use your answers from d) to deduce the symmetry of each $|I, m_I\rangle$ state under interchange of the two nuclei. You should find that all states with the same I have the same symmetry.
- Using the same reasoning we applied above to the $^{16}O_2$ molecule, which rotational states are allowed for the $^{14}N_2$ molecule for each nuclear spin state I ? Remember that the electronic wave function for N_2 is symmetric under interchange of the atoms.
- Neglecting any contribution of the nuclear spin to the energy, what is the resulting total degeneracy of each rotational state J ?
- At room temperature, how much more likely are you to find an N_2 molecule in the first excited rotational state $J = 1$ than the ground state $J = 0$? *Hint: the rotational constant of N_2 (or any other molecule for that matter) is much less than the thermal energy $k_B T$ at room temperature, such that the Boltzmann factor $\exp(-\Delta E/k_B T) \rightarrow 1$.*

29 The Pauli Exclusion Principle (10 points)

In this problem we will try to see how the requirement that the multi-electron wave function be antisymmetric under the exchange of two particles is related to the more familiar “Pauli exclusion principle”. Consider two non-interacting spin- $\frac{1}{2}$ particles in a 1D box of length 1, with the two particles in the excited configuration given by the Slater determinant:

$$\Psi_e = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1\alpha}(x_1) & \phi_{2\alpha}(x_1) \\ \phi_{1\alpha}(x_2) & \phi_{2\alpha}(x_2) \end{vmatrix} \quad (29.1)$$

The “ α ” labels here indicate that the particles have the same “up” spin. Take $\phi_1 = \sqrt{2}\sin(\pi x)$ and $\phi_2 = \sqrt{2}\sin(2\pi x)$.

- Verify that Ψ_e satisfies the time independent Schrödinger equation.
- Make a 2-dimensional plot of $|\Psi_e(x_1, x_2)|^2$. What happens when $x_1 = x_2$? Interpret your results in the context of the Pauli exclusion principle.

30 One Parameter Variation (10 points)

Consider a particle with mass m moving in the 1D harmonic oscillator potential, $V = m\omega^2 x^2/2$. Of course, we can solve this problem exactly, but this problem will explore the variational approach.

a) Show that using the trial function

$$\psi = e^{-\alpha x^2} \quad (30.1)$$

varying the parameter α to minimize the expectation value of the energy

$$W = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (30.2)$$

yields the exact result for the ground state wave function and the energy.

b) Usually, when using the variational method, we do not know the functional form of the wave function, but the efficacy of the technique is quite robust to our ignorance as long as the wave function has the right symmetries and roughly the right shape, a reasonable approximation can be found. Instead use the trial function

$$\psi = \text{sech}^2(\beta x); \quad (30.3)$$

and implement the variational method numerically to find the optimum value of β , and the resulting minimum energy and wave function. After normalizing your result, make a plot comparing the resulting optimum wave function along with the exact solution. *Hint: Don't get tripped up on units, just set $\hbar = m = \omega = 1$ for the purposes of your program. In these units the exact ground state energy of the harmonic oscillator is $1/2$.*

31 Linear Variation in an orthonormal basis (10 points)

In the linear variation method, we solve the secular equation

$$\det(\mathbf{H} - \mathbf{S}W) = 0 \quad (31.1)$$

where here \mathbf{H} and \mathbf{S} are the overlap matrices with elements in the $|f_i\rangle$ basis defined by

$$H_{ij} = \langle f_i | \hat{H} | f_j \rangle \quad (31.2)$$

$$S_{ij} = \langle f_i | f_j \rangle \quad (31.3)$$

If we take an orthonormal basis ($S_{ij} = \delta_{ij}$), equation (31.1) is simplified to

$$\det(\mathbf{H} - W\mathbf{I}) = 0 \quad (31.4)$$

where \mathbf{I} is the identity matrix with ones along the diagonal and zeros everywhere else. You should recognize equation (31.4) as that of an eigenvalue problem, and the solutions $W^{(k)}$ will now be the eigenvalues of the Hamiltonian matrix \mathbf{H} and the resulting eigenvectors found in the diagonalization problem

$$\tilde{\psi}^{(k)} = \begin{bmatrix} c_1^{(k)} \\ c_2^{(k)} \\ \vdots \\ c_N^{(k)} \end{bmatrix} \quad (31.5)$$

are eigenvectors of the Hamiltonian matrix \mathbf{H}

a) Since the solution of the time independent Schrödinger equation (TISE) are the eigenfunctions of the Hamiltonian, you might think that the linear combination found with the procedure above, $|\psi^{(k)}\rangle = \sum_i c_i |f_i\rangle$, should be eigenfunctions of the Hamiltonian and thus solutions of the TISE, with $W^{(k)}$ the energy eigenvalues. Why is this not always the case?

b) As a concrete example, use the linear variation method in the 2D basis

$$f_1(x) = \frac{\sqrt{30}}{L^{5/2}} x(L-x) \quad (31.6)$$

$$f_2(x) = \frac{132.816}{L^{9/2}} x(L-x) \left[\left(x - \frac{L}{2} \right)^2 - \frac{L^2}{28} \right] \quad (31.7)$$

on the particle in the box Hamiltonian ($V = 0$ for $0 < x < L$, $V = \infty$ otherwise). The functions f_1 and f_2 are normalized, satisfy the boundary conditions, and satisfy $\langle f_1 | f_2 \rangle = 0$, and so constitute an orthonormal basis. Find the eigenvalues and eigenvectors of \mathbf{H} in this basis, thus solving the secular equation.

c) Do the functions found in part b) solve the TISE: $\hat{H} |\psi\rangle = E |\psi\rangle$?

32 Particle with a speed bump (5 points)

Consider our old friend the 1D particle in the box, except now with a speed bump in the box so the potential now is given by.

$$V(x) = \begin{cases} 0, & 0 < x < \frac{3}{8}L \text{ and } \frac{5}{8}L < x < L \\ V_0, & \frac{3}{8}L < x < \frac{5}{8}L \\ \infty, & \text{otherwise} \end{cases} \quad (32.1)$$

where $V_0 \ll E_1$, the energy of the ground state of the particle in the box without the speed bump. Use perturbation theory to

a) Calculate the first order correction to the ground state ($n = 1$) and first excited state ($n = 2$) energies.

b) Calculate the first order correction to the ground state wave function. Do you notice a pattern in the expansion coefficients for the perturbed wave function?

33 Anharmonic Coupling and Fermi Resonance (15 points)

A polyatomic molecule with N atoms in general has $M = 3N - 6$ vibrational degrees of freedom which can be described by normal modes (linear molecules have $M = 3N - 5$ because they only have 2 rotational degrees of freedom). The *harmonic* description of normal modes goes as follows: the potential energy $U(\vec{R})$ surface that the nuclei move on near its minimum is expanded in the normal coordinates, Q_i , to read

$$U(Q_i) \approx U_0 + \frac{1}{2} F_1 Q_1^2 + \dots + \frac{1}{2} F_M Q_M^2 \quad (33.1)$$

The constant term is inconsequential for the solutions to the Schrödinger equation, so we might as well set it equal to zero. Note that there is no linear term because $Q_i = 0$ corresponds to the potential energy minimum and we need $\frac{dU}{dQ_i} = 0$ at the minimum, so equation (33.1) represents the lowest order Taylor expansion of the potential in the normal coordinates. The solution to the nuclear Schrödinger equation

$$-\sum_i \frac{\hbar^2}{2\mu_i} \frac{\partial^2 \chi}{\partial Q_i^2} + U(Q_1, \dots, Q_N) \chi = E \chi \quad (33.2)$$

in this harmonic approximation is a product of harmonic oscillator wave functions:

$$\chi(Q_1, \dots, Q_M) = \prod_{i=1}^M \phi_{\nu_i}(Q_i) = \phi_{\nu_1}(Q_1) \phi_{\nu_2}(Q_2) \dots \phi_{\nu_M}(Q_M) \quad (33.3)$$

Here $\phi_{\nu_i}(Q_i)$ corresponds to the harmonic oscillator wave function for the Q_i -th normal mode with frequency ν_i . Each normal mode can have varying number of vibrational excitation quanta.

Let's take as a concrete example the CO_2 molecule, which has three vibrational frequencies corresponding to the symmetric stretch ($\nu_1 \approx 1350 \text{ cm}^{-1}$), bend ($\nu_2 \approx 665 \text{ cm}^{-1}$), and asymmetric stretch ($\nu_3 \approx 2350 \text{ cm}^{-1}$). The ground vibrational state of the molecule can be labeled $|0, 0, 0\rangle$. The molecule with one quanta of vibrational excitation in the symmetric stretch $|100\rangle$. Two bend motion quanta $|020\rangle$, and so on and so forth. In the harmonic approximation, motions corresponding to different normal modes

are completely decoupled. For example, if you were to excite the bending motion of a (mythical) purely harmonic CO₂ molecule, you will never find it later executing a symmetric stretch motion. Real molecules, however, vibrate anharmonically.

The harmonic approximation can fail in particularly spectacular fashion when two vibrational energy levels are nearly degenerate. This is called Fermi resonance, and the above mentioned levels of CO₂ form a classic example of this, with $|020\rangle$ nearly degenerate with $|100\rangle$. We will look at the effects of adding to the harmonic potential (33.2) an anharmonic coupling term

$$U'(Q_1, Q_2) = kQ_1Q_2^2 \quad (33.4)$$

a) Find the selection rules for coupling between the (harmonic) vibrational states. In other words, show that that the matrix elements

$$\langle \nu_1, \nu_2, \dots, \nu_M | \hat{U}' | \nu'_1, \nu'_2, \dots, \nu'_M \rangle \quad (33.5)$$

are non-zero only for certain relations between the vibrational quantum numbers of the two (harmonic) states. *Hint 1: Express the normal modes in terms of \hat{a} and \hat{a}^\dagger operators. Hint 2: $|100\rangle$ and $|020\rangle$ are one such non-zero combination.*

b) Why will the influence of the anharmonic coupling be largest on (harmonic) states that are nearly degenerate, as in the Fermi resonance of CO₂?

c) Your results from a) and b) tells you that $|100\rangle$ and $|020\rangle$ will be strongly “coupled”. What this means is that they are no longer energy eigenstates of the Hamiltonian but that a linear combination of them can be:

$$|\alpha\rangle = \cos \theta |100\rangle + \sin \theta |020\rangle \quad (33.6)$$

$$|\beta\rangle = -\sin \theta |100\rangle + \cos \theta |020\rangle \quad (33.7)$$

Find the mixing angle θ that accomplishes this and the new energy eigenvalues. Express your answers in terms of the matrix element $V \equiv \langle 100 | \hat{U}' | 020 \rangle$ and the difference in the energies of the uncoupled (harmonic) eigenstates $\Delta \equiv \frac{1}{2}(E_{100}^{(0)} - E_{020}^{(0)})$.

d) Describe the resulting dynamics if the anharmonic molecule is initially placed in a superposition of the “zeroth-order bright state”, $|020\rangle$, and $|010\rangle$ such as might happen by driving the transition $(020) \leftarrow (010)$ with a short pulse of light.

34 Langevin Reactions (15 points)

In this problem we will consider the long range potential between a neutral atom or molecule and an ion. We will consider the simplest such reaction, combining a hydrogen atom and a proton to form H₂⁺.



a) Consider a proton a distance R from a Hydrogen atom. Show that when $R \gg a_0$ the Hamiltonian for the interaction between the hydrogen atom and the ion, \hat{H}' , can be written in the form:

$$\hat{H}' = -\frac{1}{4\pi\epsilon_0} \frac{z}{R^2} \quad (34.2)$$

where (x, y, z) are cartesian coordinates corresponding to the position of the electron within the hydrogen atom, R corresponds to the distance between the two protons, and the positive z-direction points from the hydrogen atom to the proton. *Hint1: Break the total Hamiltonian into terms corresponding to the hydrogen atom and its interaction with the distant proton. Hint 2: Expand the interaction in terms of powers of R^{-1} , keeping only the lowest order non-zero term.*

b) Use perturbation theory to show that the interaction energy between the proton and the hydrogen atom can be written as

$$E(R) = -\frac{C}{R^4} + (\text{higher order terms}) \quad (34.3)$$

where C is a positive constant.

c) Use perturbation theory to evaluate the constant C with the approximation that $E_1 - E_m \approx E_1$ for all $m \neq 1$, where E_m are the energy eigenvalues of the hydrogen atom. *Hint:* $|\langle \psi_m | \hat{H}' | \psi_1 \rangle|^2 = \langle \psi_1 | \hat{H}' | \psi_m \rangle \langle \psi_m | \hat{H}' | \psi_1 \rangle$.

35 Stark Effect (15 points)

When an atom or molecule is placed in a uniform external electric field, the energy levels are shifted - a phenomena known as the Stark effect. In this problem we analyze the Stark effect for the $n=1$ and $n=2$ levels of hydrogen. Let the field point in the z direction, so the potential energy of the electron due to this external field is

$$H_S = eE_0 z = eE_0 r \cos \theta \quad (35.1)$$

Treat this as a perturbation to the hydrogen atom (neglecting spin, spin-orbit coupling, etc.).

- Show that the ground state (1s) energy is not effected by the external field in first order.
- The first excited state is fourfold degenerate (2s, $2p_z$, $2p_{\pm 1}$). Using degenerate perturbation theory, determine the first order corrections to the energy. Into how many levels does E_2 split?
- What are the resulting “good” zeroth-order wave functions (i.e. the correct linear combinations of the degenerate eigenstates that the wave function approaches as the perturbing potential is smoothly turned off).

Hint: Since the degenerate subspace is 4-dimensional, there are a lot of integrals in this problem, but almost all of them are zero! So study each one carefully before doing too much math. For example if the ϕ integral vanishes, there is no point in doing the r or θ integrals. Exploit symmetry!

Congratulations, if you made it this far, you can call yourself a “Quantum Mechanic”!