Short Answer Questions: (21 questions @ 3 points each = 63 points total).

1. **Explain, in one or two sentences and (hopefully) a diagram, what Compton Scattering is. Why was the observation of Compton scattering important to the development of quantum mechanics?**
Compton Scattering is where a photon "collides with" or "scatters off of" an electron. It allows one to measure the momentum of a photon, and was important in quantum mechanics because it helped clarify the "particle nature of light." A diagram of Compton scattering is below.
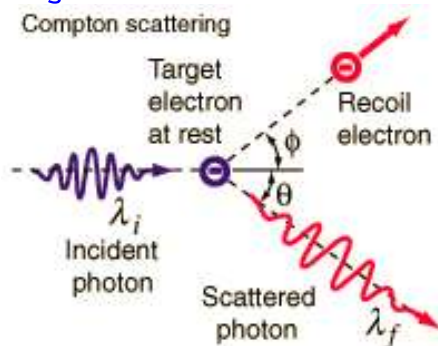
2. An experimental study of the photoelectric effect is performed on a sample of Chromium, and electrons with a kinetic energy of $2.88 \cdot 10^{-19}$ J are emitted. **What is the wavelength of the light that is shining on the Chromium surface?** The work function of Chromium is 4.40 eV.
The energy of the light goes into the (a) work function and (b) the kinetic energy of the emitted electrons. So the energy of the light is

$$E_{light} = h\nu = \Phi + T = 4.4 \text{ eV} + 2.88 \cdot 10^{-19} \text{ J}$$

$$= 4.40 \text{ eV} \left(\frac{1.602 \cdot 10^{-19} \text{ J}}{1 \text{ eV}} \right) + 2.88 \cdot 10^{-19} \text{ J}$$

$$= 9.929 \cdot 10^{-19} \text{ J}$$

and the frequency of the light is:

$$\nu = \frac{9.929 \cdot 10^{-19} \text{ J}}{h} = \frac{9.929 \cdot 10^{-19} \text{ J}}{6.626 \cdot 10^{-34} \text{ J} \cdot \text{s}} = 1.498 \cdot 10^{15} \text{ Hz}$$

so the wavelength is

$$\lambda = \frac{c}{\nu} = \frac{2.998 \cdot 10^{8} \frac{\text{m}}{\text{s}}}{1.498 \cdot 10^{15} \frac{1}{\text{s}}} = 2.001 \cdot 10^{-7} \text{m} = 200 \text{ nm} .$$

3. **What is the momentum of a photon of the characteristic yellow light (589.3 nm) emitted by a sodium vapor lamp.**
Using the De Broglie relation,

$$p = \frac{h}{\lambda} = \frac{6.6262 \cdot 10^{-34} \text{ J} \cdot \text{s}}{589.3 \cdot 10^{-9} \text{ m}} = 1.124 \cdot 10^{-27} \frac{\text{kg} \cdot \text{m}}{\text{s}}$$

4. Which of the following are <u>not</u> linear, Hermitian, operators?

(a) $\frac{d}{dx}$ **(the derivative)**

(b) $\frac{d^2}{dx^2}$ (2nd derivative)

(c) $\frac{d^4}{dx^4}$ (4th derivative)

(d) $g_+(x) = f(x) + f^*(x)$ (multiplication by $g_+(x)$, where $f(x) \in \mathbb{C}$ is any complex-valued function.

(e) $g_-(x) = f(x) - f^*(x)$ **(multiplication by $g_-(x)$, where $f(x) \in \mathbb{C}$ is any complex-valued function.**

(f) $g(x) = f(x)f^*(x)$ (multiplication by $g(x)$, where $f(x) \in \mathbb{C}$ is any complex-valued function.

(g) $ig(x) = if(x)f^*(x)$ **(multiplication by $ig(x)$, where $f(x) \in \mathbb{C}$ is any complex-valued function.**

(h) $\ln(\quad)$ **(the operator that takes the natural logarithm of a function).**

The following text and figure is relevant to questions #5 and #6.

We often model the vibrations of diatomic molecules, AB, with the Morse potential,

$$V_{\text{Morse}}(r) = e^{-2a(r-r_e)} - 2D_e e^{-a(r-r_e)} \tag{1}$$

where r is the bond length, r_e is the equilibrium (i.e., optimal) bond length, D_e is the dissociation energy of the molecule, and $a = \sqrt{k_e/2D_e}$, where k_e is the molecular force constant that binds the vibrating atoms together at the bottom of the potential well. The fundamental vibrational frequency of the Morse oscillator is

$$\nu_0 = \frac{a}{2\pi}\sqrt{\frac{2D_e}{\mu}} \tag{2}$$
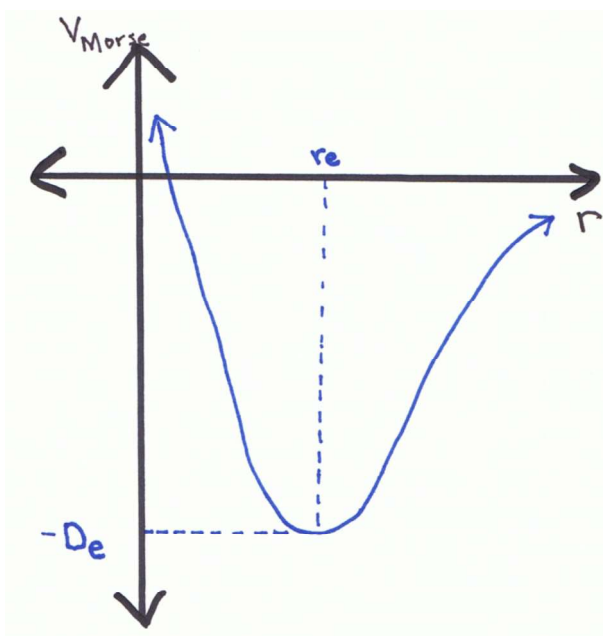
where μ is the mass of the oscillator, which is simply the reduced mass of the atoms in the diatomic molecule:

$$\mu = \frac{m_A m_B}{m_A + m_B}. \tag{3}$$

The energy eigenvalues of the Morse oscillator are

$$E(\upsilon) = -D_e + h\nu_0\left(\upsilon + \tfrac{1}{2}\right) - \frac{1}{D_e}\left(\frac{h\nu_0\left(\upsilon + \tfrac{1}{2}\right)}{2}\right)^2 \tag{4}$$

$$\upsilon = 0,1,2,3,\ldots$$

5. Write the Hamiltonian for the Morse Oscillator.

$$\hat{H}_{\text{Morse}}(r) \equiv -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \underbrace{\left(e^{-2a(r-r_e)} - 2D_e e^{-a(r-r_e)}\right)}_{\text{Morse Potential}}$$

6. What is the zero-point energy of the Morse Oscillator?

The zero-point energy is the amount that the ground-state energy of the oscillator is above the minimum value of the potential. So

$$E_{\text{zero-pt}} = E(\upsilon = 0) - \left(-D_e\right) = \tfrac{1}{2}h\nu_0 - \frac{1}{D_e}\left(\frac{h\nu_0}{4}\right)^2$$
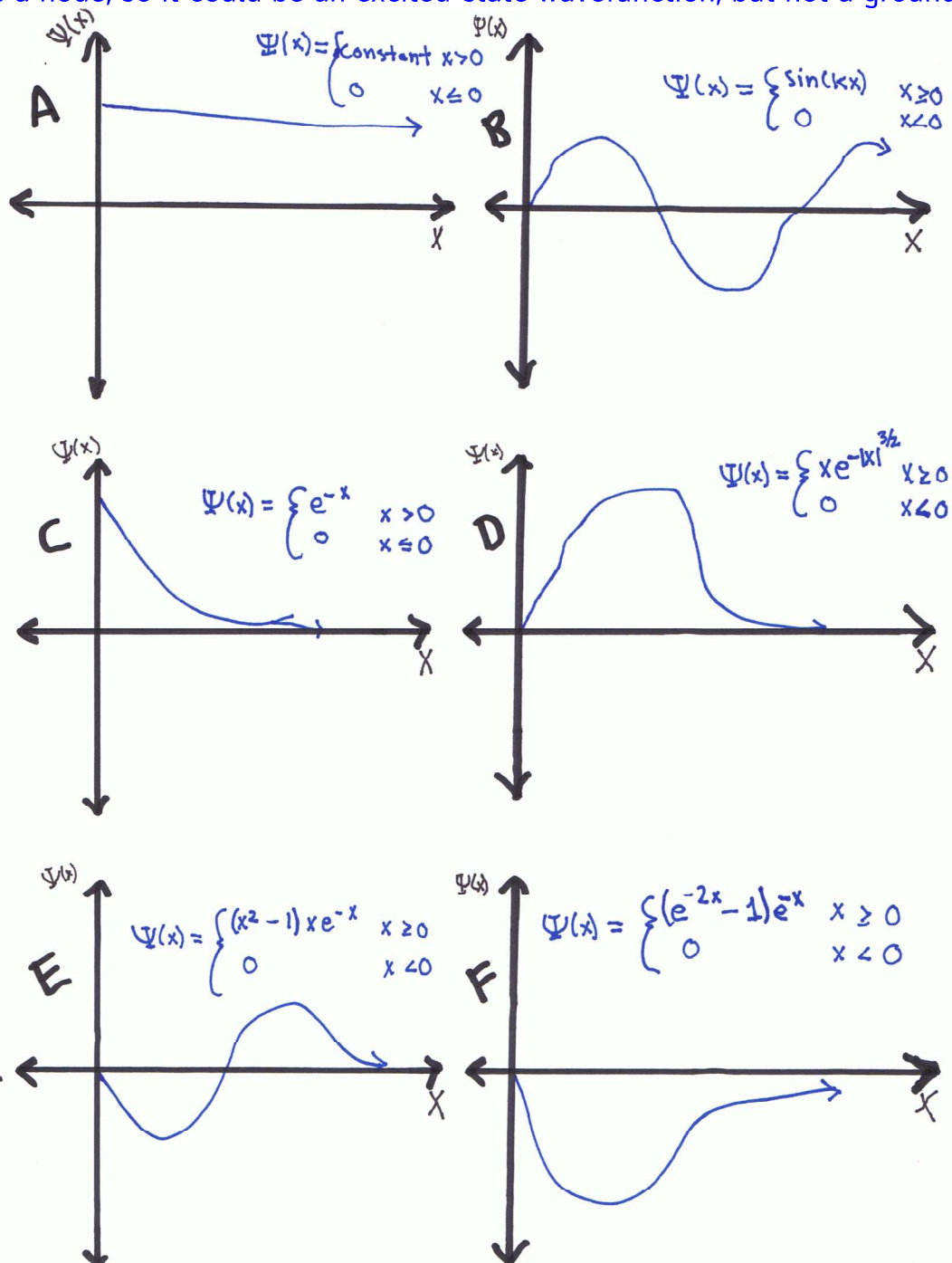
While it is technically incorrect, the definition of zero-point energy in many books (and maybe my notes) could lead you to say that the ground-state energy, $E(\upsilon = 0)$, was the zero-point energy, and I will accept that answer also.

7. Consider the following potential,

$$V(x) = \begin{cases} +\infty & x < 0 \\ x & x \geq 0 \end{cases} \qquad (5)$$

Which of the following sketches is a possible <u>ground-state</u> wavefunction for a particle bound by the potential in Eq. (5).

[Only D and F.]   A and B are not normalizable. C is not zero at the boundary. E has a node, so it could be an excited-state wavefunction, but not a ground state.

A: $\Psi(x) = \begin{cases} \text{constant} & x > 0 \\ 0 & x \leq 0 \end{cases}$

B: $\Psi(x) = \begin{cases} \sin(kx) & x \geq 0 \\ 0 & x < 0 \end{cases}$

C: $\Psi(x) = \begin{cases} e^{-x} & x > 0 \\ 0 & x \leq 0 \end{cases}$

D: $\Psi(x) = \begin{cases} xe^{-|x|^{3/2}} & x \geq 0 \\ 0 & x < 0 \end{cases}$

E: $\Psi(x) = \begin{cases} (x^2 - 1)xe^{-x} & x \geq 0 \\ 0 & x < 0 \end{cases}$

F: $\Psi(x) = \begin{cases} (e^{-2x} - 1)e^{-x} & x \geq 0 \\ 0 & x < 0 \end{cases}$

8. Write an expression for observing a particle in the first quarter of a box of length *a*. That is, write an expression for the probability that a particle-in-a-box is located between zero and *a*/4. You do not need to do the integral—just write the integral that you would do.

The integral is $\int_0^{\frac{a}{4}} \left| \psi(x) \right|^2 dx$. For an eigenstate of the particle-in-a-box, this would be

$\int_0^{\frac{a}{4}} \sin^2 \left(\frac{n\pi x}{a} \right) dx$.

The following text is relevant to problems 9-12.

One of the key steps in quantum computing is to carefully prepare systems so that we have the wavefunction that is needed to do the "computation." Suppose we tried to build a quantum computer based on the particle-in-a-box. Assume that the particle has unit mass, the box has unit length, and that the "walls" of the box are infinitely high. So

$$V(x) = \begin{cases} 0 & 0 < x < 1 \\ +\infty & \text{otherwise} \end{cases} \tag{6}$$

After a careful preparation, the wavefunction is expanded in terms of the eigenfunctions of the particle in a box,

$$\Psi(x,t) = 3\psi_1(x,t) + 4\psi_2(x,t) + 5\psi_3(x,t) \tag{7}$$

where $\psi_n(x,t)$ are the normalized eigenfunctions of the particle-in-a-box.

9. Is $\Psi(x,t)$ normalized?

Let's start by computing the candidate probability distribution function,

$$P(x,t) = \left| \Psi(x,t) \right|^2$$

$$= 9 \left| \psi_1(x,t) \right|^2 + 16 \left| \psi_2(x,t) \right|^2 + 25 \left| \psi_3(x,t) \right|^2$$

$$+ 12 \left(\psi_1^*(x,t) \psi_2(x,t) + \psi_2^*(x,t) \psi_1(x,t) \right)$$

$$+ 15 \left(\psi_1^*(x,t) \psi_3(x,t) + \psi_3^*(x,t) \psi_1(x,t) \right)$$

$$+ 20 \left(\psi_2^*(x,t) \psi_3(x,t) + \psi_3^*(x,t) \psi_2(x,t) \right)$$

We know that the eigenstates of any time-independent Hamiltonian can be written as $\psi_k(x,t) = \phi_k(x) e^{-\frac{iE_k t}{\hbar}}$ and for the special case of the particle in a box, we have:

$$\phi_k(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a} \right) \qquad\qquad E_k = \frac{h^2 n^2}{8ma^2}$$

Thus we have:

$$\left|\psi_k(x,t)\right|^2 = \left(\phi_k(x)e^{-iE_kt/\hbar}\right)^*\left(\phi_k(x)e^{-iE_kt/\hbar}\right)$$

$$= \left(\phi_k^*(x)e^{iE_kt/\hbar}\right)\left(\phi_k(x)e^{-iE_kt/\hbar}\right)$$

$$= \left|\phi_k(x)\right|^2$$

and

$$\psi_k^*(x,t)\psi_l(x,t)+\psi_l^*(x,t)\psi_k(x,t) = \phi_k^*(x)\phi_l(x)e^{-i(E_l-E_k)t/\hbar} + \phi_l^*(x)\phi_k(x)e^{-i(E_k-E_l)t/\hbar}$$

If the spatial wavefunctions are real, like they are for the particle in a box, then:

$$\psi_k^*(x,t)\psi_l(x,t)+\psi_l^*(x,t)\psi_k(x,t) = \phi_k(x)\phi_l(x)e^{-i(E_l-E_k)t/\hbar} + \phi_l(x)\phi_k(x)e^{-i(E_k-E_l)t/\hbar}$$

$$= \phi_k(x)\phi_l(x)\left(e^{i(E_k-E_l)t/\hbar} + e^{-i(E_k-E_l)t/\hbar}\right)$$

$$= 2\phi_k(x)\phi_l(x)\cos\left(\frac{(E_k-E_l)t}{\hbar}\right)$$

$$= 2\phi_k(x)\phi_l(x)\cos(\omega_{kl}t)$$

So we have:

$$\left|\Psi(x,t)\right|^2 = 9\left|\phi_1(x)\right|^2 + 16\left|\phi_2(x)\right|^2 + 25\left|\phi_3(x)\right|^2 + 24\phi_1(x)\phi_2(x)\cos(\omega_{12}t)$$
$$+30\phi_1(x)\phi_3(x)\cos(\omega_{13}t) + 40\phi_2(x)\phi_3(x)\cos(\omega_{23}t)$$

Substituting this expression into the normalization integral gives:

$$\int_0^a \left|\Psi(x,t)\right|^2 dx = \int_0^a \left(9\left|\phi_1(x)\right|^2 + 16\left|\phi_2(x)\right|^2 + 25\left|\phi_3(x)\right|^2\right)dx$$

$$\int_0^a \left(\begin{array}{c}24\phi_1(x)\phi_2(x)\cos(\omega_{12}t) + 30\phi_1(x)\phi_3(x)\cos(\omega_{13}t)\\ +40\phi_2(x)\phi_3(x)\cos(\omega_{23}t)\end{array}\right)dx$$

$$= 9(1)+16(1)+25(1)+24(0)\cos(\omega_{12}t)+30(0)\cos(\omega_{13}t)+40(0)\cos(\omega_{23}t)$$

$$= 50$$

$$\neq 1$$

This wavefunction is not normalized.

10. What is the expectation value of the energy for $\Psi(x,t)$?

Evaluating

$$\frac{\int_0^a \Psi^*(x,t)\hat{H}(x)\Psi(x,t)}{\int_0^a \Psi^*(x,t)\Psi(x,t)} = \frac{9E_1 + 16E_2 + 25E_3}{50}$$

$$= \left(\frac{9}{50}\right)\left(\frac{h^2(1)^2}{8ma^2}\right) + \left(\frac{16}{50}\right)\left(\frac{h^2(2)^2}{8ma^2}\right) + \left(\frac{25}{50}\right)\left(\frac{h^2(3)^2}{8ma^2}\right)$$

$$= \left(\frac{h^2}{8ma^2}\right)\left(\frac{9 + 64 + 225}{50}\right)$$

Using the fact that the mass and the length of the box are one, and the value of Planck's constant, we obtain

$$\langle E \rangle = \left(\frac{h^2}{8ma^2}\right)\left(\frac{9 + 64 + 225}{50}\right) = \frac{298}{400}h^2 = \frac{298}{400}\left(6.626 \cdot 10^{-34}\,\text{Js}\right) = 3.271 \cdot 10^{-67}\,\text{J}$$

Given that we had a mass of 1 kg in a box of 1 meter (which is *very* classical), the tiny size of this number is not at all surprising.

11. What is the probability of finding the system in the *n=3* state?

It is just the square of the c3 coefficient in the *normalized* wavefunction. So:

$$p_3 = \frac{|c_3|^2}{\int_0^a |\Psi(x,t)|^2\,dx} = \frac{25}{50} = .5$$

12. A stationary state is a state where the probability of observing the particle at position *x* does not depend on the time. (I.e., $P(x,t) = P(x)$.) **Does $\Psi(x,t)$ describe a stationary state of the particle-in-a-box?**

No. Looking at the expression for $|\Psi(x,t)|^2$ it is clear that the probability is changing in time.
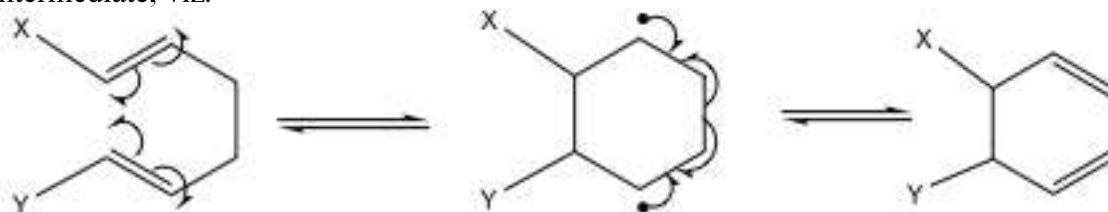
$$|\Psi(x,t)|^2 = 9|\phi_1(x)|^2 + 16|\phi_2(x)|^2 + 25|\phi_3(x)|^2 + 24\phi_1(x)\phi_2(x)\cos(\omega_{12}t)$$

$$+ 30\phi_1(x)\phi_3(x)\cos(\omega_{13}t) + 40\phi_2(x)\phi_3(x)\cos(\omega_{23}t)$$

13. Write down Fermi's Golden Rule.

W_{fi} = rate of transition from state i to state f, given that the initial state is i

$$= \frac{2\pi V^2 \left| \langle \Psi_f | \hat{\mu}_x | \Psi_i \rangle \right|^2}{\hbar} \left(g(\hbar\omega_{fi}) + g(\hbar\omega_{if}) \right)$$

14. One of the proposed mechanisms for the Cope rearrangement goes through a diyl intermediate, viz.

The highest-occupied molecular orbital and lowest-unoccupied molecular orbitals, respectively, in the diyl intermediate are sketched below[2]
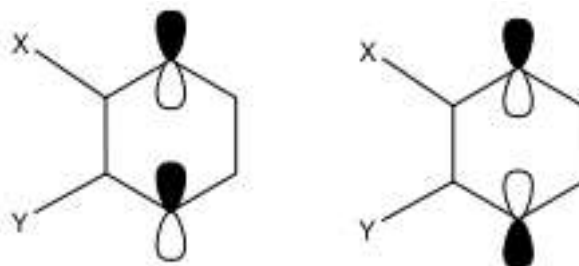
Is the excitation from the HOMO orbital (on the left) to the LUMO orbital (on the right) electric dipole allowed?

(a) yes   (b)   no

15. The time-dependent dipole moment for a particle with charge q is computed by means of the following operator:

$$\hat{\mu}(t) = \exp\left(\tfrac{i\hat{H}t}{\hbar}\right)(qx)\exp\left(\tfrac{-i\hat{H}t}{\hbar}\right). \tag{8}$$

Which "picture" of quantum mechanics is this operator most closely associated with?

(a)   Schrödinger picture.   **(b) Heisenberg picture.**

16. Write the form of the Lorentzian lineshape function.

$$L(\omega) = \frac{\alpha}{\alpha^2 + (\omega - \omega_{fi})^2}$$

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[2]   Here, the p-orbitals are perpendicular to the ring system. (Thus, if the ring system is in the plane of the paper, the p-orbitals are perpendicular to the plane of the paper.)

In problems 17 and 18, indicate which of the approximations we used in the derivation of Fermi's Golden Rule are violated.

17. One of the observed absorption lines in the spectrum of the Scandium atom ($\left[\text{Ar}\right]4s^2 3d^1$) corresponds to excitation of an electron from the *3d* orbital to the *5s* orbital. **Which of the following approximations is inadequate to explain this process?**
(a) long-wavelength approximation.
(b) weak-field approximation.
(c) long-time approximation.

18. In order to increase the efficiency of solar cells, some companies are attempting to dope their silicon wafers with Lanthanide complexes. These complexes absorb light in the blue and ultraviolet portion of the spectrum and then emit two photons in the near-infrared, with energy close to the band gap of Silicon. **The process of "two-photon emission" (i.e., going from an initial state to a final state by emitting two photons of frequency $\omega = \frac{1}{2}\omega_{fi} = \frac{1}{2\hbar}\left(E_f - E_i\right)$ cannot be explained without going beyond which of the following approximations?**
(a) long-wavelength approximation.
(b) weak-field approximation.
(c) long-time approximation.

19. High-resolution spectroscopy is performed on systems at
(a) high temperature and pressure.
(b) high temperature and low pressure.
(c) low temperature and high pressure.
(d) low temperature and low pressure.

The following text refers to problems 20-21.
The T2 relaxation process in NMR means, very roughly, that the probability that a nucleus that is initially in state *i* will still be in state *i* at time *t* decays exponentially in time, according to the law

$$P_i\left(t\right) = P_i\left(0\right)\exp\left(-t/T_2\right) \tag{9}$$

The time-correlation function for this nucleus is thus:

$$C\left(t\right) = \int_{-\infty}^{\infty}\sum_{i=0}^{\infty}P_i\left(0\right)\exp\left(-t/T_2\right)\left\langle\Phi_i\left|\hat{\mathbf{M}}_\perp\left(0\right)\cdot\hat{\mathbf{M}}_\perp\left(t\right)\right|\Phi_i\right\rangle \tag{10}$$

20. What is the expression for the spectral intensity, $I\left(\omega\right)$, in terms of the time-correlation function? You do not have to do the integral—just give me the key equation.

$$I\left(\omega\right) = 2\pi\hat{C}\left(\omega\right) = 2\pi\left(\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\omega t}C\left(t\right)dt\right)$$

21. Suppose that the only type of broadening that occurred in NMR were due to T2-relaxation. Then
(a) This is a form of <u>inhomogeneous</u> broadening and the spectral lines will have a <u>Gaussian</u> shape.
(b) This is a form of <u>inhomogeneous</u> broadening and the spectral lines will have a Lorentzian shape.
(c) This is a form of <u>homogeneous</u> broadening and the spectral lines will have a <u>Gaussian</u> shape.
(d) This is a form of <u>homogeneous</u> broadening and the spectral lines will have a <u>Lorentzian</u> shape.

Problems

Pick THREE of the following five problems. **Clearly mark which problems you wish for me to grade.**   If you do not mark which problems you wish to solve, I will mark the **first** three problems on which you have written **anything**. Each problem is worth 15 points.

1. Suppose that $\hat{A}$ and $\hat{B}$ are linear, Hermitian, operator. Consider the product of these matrices, raised to the nth power:

$$\left(\hat{A}\hat{B}\right)^n = \underbrace{\left(\hat{A}\hat{B}\right)\left(\hat{A}\hat{B}\right)\cdots\left(\hat{A}\hat{B}\right)}_{n \text{ times}} \tag{11}$$

$$n = 0,1,2,3,\ldots$$

(a) (11 pts.) Show that

$$\left\langle \Phi \left| \left(\hat{A}\hat{B}\right)^n \right| \Psi \right\rangle = \left\langle \Phi \left| \left(\hat{A}\hat{B}\right)^n \Psi \right\rangle = \left\langle \left(\hat{B}\hat{A}\right)^n \Phi \right| \Psi \right\rangle \tag{12}$$

n = 0. The result is obviously true for *n =0* because $\hat{O}^0 = 1$ for any operator and $\left\langle \Phi \left| (1)\Psi \right\rangle = \left\langle (1)\Phi \right| \Psi \right\rangle$.

n = 1.   The result is true for *n=1* by the following argument, which uses the fact that $\hat{A}$ and $\hat{B}$ are Hermitian:

$$\left\langle \Phi \left| \hat{A}\hat{B}\Psi \right\rangle = \left\langle \Phi \left| \hat{A}\left(\hat{B}\Psi\right)\right\rangle = \left\langle \hat{A}\Phi \left| \hat{B}\Psi \right\rangle = \left\langle \left(\hat{A}\Phi\right) \right| \hat{B}\Psi \right\rangle = \left\langle \hat{B}\left(\hat{A}\Phi\right) \right| \Psi \right\rangle = \left\langle \hat{B}\hat{A}\Phi \right| \Psi \right\rangle$$

Now we want to show that if the result is true for one value of *n* greater than or equal to one, it is also true for *n+1*. That is, we want to show that if $\left\langle \Phi \left| \left(\hat{A}\hat{B}\right)^k \right| \Psi \right\rangle = \left\langle \left(\hat{B}\hat{A}\right)^k \Phi \right| \Psi \right\rangle$, then $\left\langle \Phi \left| \left(\hat{A}\hat{B}\right)^{k+1} \right| \Psi \right\rangle = \left\langle \left(\hat{B}\hat{A}\right)^{k+1} \Phi \right| \Psi \right\rangle$.

n=k → n=k+1:

$$\left\langle \Phi \left| \left(\hat{A}\hat{B}\right)^{k+1} \right| \Psi \right\rangle = \left\langle \Phi \left| \left(\hat{A}\hat{B}\right)^{k+1} \Psi \right\rangle = \left\langle \Phi \left| \left(\hat{A}\hat{B}\right)^k \left(\hat{A}\hat{B}\right)\Psi \right\rangle = \left\langle \Phi \left| \left(\hat{A}\hat{B}\right)^k \left[\left(\hat{A}\hat{B}\right)\Psi\right] \right\rangle$$

$$= \left\langle \left(\hat{B}\hat{A}\right)^k \Phi \left| \left[\left(\hat{A}\hat{B}\right)\Psi\right] \right\rangle \qquad\qquad \left(\text{using } n = k \text{ case}\right)$$

$$= \left\langle \left(\hat{B}\hat{A}\right)^k \Phi \left| \hat{A}\hat{B}\Psi \right\rangle \qquad\qquad \left(\text{using } n = 1 \text{ case}\right)$$

$$= \left\langle \left(\hat{B}\hat{A}\right)\left(\hat{B}\hat{A}\right)^k \Phi \left| \Psi \right\rangle$$

$$= \left\langle \left(\hat{B}\hat{A}\right)^{k+1} \Phi \left| \Psi \right\rangle$$

This is called a proof by induction. The idea is that if you give me a value of *n* (say, *n* = 59), then I know that the result is true if the result is true for *n* = 58. In turn, I know that the result for *n* = 58 is true if the result is true for *n* = 57, and that the result for *n* = 57 is true if the result is true for *n* = 56, and …, and that the result is true for *n* = 2 if the result is true for *n* = 1. But the result is true for *n = 1* (which

was simple to show) so the result must also be true for n = 59 and, by the same argument, for any n that is a nonnegative integer.

(b) (4 pts.)Is the product of two Hermitian operators always Hermitian? If not, under what conditions is it true?

Clearly   not,   since   the $n=1$ case   of   Eq.   (12)   indicates   that $\langle \Psi | \hat{A}\hat{B}\Psi \rangle = \langle \hat{B}\hat{A}\Psi | \Psi \rangle \neq \langle \hat{A}\hat{B}\Psi | \Psi \rangle$. Obviously the product of two Hermitian operators is Hermitian if they commute, so that $\hat{A}\hat{B} = \hat{B}\hat{A}$ so that the last inequality is replaced by an equality.

2. Suppose the Hamiltonian of a system does not depend on time. (I.e., $\hat{H}(x,t) \to \hat{H}(x)$.)

    Starting from the time-dependent Schrödinger equation, derive the time-independent Schrödinger equation. Write an explicit formula for the time-dependent wavefunction in terms of the energy eigenvalue of the time-independent Schrödinger equation. (15 pts.)

If the Hamiltonian is time-independent, then replacing $\hat{H}(x,t)$ with $\hat{H}(x)$ in the time-dependent Schrödinger equation gives

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

Whenever you can "divide" a multidimensional differential equation into a sum of two terms, each of which has an explicit dependence on only a subset of the variables, you can simplify the differential equation by a technique called "separation of variables," where you assume the solution can be written as a product of the a function of the "variables in the first part" and a function of the "variables in the second part." In this case we have

$$\left[\underbrace{\hat{H}(x)}_{\text{depends only on } x} - \underbrace{i\hbar\left(\frac{\partial}{\partial t}\right)}_{\text{depends only on } t}\right]\psi(x,t) = 0$$

and so we hypothesize a form of the wavefunction like

$$\psi(x,t) = \Psi(x)\phi(t).$$

Substituting this wavefunction into the time-dependent Schrödinger equation gives

$$\phi(t)\hat{H}(x)\Psi(x) = \left(i\hbar\left(\frac{d\phi}{dt}\right)\right)\Psi(\mathbf{x})$$

Divide both sides by $\phi(t)\Psi(x)$. We obtain:

$$\frac{\hat{H}(x)\Psi(x)}{\Psi(x)} = \left(\frac{i\hbar}{\phi(t)}\left(\frac{d\phi}{dt}\right)\right)$$

The left-hand-side depends only on x; the right-hand-side depends only on t. However, the equation must hold for *all x* and *t*, which can happen only if this equation is equal to a constant. So we have:

$$\frac{\hat{H}(x)\Psi(x)}{\Psi(\mathbf{x})} = (\text{constant}) = \left(\frac{i\hbar}{\phi(t)}\left(\frac{d\phi}{dt}\right)\right)$$

or

$$\left(\frac{d\phi}{dt}\right) = \frac{1}{i\hbar}(\text{constant})\phi(t)$$

$$\hat{H}(x)\Psi(x) = (\text{constant})\Psi(\mathbf{x})$$

Identifying the second equation as the time-independent Schrödinger equation, we see that the constant must be the energy. So

$$\hat{H}(x)\Psi(x) = E\Psi(x)$$

We can solve the ordinary differential equation for the time-dependent portion of the wavefunction by explicit integration,

$$d\phi = \frac{E}{i\hbar}\phi(t)\,dt$$

$$\int \frac{1}{\phi(t)}\,d\phi = \left(\frac{-iE}{\hbar}\right)\int dt$$

$$\ln(\phi(t)) = \frac{-iEt}{\hbar} + (\text{const. of integration})$$

$$\phi(t) = e^{(\text{const. of integration})}e^{-\frac{iEt}{\hbar}}$$

$$\propto e^{-\frac{iEt}{\hbar}}$$

It is obvious that the if $\psi(x,t)$ is a solution to the Schrödinger equation, then any multiple of the wavefunction, $c\psi(x,t)$, is also. So we can ignore the constant of integration.

3. Consider a particle of mass m confined to a two-dimensional rectangular box with potential,

$$V(x,y) = \begin{cases} 0 & 0 < x < a \text{ and } 0 < y < b \\ +\infty & \text{otherwise} \end{cases} \quad (13)$$

(a) **Solve the time-independent Schödinger equation to find the eigenfunctions and the eigenvalues of this system. (11 pts.)** You should obtain:

$$\Psi_{n_x,n_y}(x,y) = \frac{2}{\sqrt{ab}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right)$$

$$E_{n_x n_y} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right) \quad (14)$$

$$n_x = 1,2,3,\ldots$$
$$n_y = 1,2,3,\ldots$$

The Hamiltonian is

$$\hat{H}(x,y) = \begin{cases} -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} - \dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial y^2} & 0 < x < a;\ 0 < y < b \\ +\infty & \text{otherwise} \end{cases}$$

and so the wavefunction must be zero outside the box,

$$\Psi(x,y) = \begin{cases} (\text{something}) & 0 < x < a;\ 0 < y < b \\ 0 & \text{otherwise} \end{cases}$$

When the Hamiltonian is the sum of two terms, each of which depends on only one variable, we should proceed by separation of variables. So we guess that the wavefunction is a product of a function of x and a function of y:

$$\Psi(x,y) = \psi(x)\phi(y)$$

and substitute into the Schrödinger equation (inside the box) to obtain:

$$\hat{H}(x,y)\psi(x)\phi(y) = E\psi(x)\phi(y)$$

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\right)\psi(x)\phi(y) = E\psi(x)\phi(y)$$

$$\phi(y)\left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}\right) + \psi(x)\left(-\frac{\hbar^2}{2m}\frac{\partial^2\phi(y)}{\partial y^2}\right) = E\psi(x)\phi(y)$$

$$\frac{1}{\psi(x)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}\right) + \frac{1}{\phi(y)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2\phi(y)}{\partial y^2}\right) = E$$

This equation indicates that sum of some function of x and some function of y, equals a constant <u>for all permissible values of x and y</u>,

$$f(x) + g(y) = \text{constant} \qquad \forall\, 0 \leq x \leq a; 0 \leq y \leq b$$

This can only happen if the individual functions are constants also. This gives the equations:

$$\frac{1}{\psi(x)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}\right) = \left(\text{constant }\#1\right)$$

$$\frac{1}{\phi(y)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2\phi(y)}{\partial y^2}\right) = \left(\text{constant }\#2\right)$$

but these equations are identical to the *one-dimensional* particle-in-a-box. So

$$\frac{1}{\psi_{n_x}(x)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi_{n_x}(x)}{\partial x^2}\right) = E_{n_x}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_{n_x}(x)}{\partial x^2} = E_{n_x}\psi_{n_x}(x)$$

$$E_{n_x} = \frac{h^2 n_x^2}{8ma^2}$$

$$\psi_{n_x}(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi x}{a}\right)$$

and similarly

$$E_{n_y} = \frac{h^2 n_x^2}{8ma^2}$$

$$\phi_{n_y}(y) = \sqrt{\frac{2}{b}}\sin\left(\frac{n_y\pi y}{b}\right)$$

So the wavefunction is

$$\Psi_{n_x,n_y}(x,y) = \frac{2}{\sqrt{ab}}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)$$

and substituting in gives:

$$E_{n_x n_y} = \frac{1}{\psi(x)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}\right) + \frac{1}{\phi(y)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2\phi(y)}{\partial y^2}\right)$$

$$= E_{n_x} + E_{n_y} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}\right)$$

(b) Suppose $b=3$ and $a=5$. **Write expressions for the transition frequencies associated with the <u>two lowest-energy</u> (lowest frequency) dipole-allowed absorptions starting from the ground state.** (That is, the initial state is $n_x = n_y = 1$). **(4 pts.)**

The lowest-energy absorptions are

$$\#1 : \left(n_x = 1, n_y = 1 \right) \rightarrow \left(n_x = 2, n_y = 1 \right): \qquad \Delta E = \frac{h^2}{8m} \left[\left(\frac{2^2}{5^2} + \frac{1^2}{3^2} \right) - \left(\frac{1^2}{5^2} + \frac{1^2}{3^2} \right) \right] = \left(\frac{h^2}{8m} \right) \left(\frac{3}{25} \right)$$

$$\#2 : \left(n_x = 1, n_y = 1 \right) \rightarrow \left(n_x = 3, n_y = 1 \right): \qquad \Delta E = \frac{h^2}{8m} \left[\left(\frac{3^2}{5^2} + \frac{1^2}{3^2} \right) - \left(\frac{1^2}{5^2} + \frac{1^2}{3^2} \right) \right] = \left(\frac{h^2}{8m} \right) \left(\frac{8}{25} \right)$$

$$\#3 : \left(n_x = 1, n_y = 1 \right) \rightarrow \left(n_x = 1, n_y = 2 \right): \qquad \Delta E = \frac{h^2}{8m} \left[\left(\frac{1^2}{5^2} + \frac{2^2}{3^2} \right) - \left(\frac{1^2}{5^2} + \frac{1^2}{3^2} \right) \right] = \left(\frac{h^2}{8m} \right) \left(\frac{1}{3} \right)$$

However, the second-lowest absorption (#2) is *not dipole allowed* because the $n_x = 1 \rightarrow n_x = 3$ transition is not allowed for the *one-dimensional* oscillator. (It also isn't allowed here, because n_y isn't changing.

4. The simplest model of molecular vibrations is the so-called Harmonic oscillator model. In the simple one-dimension harmonic oscillator, the bond between the atoms in a diatomic molecule is approximated as a spring, with force constant k_e and equilibrium constant r_e.
The resulting potential is simply a parabola, $V_{HO}(r) = \frac{1}{2} k_e \left(r - r_e \right)^2$. The eigenvalues of the simple oscillator are given by

$$E(v) = \hbar \left(\sqrt{\frac{k_e}{\mu}} \right) \left(v + \frac{1}{2} \right) \qquad\qquad v = 0,1,2,\dots \qquad (15)$$

where the reduced mass of the oscillator is simply related to the atomic masses by $\mu = \left(m_A m_B / \left(m_A + m_B \right) \right)$. The eigenfunctions of the three lowest energy states of the harmonic oscillator are given below

$$\psi_0(r) = \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{\alpha}{2}(r-r_e)^2} \qquad\qquad \psi_1(r) = \left(\frac{\alpha}{\pi} \right)^{1/4} \left(\sqrt{2\alpha} \right) (r - r_e) e^{-\frac{\alpha}{2}(r-r_e)^2}$$

$$\psi_2(r) = \left(\frac{\alpha}{\pi} \right)^{1/4} \left(\frac{1}{\sqrt{8}} \right) \left(4\alpha (r - r_e)^2 - 2 \right) e^{-\frac{\alpha}{2}(r-r_e)^2}$$

$$(16)$$

where

$$\alpha = \sqrt{\frac{k_e \mu}{\hbar^2}} \qquad\qquad (17)$$

(a) Write down the Harmonic-Oscillator Hamiltonian and show that $\psi_0(r)$ is an eigenfunction of it. (5 points)

1. The Harmonic Oscillator Hamiltonian is

$$\hat{H}_{HO} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{1}{2} k_e \left(r - r_e \right)^2$$

2. $\psi_0(r)$ is an eigenfunction of this Hamiltonian because:

$$\hat{H}_{HO}\psi_0(r) = \left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \tfrac{1}{2}k_e(r-r_e)^2\right)\left(\frac{\alpha}{\pi}\right)^{1/4}e^{-\frac{\alpha}{2}(r-r_e)^2}$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/4}\left(-\frac{\hbar^2}{2\mu}\left[\frac{d^2}{dr^2}\left(e^{-\frac{\alpha}{2}(r-r_e)^2}\right)\right] + \tfrac{1}{2}k_e(r-r_e)^2\left(e^{-\frac{\alpha}{2}(r-r_e)^2}\right)\right)$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/4}\left(-\frac{\hbar^2}{2\mu}\left[\frac{d}{dr}\left(\frac{d\left(e^{-\frac{\alpha}{2}(r-r_e)^2}\right)}{dr}\right)\right] + \tfrac{1}{2}k_e(r-r_e)^2\left(e^{-\frac{\alpha}{2}(r-r_e)^2}\right)\right)$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/4}\left(-\frac{\hbar^2}{2\mu}\left[\frac{d\left(-\alpha(r-r_e)e^{-\frac{\alpha}{2}(r-r_e)^2}\right)}{dr}\right] + \tfrac{1}{2}k_e(r-r_e)^2\left(e^{-\frac{\alpha}{2}(r-r_e)^2}\right)\right)$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/4}\left(-\frac{\hbar^2}{2\mu}\left[\left(-\alpha e^{-\frac{\alpha}{2}(r-r_e)^2}\right)+\left(-\alpha(r-r_e)\right)^2 e^{-\frac{\alpha}{2}(r-r_e)^2}\right] + \tfrac{1}{2}k_e(r-r_e)^2\left(e^{-\frac{\alpha}{2}(r-r_e)^2}\right)\right) \quad (18)$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/4}e^{-\frac{\alpha}{2}(r-r_e)^2}\left(\left[-\frac{\hbar^2}{2\mu}(-\alpha)-\frac{\hbar^2}{2\mu}(\alpha^2)(r-r_e)^2\right]+\tfrac{1}{2}k_e(r-r_e)^2\right)$$

$$= \psi_0(r)\left(-\frac{\hbar^2}{2\mu}\left(\left(\sqrt{\frac{k_e\mu}{\hbar^2}}\right)\right)+\left\{-\frac{\hbar^2}{2\mu}\left(\left(\sqrt{\frac{k_e\mu}{\hbar^2}}\right)^2\right)+\tfrac{1}{2}k_e\right\}(r-r_e)^2\right)$$

$$= \psi_0(r)\left(\frac{\hbar}{2}\sqrt{\frac{k_e}{\mu}}+\left(-\frac{k_e}{2}+\frac{k_e}{2}\right)(r-r_e)^2\right)$$

$$= \left(\frac{\hbar}{2}\sqrt{\frac{k_e}{\mu}}\right)\psi_0(r) = E_0\psi_0(r)$$

(b) Most of the vibrational absorption and emission involves the three lowest energy states given above. Which of the following transition(s) are electric dipole allowed? (3 points)
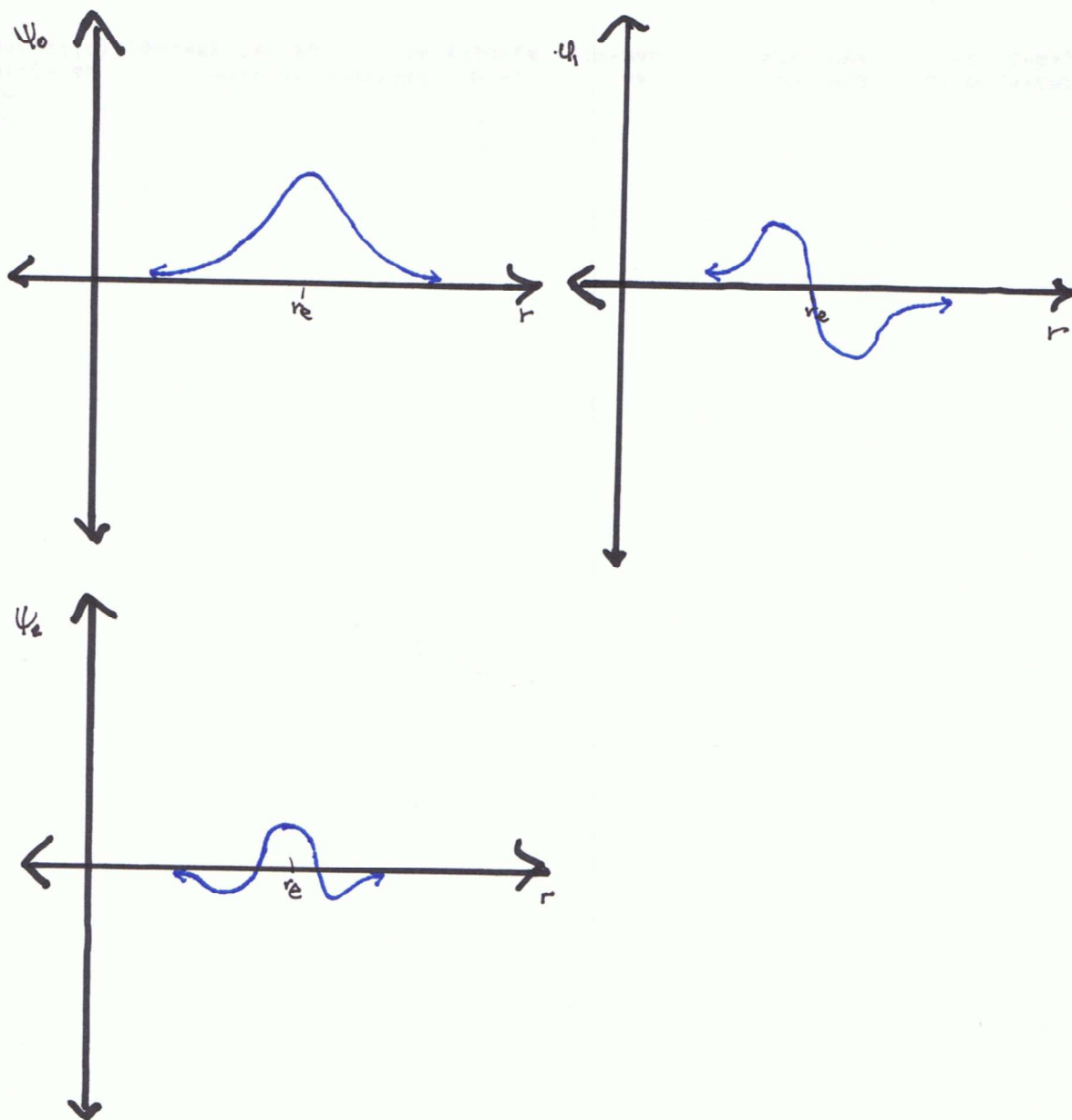
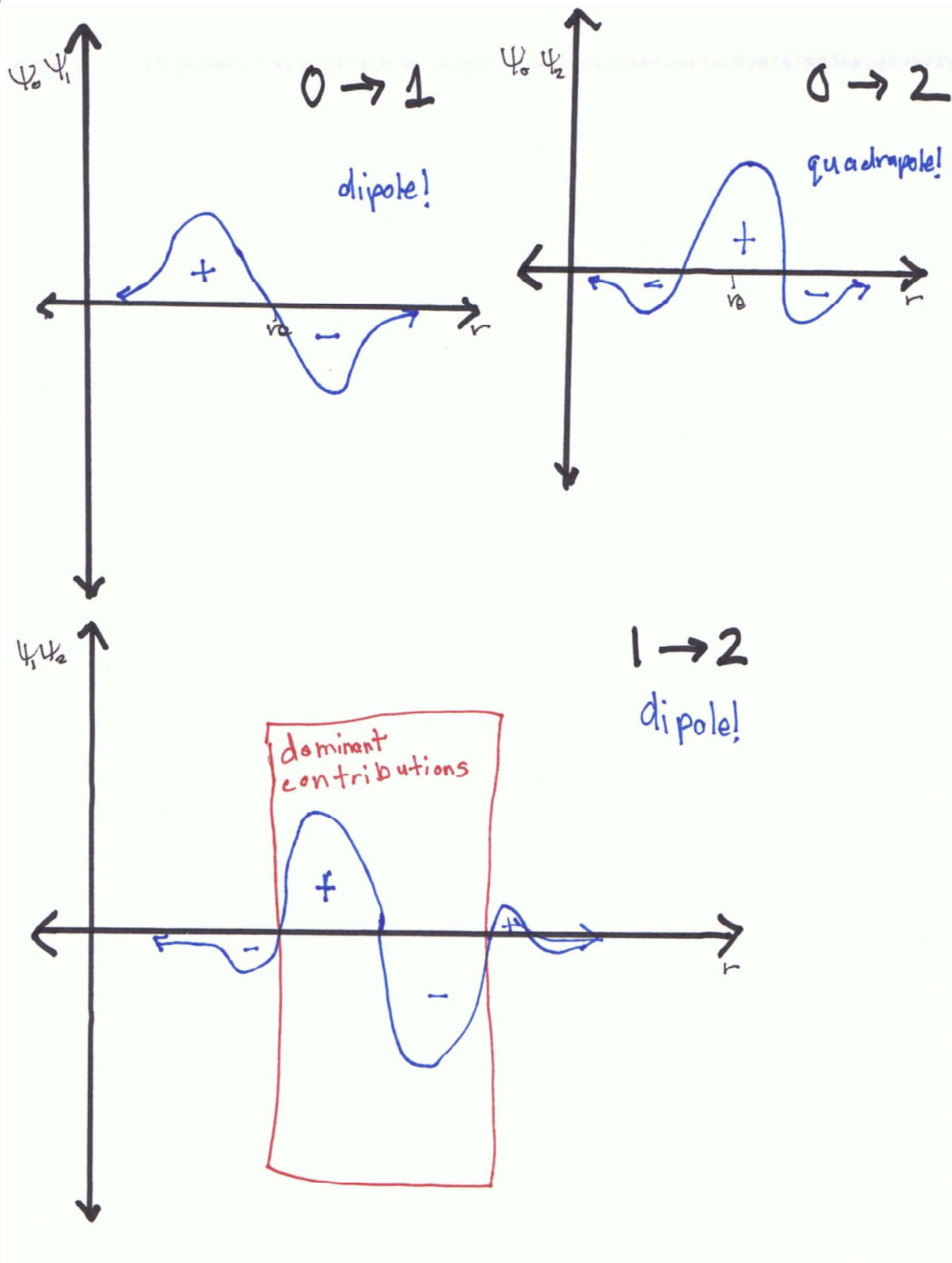(a) $0 \to 1$ (c) $1 \to 2$ (e) $2 \to 1$

(b) $0 \to 2$ (d) $2 \to 0$ (f) $1 \to 0$

If you plot the wavefunctions, you get functions that look roughly like those below.

Doing the "multiplication trick" dipole-shaped objects only when $\Delta v = \pm 1$, which explains the result indicated above.

(c) Referring to your answer in (b), what absorption frequency(ies) do you observe? (3 points)

The allowed absorptions are $0 \to 1$ and $1 \to 2$. The energies are:

$$\nu_{01} = \frac{E_1 - E_0}{h} = \frac{\hbar\left(\sqrt{\frac{k_e}{\mu}}\right)\left(1 + \frac{1}{2}\right) - \hbar\left(\sqrt{\frac{k_e}{\mu}}\right)\left(0 + \frac{1}{2}\right)}{h} = \left(\frac{1}{2\pi}\sqrt{\frac{k_e}{\mu}}\right)$$

$$\nu_{12} = \frac{E_1 - E_0}{h} = \frac{\hbar\left(\sqrt{\frac{k_e}{\mu}}\right)\left(2 + \frac{1}{2}\right) - \hbar\left(\sqrt{\frac{k_e}{\mu}}\right)\left(1 + \frac{1}{2}\right)}{h} = \left(\frac{1}{2\pi}\sqrt{\frac{k_e}{\mu}}\right)$$

The two absorption frequencies are exactly the same! So there is only one absorption frequency, which is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k_e}{\mu}}$$

(d) What is the ground-state energy and the ground-state wavefunction of the "half-oscillator" (4 points)

$$V_{\frac{1}{2}\mathrm{HO}}(r) = \begin{cases} V_{\mathrm{HO}}(r) = \frac{1}{2}k_e(r - r_e)^2 & r_e \le r < +\infty \\ +\infty & -\infty < r < r_e \end{cases}$$

Remember what we did for the particle in a box. We said that the eigenfunctions of the Hamiltonian were $\cos(kx)$ and $\sin(kx)$ for any k, but the fact that the potential was infinity for $r < 0$ and $r > a$ meant that the wavefunction had to be zero at those two values, $\psi(0) = \psi(a) = 0$. This case is similar. The solutions to the harmonic oscillator potential are given in the problem, but in the half-oscillator we also require that $\psi(r_e) = 0$. So half of the solutions of the harmonic oscillator are no longer allowed ($\upsilon = 0, 2, 4, \ldots$ do not satisfy $\psi_\upsilon(r_e) = 0$). The new ground state is thus

$$\psi_1(r) = \left(\frac{\alpha}{\pi}\right)^{1/4}\left(\sqrt{2\alpha}\right)(r - r_e)e^{-\frac{\alpha}{2}(r - r_e)^2} \quad \text{and the ground-state energy is } E(\upsilon = 1) = \frac{3\hbar}{2}\left(\sqrt{\frac{k_e}{\mu}}\right).$$

5. Suppose we use a beam of Helium-4 atoms to image a crystal, in a manner similar to *X*-ray crystallography. Assume that the ^4_2He atoms are in thermal equilibrium at temperature *T*. From fundamental thermodynamics, we know that the kinetic energy of the Helium atoms is

$$\text{kinetic energy} = \tfrac{3}{2}k_B T \tag{19}$$

where k_B is Boltzmann's constant. Suppose that the substance we want to diffract the Helium atoms from crystallizes in a simple cubic lattice with lattice constant (i.e., nearest-neighbor distance) $a = 2.0 \cdot 10^{-10}$ m.

(a) At what temperature would diffraction of the ^4_2He atoms become appreciable? (9 points)

The atoms will diffract only if the wavelength of the atoms is similar to the spacing between the atoms in the lattice. So we need to have

$$2.0 \cdot 10^{-10} \text{ m} \approx \lambda_{\text{He}}$$

The wavelength of the Helium atoms is determined by the De Broglie relation,

$$\lambda_{\text{He}} = \frac{h}{p}$$

and the momentum of the Helium atoms is determined from their kinetic energy as:

$$\frac{p^2}{2m} = (\text{k.e.})$$

$$p = \sqrt{2m_{\text{He}}(\text{k.e.})} = \sqrt{2m_{\text{He}}\left(\tfrac{3}{2}\right)k_B T} = \sqrt{3m_{\text{He}}k_B T}$$

Putting it all together

$$2.0 \cdot 10^{-10} \text{ m} \approx \lambda_{\text{He}} = \frac{h}{\sqrt{3m_{\text{He}}k_B T}}$$

$$\sqrt{3m_{\text{He}}k_B T} \approx \frac{h}{\left(2.0 \cdot 10^{-10} \text{ m}\right)}$$

$$T \approx \frac{1}{3k_B m_{\text{He}}}\left(\frac{h}{2.0 \cdot 10^{-10} \text{ m}}\right)^2$$

From this we can already answer parts (b) and (c). Colder and more massive particles have bigger De Broglie wavelengths. So if we increase the lattice spacing, we need to decrease the temperature. (Alternative viewpoint: look at the last equation. Replacing $2.0 \cdot 10^{-10}$ m with a bigger number decreases the temperature.) So the answer to (c) is (ii). If we decrease the mass of the particle we are using for diffraction, the temperature increases. (That is, all else being equal, lighter particles have less momentum and larger De Broglie wavelengths.) So the answer to (b) is (i).

Finally, substituting in for the Helium case gives

$$T \approx \frac{1}{3k_B m_{He}} \left(\frac{h^2}{2.0 \cdot 10^{-10} \text{ m}} \right)$$

$$= \frac{1}{3\left(1.381 \cdot 10^{-23} \frac{J}{K}\right)\left(4.0 \text{ u}\right)} \left(\frac{6.626 \cdot 10^{-34} \text{ J} \cdot \text{s}}{2.0 \cdot 10^{-10} \text{ m}} \right)^2$$

$$= \left(\frac{1}{4.143 \cdot 10^{-23} \text{J} \cdot \left(4.0 \text{ u}\right)\left(1.661 \cdot 10^{-27} \frac{kg}{u}\right)} \right) \left(1.098 \cdot 10^{-47}\right) \frac{\text{J}^2 \text{s}^2 \text{K}}{\text{m}^2}$$

$$= \left(39.9\right) \left(\frac{\text{J}^2 \text{s}^2 \cdot \text{K}}{\text{J} \cdot \text{kg} \cdot \text{m}^2} \right)$$

$$= 39.9 \left(\frac{\text{J} \cdot \text{s}^2 \cdot \text{K}}{\text{kg} \cdot \text{m}^2} \right)$$

$$= 39.9 \left(\frac{\left(\text{kg} \cdot \frac{\text{m}^2}{\text{s}^2}\right) \cdot \text{s}^2 \cdot \text{K}}{\text{kg} \cdot \text{m}^2} \right)$$

$$= 39.9 \text{ K}$$

Given the accuracy of this sort of heuristic argument, what we learn is that the temperature of the Helium atoms in the beam needs to be <u>**roughly 40 K.**</u>

(b) Suppose we use thermal neutrons, instead of ^4_2He to diffract off the crystal. **Would the optimal temperature of the neutrons be smaller or larger than that of the Helium atoms in part (a)? (3 points)**

<u>**(i)**</u> $T_{\text{neutrons}} > T_{\text{Helium}}$ (ii) $T_{\text{neutrons}} < T_{\text{Helium}}$

(c) Suppose we now decide to diffract ^4_2He from a cubic lattice with a slightly larger lattice constant, $a = 2.8 \cdot 10^{-10}$ m. **Should the temperature of the Helium atom beam be increased or decreased in order to optimize diffraction. (3 points)**

(i) $T_{\text{He for .28 nm}} > T_{\text{He for .20 nm}}$ (increase T)   <u>**(ii)**</u> $T_{\text{He for .28 nm}} < T_{\text{He for .20 nm}}$ **(decrease T)**