*Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.*

1. (15 points) (a) Show that the wave function for a particle in a one-dimensional box of length, a, that has an energy eigenvalue of $E = \frac{9h^2}{8ma^2}$ is an eigenfunction of the square of the linear momentum, by calculating the operation for the square of the linear momentum, p^2 on the appropriate wave function when the system is in that state.

First, one must find the wave function. It is found by noting, from the formula for the energy that the value of the quantum number must be $n = 3$. The appropriate wave function is $\psi_2(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi x}{a}\right)$. One may carry out this demonstration by first performing the operation:

$$\widehat{p^2}\sqrt{\frac{2}{a}}\sin\left(\frac{3\pi x}{a}\right) = -\hbar^2\frac{d^2}{dx^2}\left\{\sqrt{\frac{2}{a}}\sin\left(\frac{3\pi x}{a}\right)\right\} = \frac{9\pi^2}{a^2}\hbar^2\left\{\sqrt{\frac{2}{a}}\sin\left(\frac{3\pi x}{a}\right)\right\}$$

From this result, one sees that the eigenvalue of the operator for the square of the linear momentum is:

$$p^2 = \frac{9\pi^2}{a^2}\hbar^2 = \frac{9h^2}{4a^2}$$

(b) Consider the linear momentum itself, rather than the square of it. Is the state above also an eigenstate of the linear momentum? If so, what is the eigenvalue?

Again, one calculates the operation on the wave function.

$$\hat{p}\sqrt{\frac{2}{a}}\sin\left(\frac{3\pi x}{a}\right) = -i\hbar\frac{d}{dx}\left\{\sqrt{\frac{2}{a}}\sin\left(\frac{3\pi x}{a}\right)\right\} = -i\hbar\left\{\sqrt{\frac{2}{a}}\frac{d}{dx}\sin\left(\frac{3\pi x}{a}\right)\right\} = -i\frac{3\pi\hbar}{a}\left\{\sqrt{\frac{2}{a}}\cos\left(\frac{3\pi x}{a}\right)\right\}$$

In this case, the operation on the function does not return the same function. The answer is that this wave function for the particle in the one-dimensional box is NOT an eigenfunction of the operator for the linear momentum.

2. (10 points) For every phrase in Column A, find the best descriptor in Column B and insert the letter for it in the blank in Column A. (There is only one most correct

Column A	Column B
__d__ Observable	a. Model of a system exposed to no potential anywhere in the universe
__i__ de Broglie relation	b. The property that the integral of the product of a wave function and the complex conjugate of another function is zero
__f__ Classically forbidden region	c. The number of states that have the same value of a property
__g__ Completeness	d. A measurable property of a system with a corresponding operator.
__c__ Degeneracy	e. Requirement on an operator that allows it to represent an observable quantity
__e__ Hermiticity	f. Outside of the classical turning points of the harmonic oscillator
__a__ Free particle	g. Any well-behaved function can be expanded in the eigenfunctions of any quantum mechanical operator defined in the same space
__j__ Orbital	h. The concept that one cannot measure precisely both the position and momentum of a particle
__o__ Spatial quantization	i. The idea that the concept relating the wavelength of light with momentum also applies to particles
__n__ Stern-Gerlach experiment	j. For the hydrogen atom, this word is a synonym for the an eigenfunction of the Hamiltonian
	k. The property of a system to act simultaneously as a particle or a wave.
	l. Ensures that repulsion among electrons is minimized
	m. Scattering of light at frequencies other than that to which the system is exposed.
	n. Early demonstration of the existence of the property of spin of an electron
	o. In the vector model of angular momentum, the vectors can have only certain orientations in space

Score for Page

3. (15 points) Operator algebra.

a) **For each of the following pairs of functions f and g, give <u>two possible</u> forms for the operator $\hat{A}$ that allow the relation $g(x) = \hat{A}f(x)$ to be satisfied.**
1) $f = 2x^4, g = 8x^3$

$(4/x), \quad \dfrac{d}{dx}$

2) $f = x^4, g = x^2.$

$(1/x^2), \quad (4x)^{-1}\dfrac{d}{dx}, \quad (1/12)\dfrac{d^2}{dx^2}$

b) **Which of the following functions are eigenfunctions of $\partial^2/\partial x^2 + \partial^2/\partial y^2$? For each eigenfunction, give the eigenvalue. [x and y are independent variables.] (Show all work to prove your answer.)**

1) $e^{2x}e^{3y}$

$(\partial^2/\partial x^2 + \partial^2/\partial y^2)(e^{2x}e^{3y}) = 4e^{2x}e^{3y} + 9e^{2x}e^{3y} = 13e^{2x}e^{3y}.$ The eigenvalue is 13.

2) x^3y^3

$(\partial^2/\partial x^2 + \partial^2/\partial y^2)(x^3y^3) = 6xy^3 + 6x^3y.$ Not an eigenfunction.

3) $\sin 2x + \cos 3y.$

$(\partial^2/\partial x^2 + \partial^2/\partial y^2)(\sin 2x + \cos 3y) = -4\sin 2x - 9\cos 3y.$ Not an eigenfunction.

Score for Page

4. (10 points) Normalize the wave function for the lowest-energy state of the one-dimensional harmonic oscillator in terms of the characteristic length, α. (Show all work. As the final answer, write the normalized wave function.)

To begin, one must identify the wave function. According to information on page 11-2 of the handbook, the general form for the wave function of a one-dimensional harmonic oscillator is

$$\psi_n(x) = A_n H_n\left(\frac{x}{\alpha}\right) exp\left(-\frac{x^2}{2\alpha^2}\right)$$

where A_n is a normalization factor (to be determined) and $H_n\left(\frac{x}{\alpha}\right)$ is the Hermite polynomial of order n.

The lowest-energy state is the one for which $n = 0$. The Hermite polynomial of this order is just the number 1. Hence, the state to work with is:

$$\psi_0(x) = A_0 H_0\left(\frac{x}{\alpha}\right) exp\left(-\frac{x^2}{2\alpha^2}\right) = A_0 exp\left(-\frac{x^2}{2\alpha^2}\right)$$

Normalization is simply the requirement that the integral of the square of the magnitude over all space be equal to 1:

$$\int_{-\infty}^{+\infty} \psi_0^*(x)\psi_0(x)dx = 1$$

Because the wave function is real, the integral further simplifies to:

$$A_0^*A_0 \int_{-\infty}^{+\infty} exp\left(-\frac{x^2}{2\alpha^2}\right)exp\left(-\frac{x^2}{2\alpha^2}\right)dx = A_0^*A_0 \int_{-\infty}^{+\infty} exp\left(-\frac{x^2}{\alpha^2}\right)dx = 1$$

This definite integral is NOT on the integral table in the handbook. However, one may realize that, because the integrand is symmetric about $x = 0$, the integral is twice the value of the integral over the positive half of the number line:

$$2 A_0^*A_0 \int_{0}^{+\infty} exp\left(-\frac{x^2}{\alpha^2}\right)dx = 1$$

This integral is found in the inte4gral table on page 2-2 of the handbook. In terms of the characteristic length, α, this integral becomes

$$2 A_0^*A_0 \left(\frac{1}{2}\right)\sqrt{\pi\alpha^2} = 1$$

We have the opportunity to choose whether the normalization constant is real, imaginary, or complex, so we choose that it is real:

$$A_0^2\sqrt{\pi\alpha^2} = 1$$

Rearrangement gives this equation:

$$A_0^2 = \frac{1}{\sqrt{\pi}\alpha}$$

Taking the square root of both sides provides the value of the normalization constant as a real, positive number.

$$A_0 = \frac{1}{\sqrt[4]{\pi}\sqrt{\alpha}}$$

The normalized wave function is

$$\psi_0(x) = \frac{1}{\sqrt[4]{\pi}\sqrt{\alpha}} exp\left(-\frac{x^2}{2\alpha^2}\right)$$

Score for Page

5. (15 points) In a monovalent metal, one electron per atom is free to roam throughout the object. What holds such a material together – why doesn't it simply fall apart into a pile of individual atoms? The energy of the composite material must be *less* than the energy of the isolated atoms.

(a)

(a) Give a formula for the energy of N isolated atoms (Panel a), by treating each one as having an electron in the ground state of an infinite square well of width a.

a

The total energy is simply N times the ground state energy of the infinite square well.

$$E_a = N \frac{\pi^2 \hbar^2}{2ma^2}.$$

(b)

$$Na$$
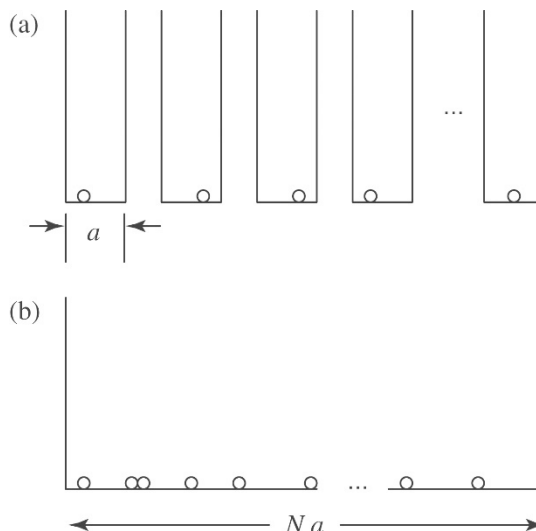
(b) When these atoms come together to form a metal, one gets *N* electrons in a much larger infinite square well of width *Na* (Panel b). Because of the Pauli exclusion principle (which we shall discuss later), there can only be one electron in each allowed state. Give a formula for the lowest energy for this system?
(Faulhaber's formula: $\sum_{k=1}^{m} k^2 = \frac{m(m+1)(2m+1)}{6}$).

Filling the lowest N energy levels of the infinite square well (with width Na) gives

$$E_b = \sum_{n=1}^{N} \frac{n^2 \pi^2 \hbar^2}{2m(Na)^2} = \frac{\pi^2 \hbar^2}{2mN^2 a^2} \sum_{n=1}^{N} n^2.$$

The sum is $N(N+1)(2N+1)/6$, therefore

$$E_b = \left(\frac{N}{3} + \frac{1}{2} + \frac{1}{6N}\right) \frac{\pi^2 \hbar^2}{2ma^2}$$

(c) The difference of these two energies is the cohesive energy of the metal – the energy it would take to tear it apart into isolated atoms. Give a formula for the cohesive energy per atom, <u>in the limit of large *N*</u>.

$$\frac{\Delta E}{N} = \frac{E_a - E_b}{N} \approx \left(\frac{N - (N/3)}{N}\right) \frac{\pi^2 \hbar^2}{2ma^2} = \frac{\pi^2 \hbar^2}{3ma^2}.$$

Score for Page

6. (15 points) Calculate the probability that a particle in a one-dimensional box of length a is found between $0.28a$ and $0.32a$ when it is described by the following wave function:

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

What would you expect for a classical particle? Compare the numerical values of the classical and quantum results.

Using the standard integral (page 2-2 in the handbook),

$$\int sin^2(ax)\, dx = \frac{x}{2} - \frac{1}{4a}sin(2ax).$$

$$P = \frac{2}{a}\int_{0.28a}^{0.32a} sin^2\left(\frac{\pi x}{a}\right) dx = \frac{2}{a}\left[\frac{x}{2} - \frac{a}{4\pi}sin\left(\frac{2\pi x}{a}\right)\right]_{0.28a}^{0.32a}$$

$$= \frac{2}{a}\left[\frac{0.32a}{2} - \frac{a}{4\pi}sin(0.64\pi) - \frac{0.28a}{2} + \frac{a}{4\pi}sin(0.56\pi)\right]$$

$$= 0.04 + \frac{1}{2\pi}\left[-sin(0.64\pi) + sin(0.56\pi)\right] = 0.052$$

Because the classical particle is equally likely to be in any given interval, the probability will be 0.04 independent of the energy. The indicated wave function corresponds to the ground state and the interval $[0.28a, 0.32a]$ is near the maximum of the wave function, therefore the quantum mechanical probability is greater than the classical probability.

Score for Page

7. (10 points) The harmonic oscillator is a model for the vibration of a bond. Consider a sample of hydrogen that contains both $^1H_2$ and $^1H^2H$ (sometimes called HD). (a) Assuming you could detect both of these molecules with vibrational spectroscopy, at what energies (in cm^{-1}) would one observe the principal absorption bands of these two molecules? (b) At what frequencies (in Hz) would you find these transitions? [Calculate these values <u>as accurately as you can</u> from information available in the handbook in the harmonic oscillator approximation.]

The principal vibrational band is the transition from $n = 0$ to $n = 1$ for the molecule.
According to an equation on page 12-2 of the handbook, this energy of transition <u>in the harmonic oscillator approximation</u> is

$$\Delta E = E_1 - E_0 = \left(1 + \frac{1}{2}\right)\hbar\omega_e - \left(\frac{1}{2}\right)\hbar\omega_e = \hbar\omega_e$$

But this is the energy in joules, not in cm^{-1}. To convert to energy in cm^{-1}, as one sees in Table 12.1, one must divide by a constant:

$$\frac{1}{\lambda} = \frac{\Delta E}{2\pi c} = \frac{\omega_e}{2\pi c}$$

(a) In table 12.1 on page 12-2 of the handbook, the information is given in cm^{-1} if ω_e is divided by $2\pi c$. Hence, the answer is:

For $^1H_2$,

$$\frac{1}{\lambda_{11}} = \frac{\Delta E}{2\pi c} = 4395.24 \ cm^{-1}$$

For $^1H^2H$,

$$\frac{1}{\lambda_{12}} = \frac{\Delta E}{2\pi c} = 3817.09 \ cm^{-1}$$

These are substantially different values for these two molecules, so one should easily distinguish them in a spectroscopic experiment.

(b) To convert these to equivalent frequencies, one must use of the following relation:

$$\nu = \frac{1}{\lambda} c$$

Plugging into this equation for each molecule the value of the speed of light gives these results for the frequencies in Hz:

For $^1H_2$,

$$\nu_{11} = \frac{1}{\lambda_{11}} c = 4395.24 \ cm^{-1}(2.99792458 \times 10^{10} \ cm \ s^{-1}) = 1.3177 \times 10^{14} \ Hz$$

For $^1H^2H$,

$$\nu_{12} = \frac{1}{\lambda_{12}} c = 3917.09 \ cm^{-1}(2.99792458 \times 10^{10} \ cm \ s^{-1}) = 1.1743 \times 10^{14} \ Hz$$

Score for Page

8. (10 points) For each phenomenon in column A, find the most specific associated quantum effect (in column B). Insert its letter in the blank.

Column A	Column B
1. non-Arrhenius behavior at low temperature __d__	a. Conduction band partially filled
2. Emission of electrons upon light shining __c__	b. Conduction band empty, small band gap
3. Electron conduction __a__	c. Photoelectric effect
4. Atomic dimerization __e__	d. Quantum tunneling
5. Semiconduction of electrons __b__	e. The valence energy level is delocalized
	f. Conduction band filled, large band gap

Score for Page

9. (5 points, extra credit) A number of students have mentioned the effect of gravity in a system such as the hydrogen atom. Consider a system like the hydrogen atom consisting of two particles, one with the mass, m_p, of the proton and a second with the mass, m_e, of the electron. For this problem, consider that neither particle is electrically charged. (The particles are isolated from any other influence; that is, they form an independent quantum system.) (a) Write down the classical Hamiltonian function for this system. (The answer to this part must be correct in order that the answers to the remainder of the question be considered for grading.)

$$H = \frac{p_p^2}{2m_p} + \frac{p_e^2}{2m_e} - G\frac{m_p m_e}{|r_e - r_p|}$$

where G is the universal gravitational constant, the momenta of the two particles are given by p_p and p_e, respectively, and the positions of the particles are indicated by r_p and r_e, respectively.

(b) Separate this classical Hamiltonian function into appropriate modes, with explanations of all symbols. (A correct answer to this section requires that the answer to part (a) be correct.)

Rewrite the Hamiltonian function in terms of the motion of the center of mass and the relative motion of the two particles, given by the center-of-mass position, R_{CM}, and the relative position, r (with corresponding linear momenta), respectively:

$$H = \frac{P_{CM}^2}{m_p + m_e} + \frac{p^2}{2\mu} - G\frac{m_p m_e}{|r|} = H_{CM}(R_{CM}) + H_{rel}(r)$$

where M is the total mass, $m_p + m_e$ and μ is the reduced mass of the system, $\mu = \frac{m_p m_e}{m_p + m_e}$.

(c) The Hamiltonian operator can also be separated into these two modes, with corresponding wave functions. What are these two modes and wave functions? Write down Schroedinger's equation for each mode, as completely as possible.

The Hamiltonian operator can be separated, in analogy to the hydrogen atom, into the center-of-mass Hamiltonian operator and into the Hamiltonian operator for the relative motion of the two particles, giving a wave function of the form:

$$\psi = \psi_{CM}(R_{CM})\psi(r)$$

The center-of-mass mode is exactly like the center-of-mass mode for the hydrogen atom.

$$H_{CM}\psi_{CM} = -\frac{\hbar^2}{2M}\nabla_{CM}^2\psi_{CM} = E_{CM}\psi_{CM}$$

The relative motion shows the effects of the gravitational interaction of the two particles.

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - G\frac{m_p m_e}{|r|}\psi = E_{rel}\psi$$

(d) Reduce the differential equation from the complex mode by making it dimensionless.

This part requires the definition of characteristic length: $a = \frac{\hbar^2}{2G\mu m_p m_e}$, the definition of which leads to the definition of y:

$$y = \frac{r}{a}$$

$$-\nabla^2\psi - \frac{1}{y}\psi = \frac{E_{rel}}{\epsilon_0}\psi$$

And the characteristic energy is given by:

$$\epsilon_0 = \frac{\hbar^2}{2\mu a^2}$$

The differential equation above is that of the hydrogen atom, so the wave functions are of the same form, except that the characteristic length is determined not by the electrostatic potential, but by the gravitational interaction of the two particles. The quantum conditions are the same as for the hydrogen atom. (That is because the gravitational potential is of the same form as the electrostatic.)

Score for Page