Chemistry 455A

First Exam
October 21, 2005

Name ___________KEY____________________________

Possibly Helpful Information:

$\hbar = 1.\cdot 10^{-34}\, J - \sec$	$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$
$m_e = 1 \cdot 10^{-30}\, Kg$	$\hbar \omega_n \phi_n = E_n \phi_n = \hat{H}\phi_n$
$c = 3 \cdot 10^8\, m/\sec$	$\frac{\partial^2 \Psi}{\partial t^2} = c^2 \frac{\partial^2 \Psi}{\partial x^2}$
$\omega = ck$	$\hat{H} = \hat{T} + \hat{V}(x)$
$\lambda \nu = c$	$T = \frac{\hat{p}^2}{2m}$
$E = \hbar\omega$	$\hat{p} = -i\hbar \frac{\partial}{\partial x}$
$E = \frac{p^2}{2m}$	
$p = \hbar k$	
$ka = \pi n$	

$$\int_x \phi_n^* \phi_m dx = \delta_{m,n}$$

$$\int_{x=0}^{a} \sin\left(\tfrac{\pi m x}{a}\right) \sin\left(\tfrac{\pi n x}{a}\right) dx = \tfrac{a}{2}\delta_{m,n}$$

$$1 = \int_x \Psi^* \Psi dx$$

$$\langle A \rangle = \frac{\int_x \Psi^* \hat{A} \Psi dx}{\int_x \Psi^* \Psi dx}$$

There are 6 pages; be sure you have all the pages before you start.
Be sure your name is on the exam before you start.
This is a timed 50 minute exam.
To receive full credit on all problems you must show your work or reasoning.

I: Problems from the text (30 points)

I.a) Demonstrate whether or not the function $f(\theta) = 3\cos^2\theta - 1$, is an eigenfunction of the operator $\hat{O} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$ (10 points)

$$\hat{O}f(\theta) = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\left(3\cos^2\theta - 1\right) = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left\{(\sin\theta)(-6\cos\theta\sin\theta)\right\}$$
$$= (-6)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\cos\theta\sin^2\theta\right) = (-6)\frac{1}{\sin\theta}\left\{-\sin^3\theta + 2\cos^2\theta\sin\theta\right\}$$
$$= (-6)\left\{2\cos^2\theta - \sin^2\theta\right\} = (-6)\left(3\cos^2\theta - 1\right)$$

Yes, it is an eigenfunctions of this operator.

I.b) If $f(\theta)$ is an eigenfunction of the operator $\hat{O}$ (of question I.a), what is the eigenvalue? If it is not an eigenfunction write N.E.F. (5 points/ consistency counts)

$$EigenValue = -6$$

I.c) The order of operations of operators is critical to the correct answer. Verify that the two operators, $\hat{A} = x$ and $\hat{B} = \frac{d}{dx}$ have different effects on a test function, $f(x)$, by showing that $\hat{A}\left(\hat{B}f(x)\right) \neq \hat{B}\left(\hat{A}f(x)\right)$ (10 points)

$$\hat{A}\left(\hat{B}f(x)\right) = x\frac{df}{dx}$$
$$\hat{B}\left(\hat{A}f(x)\right) = \frac{d}{dx}(xf) = x\frac{df}{dx} + \frac{dx}{dx}f = x\frac{df}{dx} + f$$

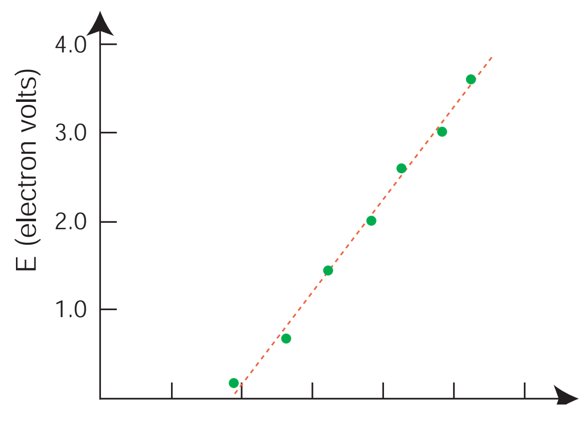
I.d) To clarify the results of problem I.c), evaluate: $\hat{B}\hat{A}f(x) - \hat{A}\hat{B}f(x)$ (5 points)

$$\hat{B}\left(\hat{A}f(x)\right) - \hat{A}\left(\hat{B}f(x)\right) == x\frac{df}{dx} + f - x\frac{df}{dx} = f$$

II: Short Answer Questions from the text (35 points)

II.a) What aspects of the experimental results on the photoelectric effect suggest that light might act like a particle? (If you draw a graph as part of your answer be sure to clearly label the axes and describe the data plotted.) (9 points)

The experiment showed the electron kinetic energy is proportional to the frequency, but the Classical theory predicts that the E is proportional to the intensity. Or any of the other ways of saying it, such as the number of electrons is actually proportional to intensity but the classical theory said it was independent of that.



The quantum mechanical solution for the motion of a particle in free space is $\Psi(x,t) = e^{i(kx-\omega t)}$. The classical mechanical solution is $x(t) = x_o + v_o t$.

II.b) In what way are these two results compatible? (7 points)

Both mechanics say the velocity/momentum are not quantized and are constants of the motion.

II.c) In what way are these two results not compatible? (5 points)

QM says we cannot know where the particle is, that all positions are equally likely. Classical mechanics says that once the initial position is given, the position as a function of time is determined. (i.e. A Probabilistic vs. a Deterministic picture of the motion.)

II.d) How did boundary conditions on the solution of the wave function lead to quantization of the energy levels for the particle in a box? (Use equations if you wish to support your arguments.) (7 points)

The wave function must vanish at the walls. The wave function is a sine function of the position. To make it vanish we require that the argument be a multiple of pi. Therefore a set of possible answers is a discrete set (even if it is unaccountably large).

II.e) What is the most general reason for quantized (or discrete) energy levels? (Use the particle in free space and then in a box to aid your argument.) (7 points)

The confinement of the particle (i.e. in a bound state) leads to quantization or discrete sets of energy levels. The particle in free space does not have quantization.

III: Wave functions for the particle of mass m in a box (35). The particle in the box illustrates most of the features of quantum mechanics.

III.a) Show that the function below, $\phi_n(x)$, is an eigenfunction for the Hamiltonian describing the particle in the box ($V(x) = 0,\ 0 \le x \le a;\ V(x) = \infty$ otherwise): (5 points)

$$\phi_n(x) = \sqrt{\tfrac{2}{a}}\sin\left(\frac{\pi n x}{a}\right)$$

$$\hat{H}\phi_n = E_n\phi_n$$

$$\hat{H}\phi_n(x) = -\sqrt{\tfrac{2}{a}}\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\sin\left(\frac{\pi n x}{a}\right) = \sqrt{\tfrac{2}{a}}\frac{\hbar^2}{2m}\left(\frac{\pi n x}{a}\right)^2\sin\left(\frac{\pi n x}{a}\right) = \frac{\hbar^2}{2m}\left(\frac{\pi n x}{a}\right)^2\phi_n$$

III.b) Compute the Eigenvalue for this eigenfunction, leave your answer in terms of n, a and any other constants you may need. (5 points)

$$EigenValue = \frac{\hbar^2}{2m}\left(\frac{\pi n x}{a}\right)^2$$

III.c) What is the energy, E_n, for the particle in this state (in terms of n, a etc.)? (5 points)

$$E_n = \frac{n^2}{2m}\left(\frac{\pi\hbar}{a}\right)^2$$

III. Continued: Now take the wave function as a sum of two of the eigenfunctions of the particle in a box, $\phi_n(x)$, for two different values of n: $\Psi(x,t=0) = c\phi_2(x) + d\phi_3(x)$, at time zero; and assume that the coefficients are: $c = \frac{i}{\sqrt{2}}$, and $d = \frac{-1}{\sqrt{2}}$ for all the subsequent parts of this problem.

III.d) Verify that this wave function $\Psi(x,t=0)$ is properly normalized at time zero. (5 points)

$$1 \stackrel{?}{=} \int \Psi^*(x,t=0)\Psi(x,t=0)\,dx$$

$$= \int \left(c\phi_2(x) + d\phi_3(x)\right)^* \left(c\phi_2(x) + d\phi_3(x)\right) dx$$

$$= c^*c\int \phi_2^*(x)\phi_2(x)\,dx + d^*d\int \phi_3^*(x)\phi_3(x)\,dx + c^*d\int \phi_2^*(x)\phi_3(x)\,dx + d^*c\int \phi_3^*(x)\phi_2(x)\,dx$$

$$= c^*c + d^*d = \left(\tfrac{i}{\sqrt{2}}\right)^*\left(\tfrac{i}{\sqrt{2}}\right) + \left(\tfrac{-1}{\sqrt{2}}\right)^*\left(\tfrac{-1}{\sqrt{2}}\right) = \tfrac{1}{2} + \tfrac{1}{2} = 1$$

Yes, it is normalized.

III.e) Express the average energy $\langle E \rangle$ for this system in terms of the E_n (i.e. the energies of the eigenstates). (5 points)

$$\langle E \rangle = c^*cE_2 + d^*dE_3 = \frac{E_2 + E_3}{2}$$

$$\langle E \rangle = \frac{1}{2m}\left(\frac{\pi\hbar}{a}\right)^2 \frac{\left\{2^2 + 3^2\right\}}{2} = \left(\frac{13}{2}\right)\frac{1}{2m}\left(\frac{\pi\hbar}{a}\right)^2$$

III.f) A single measurement of the energy is made for the system described by this $\Psi(x,t)$. List all possible values of the energy that could be measured on this system. (5 points)

$$E_2 = \frac{2^2}{2m}\left(\frac{\pi\hbar}{a}\right)^2$$

$$E_3 = \frac{3^2}{2m}\left(\frac{\pi\hbar}{a}\right)^2$$

There are only two values.

III.g) Can you measure the average energy in any single measurement? Explain please. (5 points). No, you can only measure either a 4 or a 9 (times the constants) but the average is indeed the average, which is in between at 6.5 which is not even an integer (or one squared for that matter).