Chem 452 – Exam I
September 15, 2010

Cover Sheet
Closed Book and Closed Notes

There are six problems. The point value of each part of each problem is indicated.

Useful Equations:

\[
\Psi_n(x) = \left( \frac{2}{L} \right)^{1/2} \sin \left( \frac{n\pi x}{L} \right), \quad E_n = \frac{n^2 \hbar^2}{8mL^2}
\]

\[
\Psi_{n_1,n_2}(x,y) = \left( \frac{2}{L_1} \right)^{1/2} \left( \frac{2}{L_2} \right)^{1/2} \sin \left( \frac{n_1\pi x}{L_1} \right) \sin \left( \frac{n_2\pi y}{L_2} \right)
\]

\[
E_{n_1,n_2} = \frac{\hbar^2}{8m} \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} \right)
\]

\[
\lambda = \frac{\hbar}{p}, \quad p = mv = \sqrt{2m(E-V)}
\]

\[
\hat{x} = x, \quad \hat{p}_x = -i\hbar \frac{\partial}{\partial x}, \quad \hat{I}_x = \frac{\hat{p}_x^2}{2m}
\]

\[
\int e^{ax}dx = \frac{1}{a}e^{ax} + C \quad \sin^2 x = \frac{1}{2}(1 - \cos(2x)) \quad \int \cos(ax)dx = \frac{1}{a}\sin(ax) + C
\]

Eigenvalue equation \( \hat{A} f(x) = a f(x) \)

Euler relations \( e^{iax} = \cos(ax) + i \sin(ax) \)
\( e^{-iax} = \cos(ax) - i \sin(ax) \)

Average value \( \langle a \rangle = \frac{\int_{-\infty}^{\infty} \psi^* \hat{A} \psi dx}{\int_{-\infty}^{\infty} \psi^* \psi dx} \)

Planck's distribution \( \rho = \frac{8\pi \hbar c}{\lambda^3 \left(e^{\hbar c/\lambda kT} - 1\right)} \)

Useful Constants:

\( h = 6.626 \times 10^{-34} \text{ Js} \)
\( \hbar = h/2\pi \)
\( c = 2.998 \times 10^8 \text{ m/s} \)
\( k = 1.381 \times 10^{-23} \text{ J/K} \)
\( m_e = 9.109 \times 10^{-31} \text{ kg} \)
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1. (22 points) The following questions are about the origins of quantum mechanics.

   a) (6 points) In Planck's expression for blackbody radiation, why did he have to insert the term \( \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} \) to avoid the 'ultraviolet catastrophe' that was predicted by the classical Rayleigh-Jeans expression for blackbody radiation?

   Planck recognized that light with wavelength \( \lambda \) was emitted in integer multiples of energy \( h \frac{c}{\lambda} \). Thus there must be a state with this energy to emit the light. The term \( \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} \) is related to the Boltzmann Factor which gives the probability that a state with that energy will occur, and thus be able to emit.

   b) (6 points) Davisson and Germer demonstrated that a beam of electrons moving at \( 4.5 \times 10^6 \) m/s diffract from a Ni surface because the surface acted as a diffraction grating with a groove density equal to the lattice constant of 0.91 Å. 91 pm.

   Argue from the wave-nature of matter why a beam of negatively charged BBs moving at the same velocity would not exhibit a measurable diffraction pattern if they encountered the same Ni surface. The masses of an electron and a BB are \( 9.11 \times 10^{-31} \) kg and \( 1.94 \times 10^{-4} \) kg, respectively. Justify your answer with appropriate calculations.

   \[ \lambda_B = \frac{h}{p} = \frac{6.626 \times 10^{-34} \text{ kg m}^2}{s}{9.11 \times 10^{-31} \text{ kg}} \times \frac{(4.5 \times 10^6 \text{ m/s})}{s} = 1.6 \times 10^{-10} \text{ m} \]

   \[ 160 \text{ pm} \]

   \( \lambda_B \) of e\(^-\) similar to lattice constant so clear diffraction

   \[ \lambda_B = \frac{h}{p} = \frac{6.626 \times 10^{-34} \text{ kg m}^2}{s}{1.94 \times 10^{-4} \text{ kg}} \times \frac{(4.5 \times 10^6 \text{ m/s})}{s} = 7.6 \times 10^{-37} \text{ m} \]

   So much smaller than lattice constant - diffraction negligible.
c) (6 points) Sodium metal has a work function of $3.68 \cdot 10^{-19}$ J. Make a plot of the kinetic energy of the photo-emitted electrons versus the frequency of the incident light. Label you axes.

\begin{itemize}
  \item \textbf{Label of the axes:}
  \item \textbf{Slope:} $h$
  \item \textbf{Intercept:} $3.68 \cdot 10^{-19}$ J
\end{itemize}

\begin{itemize}
  \item \textbf{Equation of the line:}
    \begin{equation}
      \text{K.E.} = h \nu - \Phi
    \end{equation}
  \item \textbf{Explanation:}
    \begin{equation}
      \Phi = \text{work Function}.
    \end{equation}
\end{itemize}

\vspace{1cm}

\textbf{d) (4 points) Write the equation describing the plot you drew in part (c).}

\begin{equation}
  \text{K.E.} = h \nu - \Phi
\end{equation}

\begin{equation}
  \Phi = \text{work Function}.
\end{equation}
2. (28 points) The following questions regard the postulates of quantum mechanics.

a) (5 points) The time-independent Schrödinger equation describing a particle moving in one dimension is, 
\[ \frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} - \frac{1}{(1+x^2)} \psi = E\psi. \]

Write the expression describing the confining potential of the particle.
\[ V(x) = \frac{1}{(1+x^2)} \]

b) (3 points) What property of the particle does the eigenvalue of the equation represent?

\[ E \text{ is the total energy} \]

c) (6 points) Indicate whether the following wavefunctions are acceptable or not. In each case, explain your reasoning. A, B, C and a are constants.

\[ \psi = Ae^{-|x-a|^2} \]

**yes, acceptable**

\[ \psi \text{ can be normalized} \]

\[ \psi \text{ is continuous} \]

\[ \psi' \text{ is continuous} \]

\[ \psi = \begin{cases} A\sqrt{x} (0 < x < a) \\ B(x-a) + C (a < x < l) \end{cases} \]

**no, unacceptable**

\[ \psi' \text{ is not continuous at} \]

\[ x = a. \]

\[ \psi = \begin{cases} A\sin(x) (0 < x < a) \\ B e^{-(x-a)^2} (a < x < l) \end{cases} \]

**yes, acceptable**

\[ \psi \text{ can be normalized and} \]

\[ \psi' \text{ is continuous} \]
d) (6 points) Explain why the Born interpretation of the wavefunction requires that the wavefunction be continuous.

The continuity restriction arises from two properties of real particles:
1) their probability distributions must vary smoothly over all space (particles do not 'jump').
2) their K.E. cannot be infinite which is what would happen at a discontinuity (2nd derivative \( \rightarrow \infty \)).

e) (8 points) Use the momentum operator to evaluate the momentum of a particle described by the wavefunction, \( \psi(x) = A(\cos(kx) + i \sin(kx)) \).

If and only if the wavefunction is not an eigenfunction of the momentum operator, then write the expression you would use to calculate the average value that would be obtained from many measurements of the momentum of the particle. Do not evaluate the expression.

\[
\hat{P}_x = -i \hbar \frac{d}{dx}
\]

\[
\hat{P}_x \psi = -i \hbar \frac{d}{dx} \left[ A(\cos(kx) + i \sin(kx)) \right]
\]

\[
= -i \hbar \left[ A(-k \sin(kx) + i k \cos(kx)) \right]
\]

\[
= k \hbar \left[ A(i \sin(kx) + \cos(kx)) \right] = \hbar k \psi
\]

(eigenvalue = momentum = \( \hbar k \))

Alternate: recognize \( \psi = Ae^{ikx} \)

\[
\hat{P}_x \psi = -i \hbar \frac{d}{dx} (Ae^{ikx}) = \hbar k (Ae^{ikx})
\]

\[\equiv\]
3. (18 points) The following questions pertain to a quantum mechanical free particle.

a) (6 points) Use the kinetic energy operator, \( \hat{T}_x = \frac{\hat{p}_x^2}{2m} \), to evaluate the kinetic energy of a free particle described by the wavefunction, \( \psi = A \exp(i 6.8x) \).

\[
\begin{align*}
\hat{T}_x & = \frac{\hat{p}_x^2}{2m} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \\
\hat{T}_x \psi & = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} (A e^{i 6.8x}) = -\frac{\hbar^2}{2m} (A (i 6.8)^2 e^{i 6.8x}) \\
& = (6.8)^2 \frac{\hbar^2}{2m} (A e^{i 6.8x}) \\
K.E. & = \frac{46.24 \hbar^2}{2m} \text{ also } \frac{(6.8)^2 \hbar^2}{2m} \text{ ok.}
\end{align*}
\]

b) (6 points) A quantum mechanical free particle moves to the left with momentum of \(2.11 \cdot 10^{-31}\) kg\cdot m/s. Calculate the momentum wave vector (which we labeled ‘k’ in class) for this state and write the corresponding wavefunction, \(\psi\).

\[
\begin{align*}
momentum = k \hbar & = 2.11 \cdot 10^{-31} \text{ kgm/s} \\
k & = \frac{2.11 \cdot 10^{-31} \text{ kgm/s}}{\frac{\hbar}{2\pi} (6.626 \cdot 10^{-34} \text{ kgm}^2/\text{s})} = 2000.8 \\
\psi & = A e^{-i 2000x}
\end{align*}
\]

(c) (6 points) Use concepts from the Heisenberg Uncertainty Principle to explain why the momentum state, \(k = 0\), is allowed for the quantum mechanical free particle.

\[
\begin{align*}
K = 0 & \text{ corresponds to a state with zero momentum.} \\
Thus, \Delta p \text{ must also be zero since zero momentum is a precise value.} \\
H.U.P. \text{ requires that } \Delta x \to \infty \text{ in this case because } \\
\Delta x \Delta p & \geq \frac{\hbar}{2}. \text{ Since the Free particle can be anywhere } \\
(\mid \psi \rangle^2 & = A^2 \text{ indep. of } x), \text{ the Free particle satisfies the H.U.P. at } k = 0.
\end{align*}
\]
4. (32 points) The following questions pertain to a quantum mechanical particle in a box.

a) (6 points) Show that the wavefunction for a 1-D particle in a box in quantum state, \( n = 3 \), is an eigenfunction of the Schrödinger equation for the particle in the region of the box,
\[
\frac{-\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = E \psi.
\]
What is the eigenvalue?

\[
-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \left( A \sin \left( \frac{3n\pi x}{L} \right) \right) - \frac{\hbar^2}{2m} \frac{d}{dx} \left( \frac{3n \pi}{L} A \cos \left( \frac{3n\pi x}{L} \right) \right) = -\frac{\hbar^2}{2m} \left( \frac{9n^2 \pi^2}{L^2} \right) \psi = \frac{9\hbar^2}{8mL^2} \psi
\]
eigenvalue is total \( E = \frac{9\hbar^2}{8mL^2} \)
also OK is \( \frac{9\hbar^2 n^2}{2mL^2} \)

b) (6 points) i. Sketch and label the values of all allowed energy levels up to the state \( n = 3 \) on the diagram below. ii. Then, sketch on the diagram the wavefunction for the state \( (n = 2) \). iii. Finally, sketch on the diagram the probability density for the state \( (n = 3) \).
c) (6 points) We derived an expression in class to calculate the probability to find a particle in a box within a range, $x = a$ to $b$, $P = \frac{1}{L} \left[ x - \frac{L}{2n\pi} \sin \left( \frac{2n\pi x}{L} \right) \right]_a^b$. Using this formula, calculate the probabilities of finding a particle in a box between $x = 0$ to $L/6$ for the following quantum states. $L$ is the length of the box. The classical probability is 0.167.

$n = 1$:

$$P = \frac{1}{L} \left[ 0 - \frac{L}{2\pi} \sin \left( \frac{2\pi x}{L} \right) \right]_0^{L/6} = \frac{1}{L} \left[ \frac{L}{6} - \frac{L}{2\pi} \sin \left( \frac{2\pi \cdot \frac{L}{6}}{L} \right) \right] - 0$$

$$= 0.0288$$

$n = 2$:

$$P = \frac{1}{L} \left[ \frac{L}{6} - \frac{L}{4\pi} \sin \left( \frac{4\pi x}{L} \right) \right]_0^{L/6} - 0 = 0.0978$$

$n = 3$:

$$P = \frac{1}{L} \left[ \frac{L}{6} - \frac{L}{6\pi} \sin \left( \frac{6\pi x}{L} \right) \right]_0^{L/6} - 0 = 0.167$$

d) (6 points) Discuss the trend in calculated probabilities in terms of the shapes of the probability densities of the corresponding wavefunctions.

$\Psi_{n=1}$ has most of its density around $\frac{L}{2}$ and so has little density at edges.

$\Psi_{n=3}$ has a node at $\frac{L}{3}$, so $x = \frac{L}{6}$. Falls at the peak of the first of 3 identical lobes. So by symmetry, the prob. is exactly $\frac{1}{6}$.

$\Psi_{n=2}$ is intermediate between these.
e) (8 points) Consider an electron as a quantum mechanical particle in a box of length, \( L = 0.566 \) nm. A photon of energy, \( E = 3.20 \times 10^{-18} \) J, excites the electron from the quantum state, \( n - 1 \), to the next highest quantum state, \( n \). Calculate the value of the final quantum number, \( n \).

transition between quantum states using Planck's quantum condition

\[
\Delta E = h \nu = E_n - E_{n-1} = (n^2 - (n-1)^2) \frac{h^2}{8mL^2} = (2n - 1) \frac{h^2}{8mL^2}
\]

solve for \( n \):

\[
(2n - 1) = \frac{\Delta E (8mL^2)}{h^2}
\]

\[
(2n - 1) = \left(\frac{3.20 \times 10^{-18} \frac{kg \cdot m^2}{s^2}}{5^2}\right) \left(8\right) \left(9.11 \times 10^{-31} \text{kg}\right) \left(0.566 \times 10^{-9} \text{m}\right)^2 \left(6.626 \times 10^{-34} \frac{kg \cdot m^2}{s}\right)^2
\]

\[
= 17.02 \text{ round to } 17
\]

\[
n = \frac{17 + 1}{2} = 9
\]