PHYSICAL CHEMISTRY 3520  
EXAM 1  
February 8, 2008

Please write neatly and clearly, and show all working. Allocate time to each question in proportion to the available credit. Keep explanations brief and to the point.

Your name: SOLUTIONS

SOME POSSIBLY USEFUL INFORMATION:

\[ N_A \text{ or } L = 6.022 \times 10^{23} \text{ mol}^{-1} \quad h = 6.626 \times 10^{-34} \text{ J s} \]
\[ k = 1.38 \times 10^{-23} \text{ J K}^{-1} \quad c = 2.998 \times 10^{8} \text{ m s}^{-1} \]
\[ \text{H atom mass} = 1.66 \times 10^{-27} \text{ kg} \quad \text{electron mass} = 9.11 \times 10^{-31} \text{ kg} \]
\[ R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \]

Planck: \( E = h \nu \)  Schrodinger: \( \hat{H}\psi = E\psi \)  de Broglic: \( \lambda = h/\rho \)

\( \hat{x} \) operator is multiply by \( x \)  \( \hat{p} \) operator is \( h/(2\pi i) d/dx \)
\( \hat{E}_K \) operator is \( -\hbar^2/(8\pi^2m) d^2/dx^2 \)  \( \hat{V} \) operator is multiply by \( V \)

\[ \sin^2 \theta = (1 - \cos \theta)/2 \quad \cos^2 \theta = (1 + \cos 2\theta)/2 \]
1) 40 points
A particle of mass \( m \) is confined by infinite potential barriers to the one-dimensional region of space \( x = -L \) to \( x = +L \), where the potential energy is zero. Its wavefunction is given by
\[
\psi(x) = A \cos \left( \frac{\pi x}{2L} \right)
\]
where \( A \) is a constant. The potential energy is zero for \( -L < x < L \).

a) Verify that this \( \psi \) satisfies the Schrodinger equation and find the total energy \( E \) of the particle.

b) Find what value of \( A \) normalizes the wavefunction.

\[
\begin{align*}
\hat{H} \psi &= \left( -\frac{\hbar^2}{8m^2} \frac{d^2}{dx^2} + V \right) \psi = \frac{-\hbar^2}{8m^2} \frac{d^2}{dx^2} A \cos \left( \frac{\pi x}{2L} \right) \\
&= \frac{-\hbar^2}{8m^2} \left( \frac{\pi^2}{4L^2} A \cos \left( \frac{\pi x}{2L} \right) \right) \\
&= E \psi \quad \text{where} \quad E = \frac{\hbar^2}{8mL^2}.
\end{align*}
\]

b) We want \( 1 = \int_{-L}^{+L} |\psi|^2 dx = \frac{A^2}{\pi} \int_{-L}^{+L} \cos^2 \left( \frac{\pi x}{2L} \right) dx \).

Substitute \( \theta = \frac{\pi x}{2L} \), so \( d\theta = \frac{\pi}{2L} dx \):
\[
\begin{align*}
1 &= \frac{A^2}{\pi} \int_{-L}^{L} \cos^2 \theta \, d\theta \\
&= \frac{A^2}{\pi} \int_{-\pi/2}^{\pi/2} \cos^2 \theta \, d\theta \\
&= \frac{A^2}{\pi} \left[ \frac{\theta}{2} + \frac{\sin 2\theta}{4} \right]_{-\pi/2}^{\pi/2} \\
&= \frac{A^2}{\pi} \left( \frac{\pi}{2} - \frac{\pi}{2} \right) = \frac{A^2 L^2 \pi}{\pi} \\
&= \frac{A^2 L^2 \pi}{\pi} . \quad \pi = A^2 L
\end{align*}
\]

\[ A = \frac{1}{\sqrt{L}} \]
2) 30 points
a) Do the position and linear momentum operators commute? What are the implications for the observables of position and linear momentum?

b) A particle is described by the wavefunction \( \psi = \cos ikx \). Is this wavefunction an eigenfunction of the momentum operator? What can be learned about the observed momentum for this wavefunction?

\[ \hat{p} \psi = \frac{\hbar}{2\pi i} \frac{d}{dx} (\cos ikx) = \frac{\hbar}{2\pi i} (-ik \sin ikx) \]

\[ \hat{x} \hat{p} \psi = x \cdot \frac{\hbar}{2\pi i} \frac{d}{dx} \]

There are different, so the operators do not commute.

The consequence is that \( p \) and \( x \) cannot be known simultaneously and exactly, an example of complementary observables.

\[ \hat{p} \psi = \frac{\hbar}{2\pi i} \frac{d}{dx} (\cos ikx) = \frac{\hbar}{2\pi i} \]

\[ = \frac{\hbar}{2\pi i} \]

i.e., no, not an eigenfunction.

You cannot obtain the exact value of \( p \), only an average or expectation value.
A photon of wavenumber $4 \times 10^4 \text{ cm}^{-1}$ knocks an electron out of a piece of metal whose work function is 300 kJ mol$^{-1}$. Calculate the speed of this electron.

**Energy Balance:**
\[ \text{photon energy} = \text{work function} + \text{e}^- \text{ energy} \]

**Photon Frequency**
\[ \nu = \frac{\lambda}{\lambda} = 2.998 \times 10^8 \text{ cm s}^{-1} = 1.199 \times 10^5 \text{ Hz} \]

**Photon Energy**
\[ E = h\nu = 1.199 \times 10^5 \text{ Hz} \times 6.626 \times 10^{-34} \text{ J s} \]
\[ = 7.946 \times 10^{-19} \text{ J} \]

**Work Function**
\[ = 300 \text{ kJ mol}^{-1} \] or \[ \frac{300 \times 10^3 \text{ J mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 4.982 \times 10^{-19} \text{ J} \]

**e^- Kinetic Energy** is the difference,
\[ (7.946 - 4.982) \times 10^{-19} \text{ J} \]
\[ = 2.964 \times 10^{-19} \text{ J} \]

\[ E_K = \frac{1}{2} mv^2 \]
\[ m = 9.11 \times 10^{-31} \text{ kg} \] for an e$^-$.

\[ v = \sqrt{\frac{2E_K}{m}} = \sqrt{\frac{2 \times 2.964 \times 10^{-19}}{9.11 \times 10^{-31}}} = 8.07 \times 10^5 \text{ m s}^{-1} \]