PHYSICAL CHEMISTRY 3520
EXAM 1
February 17, 2014

It is important to write neatly and clearly, and to 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:

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

Planck: \( E = h\nu \)

Schrödinger: \( \hat{H}\psi = E\psi \)

de Broglie: \( \lambda = h/p \)

Particle in 1-D box:
\[ \psi_n = (2/a)^{1/2} \sin(n\pi x/a), \quad E_n = h^2 n^2/(8ma^2) \]

Harmonic oscillator:
\[ E_n = (\nu + 1/2) h\nu; \quad \nu = (k/\mu)^{1/2}/(2\pi) \]

Rigid rotor \( |L^2| = l(l + 1)h^2/(4\pi^2) \)

\( L_\phi = m_l h/(2\pi) \)

\( E = L^2/(2l) \)

\( \hat{x} \text{ operator is multiply by } x \)

\( \hat{p} \text{ operator is } h/(2\pi) d/dx \)

\( \hat{E}_K \text{ operator is } -h^2/(8\pi^2 m) d^2/dx^2 \)

\( \hat{V} \text{ operator is multiply by } V \)

\( \sin^2 \theta = (1 - \cos 2\theta)/2 \quad \cos^2 \theta = (1 + \cos 2\theta)/2 \)
1) 20 points
A particle of mass $m$ moves in a one-dimensional system defined by the $x$ coordinate, and is confined to the range $x = 0 - L$. The wavefunction is given by

$$\psi(x) = A \left( xL - x^2 \right)$$

where $A$ is a constant. What value of $A$ normalizes the wavefunction? Show work.

We want

$$1 = \int_{-L}^{L} \psi^* \psi \, dx = A^2 \int_{-L}^{L} \left( xL - x^2 \right)^2 \, dx$$

$$= A^2 \int_{0}^{L} x^2 L^2 - 2x^3 L + x^4 \, dx$$

$$= A^2 \left[ \frac{x^3 L^2}{3} - \frac{x^4 L}{2} + \frac{x^5}{5} \right]_0^L$$

$$= A^2 \cdot L^5 \left( \frac{1}{3} - \frac{1}{2} + \frac{1}{5} \right)$$

$$= A^2 \cdot L^5 \cdot \frac{1}{30}$$

$$\therefore A^2 = \frac{30}{L^5} \quad A = \sqrt{\frac{30}{L^5}}$$
30 points

2) Consider the wavefunction for $0 \leq x \leq L$ where the potential energy is zero

$$\psi(x) = A \sin \left( \frac{n\pi x}{L} \right)$$

and $\psi(x) = 0$ elsewhere, where the potential energy is infinite.

a) Prove that $\psi$ is an eigenfunction of the Hamiltonian operator and deduce that the allowed values of the total energy are $E_n = \frac{n^2\hbar^2}{8mL^2}$. Show work.

b) Use this result to find the energy difference between the $n=4$ and $n=5$ levels for an electron confined in a one-dimensional box 0.8 nm wide, in J.

a) $\hat{H}\psi = (E \psi) \psi$ and have $V=0$

$$\hat{H}\psi = \frac{-\hbar^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2} A \sin \left( \frac{n\pi x}{L} \right)$$

$$= \frac{-\hbar^2}{8\pi^2 m} \frac{n^2\pi^2}{L^2} A \sin \left( \frac{n\pi x}{L} \right)$$

$$= \frac{\hbar^2}{8\pi^2 m L^2} \psi = E \psi \text{ with } E = \frac{n^2\hbar^2}{8mL^2}.$$

b) $m = 9.11 \times 10^{-31}$ kg, $L = 8 \times 10^{-10}$ m.

From $n=4$ to $n=5$, $\Delta E = \frac{\hbar^2}{8mL^2} (25-16) = \frac{9 \times (6.626 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31} \times (8 \times 10^{-10})^2} = 8.47 \times 10^{-19}$ J.
3) 20 points
Do the position and momentum operators commute? *Show work.* What is the physical consequence of this result?

Are $\hat{\mathbf{p}} \hat{x} \psi$ and $\hat{x} \hat{\mathbf{p}} \psi$ equal?

$\hat{x} \psi = x \psi$

$\hat{\mathbf{p}} (\hat{x} \psi) = \frac{\hbar}{2\pi i} \frac{d}{dx} (x \psi) = \frac{\hbar}{2\pi i} \left( x \frac{d\psi}{dx} + \psi \right)$.

$\hat{\mathbf{p}} \psi = \frac{\hbar}{2\pi i} \frac{d\psi}{dx}$

$\hat{x} (\hat{\mathbf{p}} \psi) = \frac{\hbar}{2\pi i} x \frac{d\psi}{dx}$.

These are not equal so the operators do not commute.

The observables are therefore complementary and there is an uncertainty relation between them.
4) 30 points
Consider a quantized harmonic oscillator with a force constant of 800 N m\(^{-1}\) and a reduced mass of 3 \times 10^{-27} \text{ kg}.

a) What is the lowest possible vibrational energy for this system, in J?

b) Sketch the shapes of the two lowest energy wavefunctions, and label them by their quantum numbers.

c) What is the wavenumber of the photon whose energy matches the difference between these two energy levels? Give your answer in cm\(^{-1}\).

\[
v = \frac{1}{2\pi} \sqrt{\frac{k}{m}} = \frac{1}{2\pi} \sqrt{\frac{800 \text{ N m}^{-1}}{3 \times 10^{-27} \text{ kg}}} = 8.22 \times 10^{17} \text{ Hz}
\]

a) Lowest energy is when \( v = 0 \) i.e. \( \frac{1}{2} hv 

= \frac{1}{2} \times 6.626 \times 10^{-34} \text{ Js} \times 8.22 \times 10^{17} \text{ Hz} = 2.72 \times 10^{20} \text{ J}

b)

\[
\begin{align*}
\text{v} &= 0 \\
\text{v} &= 1
\end{align*}
\]

c) \( \Delta E = \frac{3}{2} hv - \frac{1}{2} hv = hv 

To convert Hz to cm\(^{-1}\) directly, divide by \( c \) in cm s\(^{-1}\)

so \( \Delta E = \frac{8.22 \times 10^{17} \text{ Hz}}{2.998 \times 10^{10} \text{ cm s}^{-1}} = 2742 \text{ cm}^{-1} \).