PHYSICAL CHEMISTRY 3520
EXAM 1
February 6, 2013

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: \[ E = hv \quad \text{Schroedinger: } \hat{H}\psi = E\psi \quad \text{de Broglie: } \lambda = h/p \]

x operator is multiply by x \quad p operator is \quad h/(2\pi i) d/dx

E_k operator is \(-h^2/(8\pi^2 m) d^2/dx^2\) \quad V operator is multiply by V

\[ \sin^2 \theta = (1 - \cos 2\theta)/2 \quad \cos^2 \theta = (1 + \cos 2\theta)/2 \]
1) **30 points**

A particle of mass $m$ moves in a circle whose circumference is $L$. The potential energy is zero. In terms of distance $x$ around the ring, the wavefunction is given by

$$\psi(x) = A \cos \left( \frac{2n\pi x}{L} \right)$$

where $A$ is a constant and $n$ is the quantum number. $0 \leq x \leq L$.

What value of $A$ normalizes the wavefunction?

$$\Theta = \frac{2n\pi x}{L}$$
$$d\Theta = \frac{2n\pi}{L} \, dx$$

$$\psi(x) = A \cos \left( \frac{2n\pi x}{L} \right)$$

So,

$$\int_{0}^{L} \psi^* \psi \, dx = 1 = \int_{0}^{L} A^2 \cos^2 \left( \frac{2n\pi x}{L} \right) \, dx = A^2 \left[ \frac{L}{2n\pi} \cos 2\Theta \right]_0^{2n\pi}$$

$$= A^2 \frac{L}{2n\pi} \left[ \frac{1}{2} \left[ 1 + \cos 2\Theta \right] \right]_0^{2n\pi} = \frac{A^2 L}{4n\pi} \left[ \Theta + \frac{\sin 2\Theta}{2} \right]_0^{2n\pi}$$

$$= \frac{A^2 L}{4n\pi} \left( -1 + 1 \right) = \frac{A^2 L}{2} = 1 \implies A = \sqrt{\frac{2}{L}}$$

See problem 7.15
30 points

2) Consider the wavefunction for \(0 \leq x \leq L\)
\[\psi(x) = A \sin\left(\frac{n\pi x}{L}\right)\]

a) Prove that the allowed values of the total energy are \(E_n = \frac{n^2\hbar^2}{8mL^2}\).

b) Use this result to find the energy difference between the \(n=3\) and \(n=4\) levels for an electron confined in a box 1 nm wide, in J.

c) For the energy gap in part (b), what is the frequency and wavelength of a photon whose energy matches this gap?

\[E_k = -\frac{\hbar^2}{8\pi^2 m} \frac{d^2}{dx^2} \psi \]
\[E_k \psi = -\frac{\hbar^2}{8\pi^2 m} \frac{d}{dx} A \cos\left(\frac{n\pi x}{L}\right) \frac{n\pi x}{L} \]
\[= -\frac{\hbar^2}{8\pi^2 m} \left(\frac{n\pi}{L}\right)^2 A \sin\left(\frac{n\pi x}{L}\right) \]
\[\text{constant} \quad A \psi \]
\[= \frac{\hbar^2 n^2}{8mL^2}\]

b) \[E_{n=4} - E_{n=3} = \frac{\hbar^2}{8mL^2} \left(4^2 - 3^2\right) = \left(\frac{6.626 \times 10^{-34} \text{ J s}}{8.91 \times 10^{-31} \text{ kg}} \right) \left(1 \times 10^{-9}\right)\]
\[= 4.22 \times 10^{-19} \text{ J}\]

C) \(E = h\nu\) so \(\nu = \frac{E}{h} = \frac{4.22 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 6.36 \times 10^{14} \text{ s}^{-1}\)
\[\lambda = \frac{C}{\nu} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{6.36 \times 10^{14} \text{ s}^{-1}} = 4.71 \times 10^{-7} \text{ m} \quad \text{or} \quad 471 \text{ nm}\]
3) 20 points
a) Consider the wavefunction $\psi = A \exp(kx)$. Is this $\psi$ an eigenfunction of the operator $d/dx$? Show work. If yes, give the eigenvalue.

b) Do the position and momentum operators commute? Show work. What is the physical consequence of this result?

\[
\frac{d}{dx} \frac{Ae^{kx}}{\psi} = k \frac{Ae^{kx}}{\psi}
\]

Yes, and the eigenvalue is $k$

see problem 7.17

b) does $\hat{\rho} \hat{x} \psi = \hat{x} \hat{\rho} \psi$?

\[
\hat{\chi}(\hat{\rho} \psi) = \hat{x} \left( \frac{\hbar}{2\pi i} \frac{d\psi}{dx} \right) = \chi \frac{\hbar}{2\pi i} \frac{d\psi}{dx}
\]

\[
\hat{\rho}(\hat{x} \psi) = \frac{\hbar}{2\pi i} \frac{d(x\psi)}{dx} = \frac{\hbar}{2\pi i} \left( \chi \frac{d\psi}{dx} + \psi \right) \neq \chi \frac{\hbar}{2\pi i} \frac{d\psi}{dx}
\]

No, position and momentum operators do not commute.
This means that they are complementary observables, and therefore both cannot be known exactly.
4) 20 points
A metal with a work function of $5 \times 10^{-19}$ J is exposed to light at a wavelength of 300 nm. What is the kinetic energy of the emitted photo-electrons? What is their momentum?

$$E = h\nu = h \frac{c}{\lambda} = 6.626 \times 10^{-34} \text{Js} \times \frac{2.998 \times 10^8 \text{m/s}}{300 \times 10^{-9} \text{m}} = 6.62 \times 10^{-19} \text{J}$$

incident photon \quad \downarrow \quad \text{work}\ P_w \quad \downarrow \quad \text{emitted electron\ } E_k

$$6.62 \times 10^{-19} \text{J} - 5 \times 10^{-19} \text{J} = 1.62 \times 10^{-19} \text{J}$$

$$E_k = \frac{p^2}{2m} \implies p = \sqrt{2mE_k} = \sqrt{2 \times 9.11 \times 10^{-31} \text{kg} \times 1.62 \times 10^{-19} \text{J}}$$

$$= 5.44 \times 10^{-25} \text{kg m/s}$$

See exercise 7.8