Name:______________________________

CHEM3141 PHYSICAL CHEMISTRY: EXAM I

September 26, 2005 Time: 110 Minutes 100 points total
Answer all questions in detail and SHOW ALL WORK! Please write answers on your paper.

Planck's constant $h = 6.626\times10^{-34}$ Js speed of light $c = 2.998\times10^{8}$ ms^{-1} $R_H = 109677.581$ cm^{-1}
$k_B = 1.380658\times10^{-23}$ J K^{-1} electron's mass $m_e = 9.109\times10^{-31}$ Kg 1 cm^{-1} = 1.986×10^{-23} J
1 eV = $1.602\text{x}10^{-19}$ J 350 cm^{-1} = 1 Kcal mol^{-1}, 1 Hartree (E_h) = 219470 cm^{-1}

Particle-in-box energy states and energy levels: $\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$ $E_n = \frac{n^2h^2}{8mL^2}$

$$\frac{d\cos x}{dx} = -\sin x \qquad \frac{d\sin x}{dx} = \cos x \qquad \int_0^a \sin\frac{n\pi x}{a}\sin\frac{m\pi x}{a}\,dx = \frac{a}{2}\delta_{nm} \qquad \int_0^a \cos\frac{n\pi x}{a}\sin\frac{m\pi x}{a}\,dx = 0$$

$$\int_0^a x\sin^2\frac{n\pi x}{a}dx = \frac{a^2}{4} \qquad \hat{P}_x = -i\hbar\frac{\partial}{\partial x} \qquad e^{\pm i\theta} = \cos\theta \pm i\sin\theta$$

Multiple Choice: Choose the best possible answer and write this on *your* answer sheet.

1. (3 Pts) The molecular process most similar to the photoelectric effect is:
a. photoreduction – reduction following the absorption of a photon.
b. photoionization – loss of an electron following absorption of a photon.
c. photoemission - loss of a photon (fluorescence) following absorption of a photon
d. photopolymerization – polymerization following absorption of a photon

2. (3 pts) *Young's Double Slit Experiment* involves the generation of an interference pattern by electrons passing through two slits. This is a good example of:
a. A blackbody radiator.
b. A particle in a box.
c. Phenomena classically considered as waves demonstrating particle-like properties.
d. Phenomena classically considered as particles demonstrating wave-like properties.
e. Ultraviolet Catastrophe

3. (3 pts) Which of the following is **NOT** a characteristic of a well-behaved wavefunction.
a. multivalued.
b. normalizable
c. continuous
d. no singularities:

4. (3 pts) Which of the following is **NOT necessarily true** for two *degenerate* eigenfunctions Ψ_m and Ψ_n of **H**.
a. $c_1\Psi_m + c_2\Psi_n$ is also an eigenfunction of **H**.
b. Ψ_m and Ψ_n are mutually orthogonal.
c. Both Ψ_m and Ψ_n are normalized.
d. Ψ_m and Ψ_n are have the same energy eigenvalue.

5. (7 pts) Answer the following questions for a particle in a three dimensional box.
a. (5 pts) If $\Psi(x,y,z)$ is the wavefunction for the particle in the 3D box, describe the useful meaning of $\Psi^*(x,y,z)\,\Psi(x,y,z)\,dx\,dy\,dz$.
b. (2 pts) What is the value of the potential V(x,y,z) within the box.?

- End of qualitative section- **↓Beginning of quantitative section↓**

Answer all questions in detail and SHOW ALL WORK to receive full credit!

6. (17 pts) If the Balmer series for H atom transitions are given in wavenumbers by:

$$\tilde{\nu}_n = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad n = 3, 4, 5, 6\ldots$$

a. (6 pts) Determine the longest wavelength for this series in nm units.
b. (6 pts) Determine the ionizing wavelength for this series in nm units.
c. (5 pts) Transform the above equation into the equivalent expression in frequency, i.e. express ν on the left hand side in terms of R_H, n and possibly other variables on the right hand side.

7. (14 pts) a. (8 pts) Determine the value of the commutator $[\mathbf{p_x}, \mathbf{x^2}]$ by using a general function $\psi(x)$.
b. (6 pts) Are the 1-D particle-in-a-box wavefunctions eigenfunctions (listed at the top of the exam) of the $[\mathbf{p_x}, \mathbf{x^2}]$ operator? If so state the eigenvalue? **Justify your answer**!

8. (30 pts) The 1-D Particle-in-a-box Schrodinger equation is given as: $-\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}\psi(x) = E\psi(x)$

a. (8 pts) Show by explicit substitution of $\psi_n(x) = \sqrt{\dfrac{2}{L}}\sin\left(\dfrac{n\pi x}{L}\right)$ and $E_n = \dfrac{n^2h^2}{8mL^2}$ that ψ_n is a solution to this 1-D PIB Schrodinger equation. DO NOT SOLVE A DIFFERENTIAL EQUATION, rather insert and show that the LHS equals the RHS!
b. (8 pts) Explicitly show via **explicit integral substitution** that these $\psi_n(x)$ PIB functions are normalized.
c. (10 pts) Show that the expectation value of $\mathbf{p_x^2}$ using these $\psi_n(x)$ PIB basis functions is equal to $\left(\dfrac{n\pi\hbar}{L}\right)^2$
d. (4 pts) Explain why we obtain the trivial solution for ψ_n for the case of n = 0.

9. (12 pts) If $\mathbf{H}\psi_1 = E\psi_1$, $\mathbf{H}\psi_2 = E\psi_2$, and $\mathbf{H}\psi_3 = 3E\psi_3$,
Show whether each function below is an eigenfunction of **H** and if so state the eigenvalue.
Note c_1, c_2, c_3, are constants.

a. $c_1\psi_1 - c_2\psi_2$ b. $c_2\psi_2 + c_3\psi_3$ c. $3c_1\psi_1 + c_3\psi_3$

10. (8 pts) A metal absorbs two 460 nm photons and ejects an electron with 0.805 eV. What is the work function of the metal in eV units?

--- ANSWER KEY ---

1. (3 Pts) The molecular process most similar to the photoelectric effect is:
b. photoionization – loss of an electron following absorption of a photon.

2. (3 pts) *Young's Double Slit Experiment* involves the generation of an interference pattern by electrons passing through two slits. This is a good example of:
d. Phenomena classically considered as particles demonstrating wave-like properties.

3. (3 pts) Which of the following is **NOT** a characteristic of a well-behaved wavefunction.
a. multivalued.

4. (3 pts) Which of the following is **NOT necessarily true** for two *degenerate* eigenfunctions Ψ_m and Ψ_n of **H**.
c. Both Ψ_m and Ψ_n are normalized.

5. (7 pts) Answer the following questions for a particle in a three dimensional box.
a. (5 pts) If $\Psi(x,y,z)$ is the wavefunction for the particle in the 3D box, describe the useful meaning of $\Psi^*(x,y,z)\,\Psi(x,y,z)\,dx\,dy\,dz$.
This represents the probability of finding the particle between x and x+dx, y and y+dy, and z and z+dz.
b. (2 pts) What is the value of the potential V(x,y,z) within the box.?
Zero!

6. (17 pts) If the Balmer series for H atom transitions are given in wavenumbers by:

$$\tilde{\nu}_n = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad n = 3, 4, 5, 6\ldots$$

a. (6 pts) Determine the longest wavelength for this series in nm units.
First let's convert this into a wavelength equation and compute the transition to the next energy level (n=3) for the longest wavelength.

$$\lambda = \tilde{\nu}_n^{-1} = \left[R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)\right]^{-1}\left(\frac{1\,m}{100\,cm}\right)\left(\frac{10^9\,nm}{1\,m}\right)$$

$$\lambda = \left[109677.581\,cm^{-1}\left(\frac{1}{2^2} - \frac{1}{3^2}\right)\right]^{-1}\left(\frac{1\,m}{100\,cm}\right)\left(\frac{10^9\,nm}{1\,m}\right) = 656\,nm$$

b. (6 pts) Determine the ionizing wavelength for this series in nm units.
Now let n = ∞

$$\lambda = \left[109677.581\,cm^{-1}\left(\frac{1}{2^2} - \frac{1}{\infty^2}\right)\right]^{-1}\left(\frac{1\,m}{100\,cm}\right)\left(\frac{10^9\,nm}{1\,m}\right) = 365\,nm$$

c. (5 pts) Transform the above equation into the equivalent expression in frequency, i.e. express ν on the left hand side in terms of R_H, n and possibly other variables on the right hand side.

$$\tilde{\nu}_n = R_H\left(\frac{1}{2^2}-\frac{1}{n^2}\right) \qquad c = \lambda\nu \qquad c\frac{1}{\lambda}=\nu \qquad c\tilde{\nu}_n=\nu_n$$

$$\nu_n = c\,R_H\left(\frac{1}{2^2}-\frac{1}{n^2}\right)$$

7. (14 pts)

a. (8 pts) Determine the value of the commutator $[\mathbf{p_x}, \mathbf{x^2}]$ by using a general function $\psi(x)$.

$$\left[p_x, x^2\right]\Psi(x) = p_x x^2\Psi(x) - x^2 p_x\Psi(x) = -i\hbar\frac{\partial}{\partial x}\left(x^2\Psi\right) - x^2\left(-i\hbar\frac{\partial\Psi}{\partial x}\right)$$

$$-i\hbar\left\{\left(2x\Psi + x^2\frac{\partial\Psi}{\partial x}\right) - \left(x^2\frac{\partial\Psi}{\partial x}\right)\right\} = -i\hbar 2x\Psi$$

b. (6 pts) Are the 1-D particle-in-a-box wavefunctions eigenfunctions (listed at the top of the exam) of the $[\mathbf{p_x}, \mathbf{x^2}]$ operator? If so state the eigenvalue? **Justify your answer**!

Based on the answer to part a we may use.

$$\left[p_x, x^2\right]\Psi(x)_{PIB} = -i\hbar 2x\Psi(x)_{PIB}$$

This is not an eigenvalue since the factor preceding $\Psi(x)_{PIB}$ is not a constant, but a function of x: $-i\hbar 2x$

8. (30 pts) The 1-D Particle-in-a-box Schrodinger equation is given as: $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$

a. (8 pts) Show by explicit substitution of $\psi_n(x)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$ and $E_n = \frac{n^2h^2}{8mL^2}$ that ψ_n is a solution to this 1-D PIB Schrodinger equation. DO NOT SOLVE A DIFFERENTIAL EQUATION, rather insert and show that the LHS equals the RHS!

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$$

$$LHS = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left\{\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\right\} = -\frac{\hbar^2}{2m}\sqrt{\frac{2}{L}}\frac{d}{dx}\left\{\frac{d}{dx}\sin\left(\frac{n\pi x}{L}\right)\right\} = -\frac{\hbar^2}{2m}\sqrt{\frac{2}{L}}\frac{d}{dx}\left\{\frac{n\pi}{L}\cos\left(\frac{n\pi x}{L}\right)\right\}$$

$$= -\frac{\hbar^2}{2m}\frac{n\pi}{L}\sqrt{\frac{2}{L}}\frac{d}{dx}\left\{\cos\left(\frac{n\pi x}{L}\right)\right\} = -\frac{\hbar^2}{2m}\frac{n\pi}{L}\sqrt{\frac{2}{L}}\left\{-\frac{n\pi}{L}\sin\left(\frac{n\pi x}{L}\right)\right\} = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{L^2}\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

$$= \frac{h^2}{4\pi^2 2m}\frac{n^2\pi^2}{L^2}\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) = \frac{n^2h^2}{8mL^2}\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) = \frac{n^2h^2}{8mL^2}\psi(x) = E\psi(x) = RHS$$

$$\therefore LHS = RHS$$

b. (8 pts) Explicitly show via **explicit integral substitution** that these $\psi_n(x)$ PIB functions are normalized.

$$\int_{x=0}^{x=L} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx = \frac{2}{L} \int_{x=0}^{x=L} \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{2}{L}\left(\frac{L}{2} \delta_{nn}\right) = \frac{2}{L}\left(\frac{L}{2} \times 1\right) = 1$$

c. (10 pts) Show that the expectation value of p_x^2 using these $\psi_n(x)$ PIB basis functions is equal to $\left(\frac{n\pi\hbar}{L}\right)^2$

$$\int_{x=0}^{x=L} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)\left(-i\hbar \frac{\partial}{\partial x}\right)^2 \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx = -\frac{2\hbar^2}{L} \int_{x=0}^{x=L} \sin\left(\frac{n\pi x}{L}\right) \frac{\partial}{\partial x}\left\{\frac{\partial}{\partial x} \sin\left(\frac{n\pi x}{L}\right)\right\} dx$$

$$= -\frac{2\hbar^2}{L} \frac{n\pi}{L} \int_{x=0}^{x=L} \sin\left(\frac{n\pi x}{L}\right) \frac{\partial}{\partial x} \cos\left(\frac{n\pi x}{L}\right) dx = \frac{2\hbar^2}{L} \frac{n^2\pi^2}{L^2} \int_{x=0}^{x=L} \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{2\hbar^2}{L} \frac{n^2\pi^2}{L^2}\left(\frac{L}{2}\right) = \left(\frac{n\pi\hbar}{L}\right)^2$$

(4 pts) Explain why we obtain the trivial solution for ψ_n for the case of n = 0.

For n=0 we see that the wavefunction ψ_n is $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{0\pi x}{L}\right) = \sqrt{\frac{2}{L}} \times 0 = 0$ is zero everywhere irrespective of the value of x, i.e. the function (system or particle) does not exist.

9. (12 pts) If $\mathbf{H}\psi_1 = E\psi_1$, $\mathbf{H}\psi_2 = E\psi_2$, and $\mathbf{H}\psi_3 = 3E\psi_3$,
Show whether each function below is an eigenfunction of **H** and if so state the eigenvalue. Note c_1, c_2, c_3, are constants.

a. $c_1\psi_1 - c_2\psi_2$ b. $c_2\psi_2 + c_3\psi_3$ c. $3c_1\psi_1 + c_3\psi_3$ d. $3c_3\psi_3$

a. $\mathbf{H}\{c_1\psi_1 - c_2\psi_2\} = c_1\mathbf{H}\psi_1 - c_2\mathbf{H}\psi_2 = c_1 E\psi_1 - c_2 E\psi_2 = E\{c_1\psi_1 - c_2\psi_2\}$, This **is** an eigenfunction with eigenvalue = E.

b. $\mathbf{H}\{c_2\psi_2 + c_3\psi_3\} = c_2\mathbf{H}\psi_2 + c_3\mathbf{H}\psi_3 = c_2 E\psi_2 + c_3 3E\psi_3 = E\{c_2\psi_2 + c_3 3\psi_3\}$ This **is not** an eigenfunction since $c_2\psi_2 + c_3 3\psi_3 \neq c_2\psi_2 + c_3\psi_3$

c. $\mathbf{H}\{3c_1\psi_1 + c_3\psi_3\} = 3c_1\mathbf{H}\psi_1 + c_3\mathbf{H}\psi_3 = 3c_1 E\psi_1 + c_3 3E\psi_3 = 3E\{c_1\psi_1 + c_3\psi_3\}$, This **is not** an eigenfunction since $c_1\psi_1 + c_3\psi_3 \neq 3c_1\psi_1 + c_3\psi_3$

10.(8 pts)

$$E_{el} = E_{ph} - \phi \quad \rightarrow \quad \phi = E_{ph} - E_{el} \quad \rightarrow \quad \phi = nh\nu - E_{el} \quad \rightarrow \quad c = \lambda\nu \quad \rightarrow \quad \nu = \frac{c}{\lambda}$$

$$\phi = \frac{nhc}{\lambda} - E_{el} = \frac{2hc}{\lambda} - E_{el} = \frac{2 \times 6.626 \times 10^{-34}\,J\,s \times 2.998 \times 10^{8}\,m\,s^{-1}}{460\,nm}\left(\frac{10^9\,nm}{1\,m}\right)\frac{1\,eV}{1.602 \times 10^{-19}\,J} - 0.805\,eV$$

$$\phi = 5.391\,eV - 0.805\,eV = 4.59\,eV$$