Chem 361
Quantum Chemistry
Midterm Exam
November 15, 2006

Name ___________

Full credit will be given to correct answers only when ALL the necessary steps are shown. DO NOT GUESS THE ANSWER.

This is a closed book and closed notes exam, and you are responsible to be sure that your exam has no missing pages (6 pages).

If you consider that there is not enough information to solve a problem, you have to specify the missing information and describe the problem solving procedure.

No one can make you feel inferior without your consent
- Eleanor Roosevelt -

Honor Statement

I have neither give nor received aid in this examination.

Full signature ________________________________

Problem 1 (25 Points)

P19.24) Selection rules in the dipole approximation are determined by the integral $\mu_x^{mn} = \int \psi_m^*(\tau)\,\mu_x(\tau)\,\psi_n(\tau)\,d\tau$. If this integral is nonzero, the transition will be observed in an absorption spectrum. If the integral is zero, the transition is "forbidden" in the dipole approximation. It actually occurs with low probability because the dipole approximation is not exact. Consider the particle in the one-dimensional box and set $\mu_x = -ex$.

a) Calculate μ_x^{12} and μ_x^{13} in the dipole approximation. Can you see a pattern and discern a selection rule? You may need to evaluate a few more integrals of the type μ_x^{1m}. The standard integral

$$\int x \sin\frac{\pi x}{a}\sin\frac{n\pi x}{a}dx = \frac{1}{2}\left(\frac{a^2\cos\frac{(n-1)\pi x}{a}}{(n-1)^2\pi^2} + \frac{(n-1)ax\sin\frac{(n-1)\pi x}{a}}{(n-1)\pi}\right) - \frac{1}{2}\left(\frac{a^2\cos\frac{(n+1)\pi x}{a}}{(n+1)^2\pi^2} + \frac{ax\sin\frac{(n+1)\pi x}{a}}{(n+1)\pi}\right)$$

is useful for solving this problem.

b) Determine the ratio μ_x^{12}/μ_x^{14}. On the basis of your result, would you modify the selection rule that you determined in part (a)?

a) $\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)$

$$\mu^{1n} = -e\frac{2}{a}\int_0^a \sin\left(\frac{\pi}{a}x\right) x \sin\left(\frac{n\pi}{a}x\right)dx = -\frac{e2}{a}\left\{\frac{a^2\cos[(n-1)\pi]}{2(n-1)^2\pi^2} - \frac{a^2\cos[(n+1)\pi]}{2(n+1)^2\pi^2} - \frac{a^2}{2(n-1)^2\pi^2} + \frac{a^2}{2(n+1)^2\pi^2}\right\}$$

$$\boxed{\mu^{12} = -\frac{e2}{a}\left\{-\frac{a^2}{2\pi^2} + \frac{a^2}{2\,9\pi^2} - \frac{a^2}{2\pi^2} + \frac{a^2}{2\,9\pi^2}\right\}}$$

$$= -\frac{2e}{a}\left\{\frac{a^2}{9\pi^2} - \frac{a^2}{\pi^2}\right\} = \frac{16}{9\pi^2}ae$$

$$\mu^{14} = \frac{ae}{\pi^2}2\left\{\frac{1}{3^2} - \frac{1}{5^2}\right\} = \frac{32}{9\cdot 25}\frac{ae}{\pi^2}$$

$$\frac{\mu^{12}}{\mu^{14}} = \frac{16}{9}\,\frac{9.25}{32} = \frac{25}{2} = 12.5$$

Transition dominated by $1 \to 2$

Problem 2 (25 Points)

P20.7) In this problem, you will calculate the probability density of finding the electron within a sphere of radius r for the H atom in its ground state.

a) Show using integration by parts, $\int u\,dv = uv - \int v\,du$, that

$$\int r^2 e^{-\frac{r}{a}}dr = e^{-\frac{r}{a}}\left(-2a^3 - 2a^2 r - ar^2\right)$$

c) Evaluate this probability density for $r = 0.10\,a_0$, $r = 1.0$

a) $I \equiv \int r^2 e^{-\frac{r}{\alpha}}dr = -\alpha r^2 e^{-\frac{r}{\alpha}} + 2\alpha \int r e^{-r/\alpha}dr$

$u = r^2 \quad du = 2r\,dr$ || $u = r \quad du = dr$

$dv = e^{-r/\alpha}dr \quad v = -\alpha e^{-r/\alpha}$ || $dv = e^{-r/\alpha} \quad v = -\alpha e^{-r/\alpha}$

$I = -\alpha r^2 e^{-\frac{r}{\alpha}} - 2\alpha^2 r e^{-r/\alpha} + 2\alpha^2 \int e^{-r/\alpha}dr$

$= -\alpha r^2 e^{-\frac{r}{\alpha}} - 2\alpha^2 r e^{-\frac{r}{\alpha}} - 2\alpha^3 \int e^{-\frac{r}{\alpha}}\left(-\frac{dr}{\alpha}\right)$

$$\boxed{I = -e^{-\frac{r}{\alpha}}\left(\alpha r^2 + 2\alpha^2 r + 2\alpha^3\right)}$$

c) $P(r,\theta,\varphi)dV = |\psi_{100}|^2 \sin\theta\, d\theta\, d\varphi\, r^2 dr$

FOR A SPHERE OF RADIUS r AND THICKNESS dr

$p(r)dr = 4\pi |\psi_{100}|^2 r^2 dr = 4\pi \frac{1}{\pi a_0^3} r^2 e^{-\frac{2r}{a_0}}dr$

$\text{Prob}\{R \le R\} = \int_0^R \frac{4}{a_0^3} r^2 e^{-\frac{2r}{a_0}}dr = \frac{1}{2}\int_0^R \left(\frac{2r}{a_0}\right)^2 e^{-\frac{2r}{a_0}}\left(\frac{2dr}{a_0}\right)$

$= \frac{1}{2}\int_0^{\frac{2R}{a_0}} u^2 e^{-u}du = \frac{1}{2}(-1)e^{-u}\left(u^2 + 2u + 2\right)\Big|_0^{\frac{2R}{a_0}} = 1 - \frac{e^{-\frac{2R}{a_0}}}{2}\left(2 + \frac{4R}{a_0} + \frac{4R^2}{a_0^2}\right)$

Let $R = x a_0$

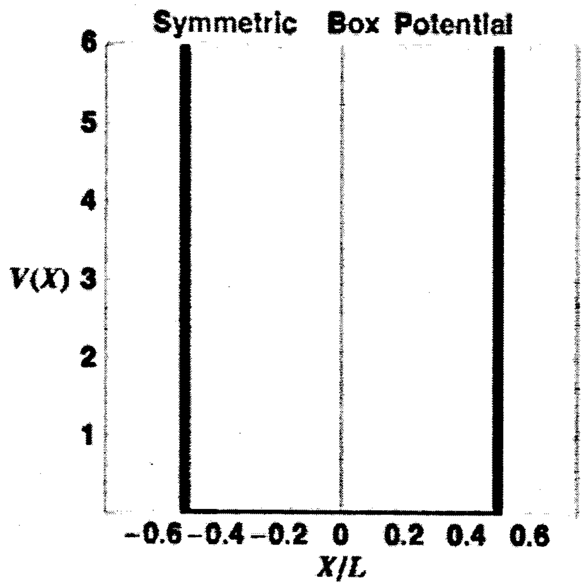
$$\boxed{\text{Prob}\{r \le x a_0\} = 1 - e^{-2x}\left[1 + 2x + 2x^2\right]}$$

a) $R = x = 0.10$

$\text{Prob} = 1 - e^{-0.2}(1.22) = \boxed{0.0011}$

b) $x = 1.0 \quad \text{Prob} = 1 - e^{-2}\,5 = \boxed{0.32}$

Problem 3 (25 Points)
Solve the Schrödinger equation for a particle in a symmetric box.



Notice that the boundary conditions are at x=-L/2 and x=L/2.
a) Find a general expression for the normalized eigenfunctions.
b) Find the energy levels.

Solution OF THE SE. $\Psi(x) = A\sin(kx) + B\cos(kx)$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi = E\Psi \Rightarrow k = \sqrt{\frac{2mE}{\hbar^2}} = \sqrt{\frac{8m\pi^2L^2}{h^2L^2}E} = \frac{\pi}{L}\sqrt{\frac{E}{apb}}$$

B.C. $\Psi(-L/2) = \Psi(L/2) = 0$

$$\left.\begin{array}{l} A\sin\left(\frac{kL}{2}\right) + B\cos\left(\frac{kL}{2}\right) = 0 \\ -A\sin\left(\frac{kL}{2}\right) + B\cos\left(\frac{kL}{2}\right) = 0 \end{array}\right\} \Rightarrow \begin{array}{l} 2B\cos\left(\frac{kL}{2}\right) = 0 \\ 2A\sin\left(\frac{kL}{2}\right) = 0 \end{array}$$

i) $A \neq 0$ $B = 0$ $\sin\left(\frac{kL}{2}\right) = 0 \Rightarrow \frac{kL}{2} = n\pi$ $n = 1, 2, \ldots$

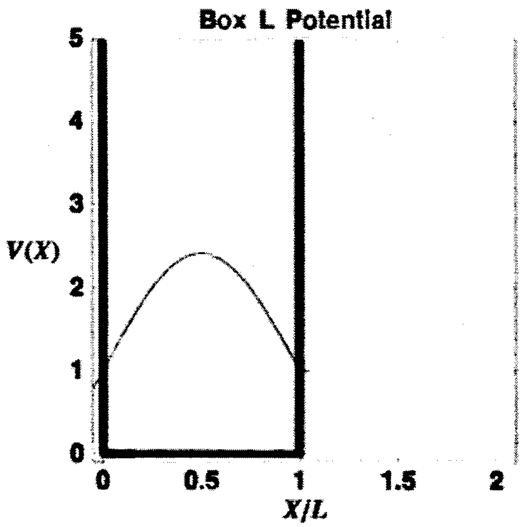
OR ii) $A = 0$ $B \neq 0$ $\cos\left(\frac{kL}{2}\right) = 0 \Rightarrow \frac{kL}{2} = (2n+1)\frac{\pi}{2}$ $n = 0, 1, 2, \ldots$

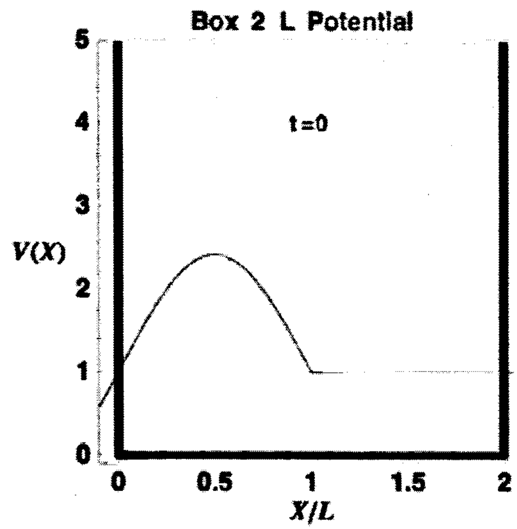
ODD SOL. $k^2 = \frac{4\pi^2}{L^2}n^2 = \frac{\pi^2}{L^2}\frac{E}{apb} \Rightarrow E_n = apb\,4n^2$ $n = 1, 2.$
$\{4, 16, 36, 64, \ldots\}$

EVEN SOL $k^2 = \frac{4}{L^2}(2n+1)^2\frac{\pi^2}{4} = \frac{\pi^2}{L^2}\frac{E}{apb} \Rightarrow E_n = apb(2n+1)^2$ $n = 0, 1, \ldots$
$\{1, 9, 25, 49 \ldots\}$

ODD $\Psi_n^O(x) = \sqrt{\frac{2}{L}}\cos\left(\frac{(2n+1)\pi}{L}x\right)$ EVEN $\Psi_n^E(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{2n\pi}{L}x\right)$

Problem 4 (25 Points)
Nonadiabatic transition and superposition principle
Sudden changes in the potential may be so fast that the system is not able to adjust instantaneously, as in the case illustrated below, where a box of size L is change to size 2L. Before the change, the system is in its ground state, but after the change the intitial function is not an eigenfunction of the bigger box. In particular notice that the function is zero for L <x 2L.





After the change, if we measure the energy the system would collapse into one of the new eigenstates. What is the probability of finding the state in the ground state, and first excited state of the new potential?

FOR THE NEW BOX AT $t=0$ $\Psi(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi}{L}x\right)$ $0<x<L$

ZERO OTHERWISE

SUPERPOSITION PRINCIPLE

$$\Psi(x) = \sum_{m=1}^{\infty} C_m \sqrt{\frac{2}{2L}} \sin\left(\frac{m\pi}{2L}x\right) = \sum_{m=1}^{\infty} C_m \phi_m(x)$$

$$C_m = \langle \phi_m | \Psi \rangle = \int_0^L \sqrt{\frac{1}{L}}\sin\left(\frac{m\pi x}{2L}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)dx$$

$$C_1 = \frac{\sqrt{2}}{L}\int_0^L \sin\left(\frac{\pi x}{2L}\right)\sin\left(\frac{\pi x}{L}\right)dx = \frac{\sqrt{2}}{L} \qquad = \frac{\sqrt{2}}{\cancel{L}}\left(\frac{4\cancel{L}}{3\pi}\right) = \frac{4\sqrt{2}}{3\pi}$$

$$C_2 = \frac{\sqrt{2}}{L}\int_0^L \sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right)dx = \frac{\sqrt{2}}{L}\frac{L}{2} = \sqrt{2}$$

$$P_1 = |C_1|^2 = \frac{32}{9}\frac{1}{\pi^2} = 0.36$$

$$P_2 = |C_2|^2 = \frac{1}{2}$$