Quantum Chemistry
Midterm I Exam
October 14 2008

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)**

Calculate the speed that a gas-phase nitrogen molecule would have if it had the same energy as an infrared photon ($\lambda = 1.00 \times 10^4$ nm), a visible photon ($\lambda = 500$ nm), an ultraviolet photon ($\lambda = 100$ nm), and an X-ray photon ($\lambda = 0.100$ nm). What temperature would the gas have if it had the same energy as each of these photons? Use the root mean square speed, $V_{rms} = \langle V^2 \rangle^{1/2} = \sqrt{3k_B T / m}$, for this calculation.

$$v = \sqrt{\frac{2E}{m}} = \sqrt{\frac{2hc}{m\lambda}} = \sqrt{\frac{2\times 6.626\times10^{-34}\,\mathrm{J\,s}\times 2.998\times10^{8}\,\mathrm{m\,s^{-1}}}{28.02\ \mathrm{amu}\times1.661\times10^{-27}\ \mathrm{kg}\ (\mathrm{amu})^{-1}\times1.00\times10^{4}\times10^{-9}\ \mathrm{m}}}$$

$= 924\ \mathrm{m\ s^{-1}}$

for $\lambda = 1.00 \times 10^4$ nm.

The results for 500. nm, 100. nm and 0.100 nm are $4.13\times10^3\ \mathrm{m\,s^{-1}}$, $9.24\times10^3\ \mathrm{m\,s^{-1}}$, and $2.92\times10^5\ \mathrm{m\,s^{-1}}$.

We calculate the temperature using the formula

$$T = \frac{M v_{rms}^2}{3R} = \frac{28.02\times10^{-3}\,\mathrm{kg\ mol^{-1}}\times\left(924\mathrm{m\,s^{-1}}\right)^2}{3\times8.314\ \mathrm{J mol^{-1}\,K^{-1}}} = 959\ \mathrm{K}$$

For $\lambda = 1.00 \times 10^4$ nm. The results for 500. nm, 100. nm and 0.100 nm are 1.92×10^4 K, 9.59×10^4 K, and 9.59×10^7 K.

Problem 2 **(30 points)**

Find the result of operating with $\frac{d^2}{dx^2} - 4\,x^2$ on the function $Exp[-\alpha\, x^2]$. What must the value of α be to make this function an eigenfunction of the operator?

$$\frac{d^2 e^{-ax^2}}{dx^2} - 4x^2 e^{-ax^2} = -2ae^{-ax^2} - 4x^2 e^{-ax^2} + 4a^2 x^2 e^{-ax^2} = -2ae^{-ax^2} + 4\left(a^2 - 1\right) x^2 e^{-ax^2}$$

For the function to be an eigenfunction of the operator, the terms containing $x^2 e^{-ax^2}$ must vanish. This is the case if $a = \pm 1$.

Problem 3 **(25 points)**

The smallest observed frequency for a transition between states of an electron in a one-dimensional box is $3.5\times10^{14}\ s^{-1}$. What is the length of the box?

Because the energy spacing between adjacent levels increases with the quantum number, the lowest energy transition is between $n = 1$ and $n = 2$.

$$E = h\nu = \frac{h^2}{8ma^2}\left(n_2^2 - n_1^2\right) \quad a = \sqrt{\frac{h}{8m\nu}\left(n_2^2 - n_1^2\right)}$$

$$a = \sqrt{\frac{6.26\times10^{-34}\ \text{J s}}{8\times9.109\times10^{-31}\ \text{kg}\times3.5\times10^{14}\ \text{s}^{-1}}\left(2^2 - 1^2\right)} = 8.8\times10^{-10}\ \text{m}$$

Problem 4 **(10 points)**

Calculate the root mean square speed $V_{rms} = \langle V^2 \rangle^{1/2}$ of an electron in the ground state in a dimensional box. Use the data from Problem 3. This value tells us how fast is the electron moving inside the box. Should we worry about relativistic effects? Explain your answer.

$$E_1 = \frac{p^2}{2m}$$

$$p = mv = \sqrt{2mE_1}$$

$$\langle v^2 \rangle^{1/2} = \sqrt{\frac{2E_1}{m}} = \sqrt{\frac{2h^2}{8m^2L^2}}$$

$$v_{rms} = \frac{h}{2mL}$$

$$= \frac{6.26 \times 10^{-34} Js}{2(9.109\times10^{-31} kg)(8.8\times10^{-10} m)}$$

$$= \frac{6.26 \times 10^{-34+31+10}}{2(9.109)(8.8)} m/s$$

$$\boxed{v_{rms} = 3.90 \times 10^{-36+41} \frac{m}{s}} = \boxed{3.90\times10^5 m/s}$$

$$c = 300\,000 \frac{km}{s} = 3\times10^8 \frac{m}{s}$$

$v_{rms} << c$ no relativistic effects.

$$v_{rms} = 390 \frac{km}{s} =$$

For a H atom $v_{rms} \sim \frac{3.90\times10^5 m/s}{2000} = 195 \frac{m}{s} \sim 200 \frac{m}{s}$

Problem 5 **(10 points)**
In this problem we consider an electron in a one-dimensional infinite potential box of length L in its ground state. All of the sudden, we double the size of the box. What is the probability of finding the electron in the ground state of the bigger box?

In order to find the probability we need to take the following steps:

a) First, we need to write down the wave function before the size change. Remember that the electron is in its ground state so the wave function is the eigenfunction for n=1.
b) Consider that the change in size is so fast that the system does not have time to react, and we can freeze the wave function. What is the wave function just after the size change and before the systems reacts to the change? To find the new wave function consider the frozen systems and two regions: a) $0<x<L$, and $L<x<2L$. This new wave function is not an eigenfunction of the new larger box.
c) What is the new ground state eigenfunction of the larger box?
d) In principle we can expand the wave function in b) in term of the eigenfunctions of the larger box. So the probability of finding the electron after the sudden increase in box size is the square of the C_1. So what is the probability of finding the electron in the ground state of the larger box?
e) You may need the following integral:

$$\int_0^S Sin[a\,x]\,Sin[b\,x]\,dx = \frac{b\,Cos[S\,b]Sin[S\,a] - a\,Cos[S\,a]Sin[S\,b]}{a^2 - b^2}$$

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DateList[]
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{2009, 10, 19, 12, 35, 3.457034}
```

Box 0 < x < L -> 2 L

Consider the case when we have a particle in the ground state of PIB of length L.

$$\Psi 1[x\_, L\_] := \sqrt{\frac{2}{L}}\ \mathrm{Sin}\left[\frac{\pi x}{L}\right]$$

Definitions:

$$\Phi[x\_, L\_] := \mathrm{If}[0 < x < L,\ \Psi 1[x, L],\ 0]$$

$$\phi[m\_][x\_, L\_] := \sqrt{\frac{1}{L}}\ \mathrm{Sin}\left[\frac{m \pi x}{2 L}\right]$$

Now we have two normalized functions

$$\int_0^L \Psi 1[x, L]\ \Psi 1[x, L]\ dx$$

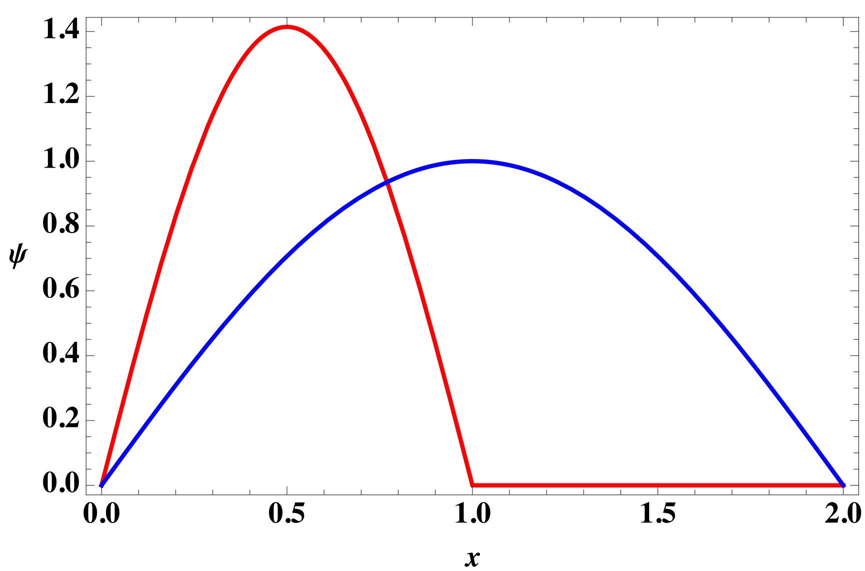
$$1$$

$$\int_0^{2 L} \phi[m][x, L]\ \phi[m][x, L]\ dx$$

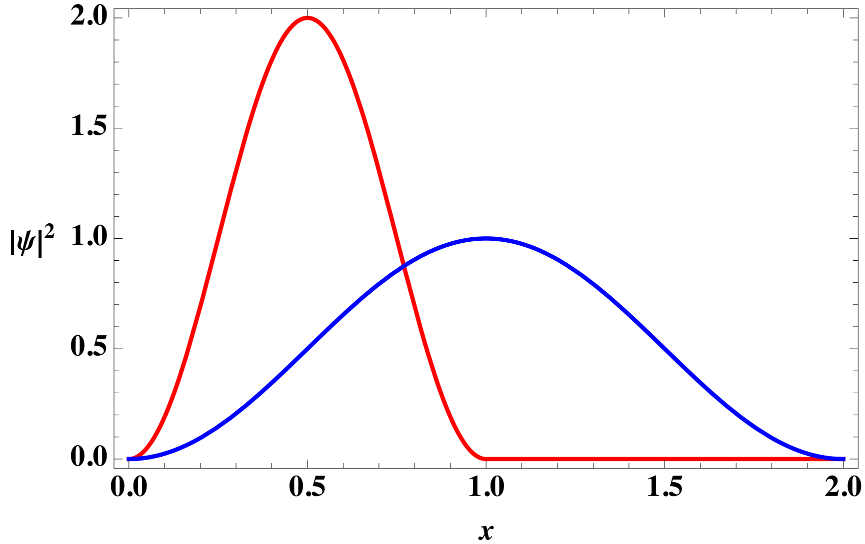
$$1 - \frac{\mathrm{Sin}[2 m \pi]}{2 m \pi}$$

For completeness we plot the functions and the square of the functions, assuming that L =1 .

```
Plot[{Φ[x, 1], (ϕ[1][x, 1])}, {x, 0, 2}, PlotStyle → {{Thick, Red}, {Thick, Blue}},
 BaseStyle → {Bold, 14}, Frame → True, FrameLabel → {x, ψ}, RotateLabel → False, ImageSize → 400]
```



```
Plot[{Ψ[x, 1]^2, (ϕ[1][x, 1]^2)}, {x, 0, 2},
 PlotStyle → {{Thick, Red}, {Thick, Blue}}, BaseStyle → {Bold, 14},
 Frame → True, FrameLabel → {x, "|ψ|^2"}, RotateLabel → False, ImageSize → 400]
```



To find the expansion coefficients and the probabilities, we first need to define the coefficients in the new basis set of the bigger box:

```
c[m_, L_] := Simplify[∫_0^L ϕ[m][x, L] Ψ1[x, L] ⅆx, Assumptions → {m ∈ Integers}]
```

In general the coefficients are given by the following expression:

```
c[m, L]
```

$$\frac{4\sqrt{2}\ \mathrm{Sin}\left[\frac{m\pi}{2}\right]}{4\pi - m^2\pi}$$

Notice that n=2 may give us a problem.

Now we calculate the probabilities as the square of the coefficients

```
prob1 = Table[{n, c[n, 1]^2} // N, {n, 1, 10}];
```

and show them in a tabular form

```
TableForm[prob1, TableHeadings →
  {{"n =", "n =", "n =", "n =", "n =", "n =", "n =", "n =", "n =", "n ="}, {n, Prob1}}]
```

	n	Prob1
n =	1.	0.360253
n =	2.	0.5
n =	3.	0.129691
n =	4.	0.
n =	5.	0.0073521
n =	6.	0.
n =	7.	0.00160112
n =	8.	0.
n =	9.	0.000546851
n =	10.	0.

Bonus question (5 points)

Who is my favorite painter?

Frida Khalo