CHM 3411 – Problem Set 4

Due date: Wednesday, February 6st. (NOTE: The first hour exam is in class on Friday, February 8th. It will cover material from Chapters 7 and 8 of Atkins, including handouts.)

Do all of the following problems. Show your work.

1) Consider the following function as a possible solution to the particle on a ring TISE

$$f(\phi) = A \sin(2\phi) \quad (1.1)$$

a) What value for A makes f(x) a normalized function?

b) Is f(x) an eigenfunction for the Hamiltonian operator for the particle on a ring? Recall that for this system

$$H = T + V = - (\hbar^2/2mr^2)\, d^2/d\phi^2 \quad (1.2)$$

If your answer is yes, what is the corresponding eigenvalue?

c) Is f(x) an eigenfunction for the operator L_z? Recall that

$$L_z = - i\hbar\, d/d\phi \quad (1.3)$$

If your answer is yes, what is the corresponding eigenvalue?

2) What is the value for the following commutator

$$[\phi, L_z] \quad (2.1)$$

where L_z is the z-component of the angular momentum vector (defined in the previous problem).

3) The solutions to the particle on a sphere TISE are the spherical harmonics $Y_{\ell,m_\ell}(\theta,\phi)$ (see Table 8.2 of Atkins), where the energy and possible values for the quantum numbers are

$$E_\ell = [\, \ell(\ell+1)\,] \frac{\hbar^2}{2mr^2} = [\, \ell(\ell+1)\,]\, E_0 \;, \text{ where } E_0 = \hbar^2/2mr^2 \quad (3.1)$$

where $\ell = 0, 1, 2, \ldots$

$m_\ell = 0, \pm 1, \pm 2, \ldots \pm \ell$

Note that in the above expression the units for energy are J (Joule).

a) What is the energy and the degeneracy for the $\ell = 3$ states of the particle on a sphere? You may give your energy in terms of E_0 (defined above).

b) The wavefunction for the $\ell = 2$, $m_\ell = 2$ state of the particle on a sphere TISE is

$$Y_{2,2}(\theta,\phi) = (15/32\pi)^{1/2} \sin^2\theta \exp(2i\phi) \quad (3.2)$$

Show by substitution into the eigenvalue equation that $Y_{2,2}(\theta,\phi)$ is an eigenfunction of the operator L_z (defined in problem 1), and find the corresponding eigenvalue.

4) The particle on a sphere is a good model for rotation of a diatomic molecule. Spectroscopic measurements can determine an experimental value for B, the rotational constant for the molecule. Since

$$B = \frac{h}{8\pi^2 c\mu r_e^2} \qquad (4.1)$$

where B is in wavenumbers, and μ, the reduced mass of a diatomic molecule AB, is defined as

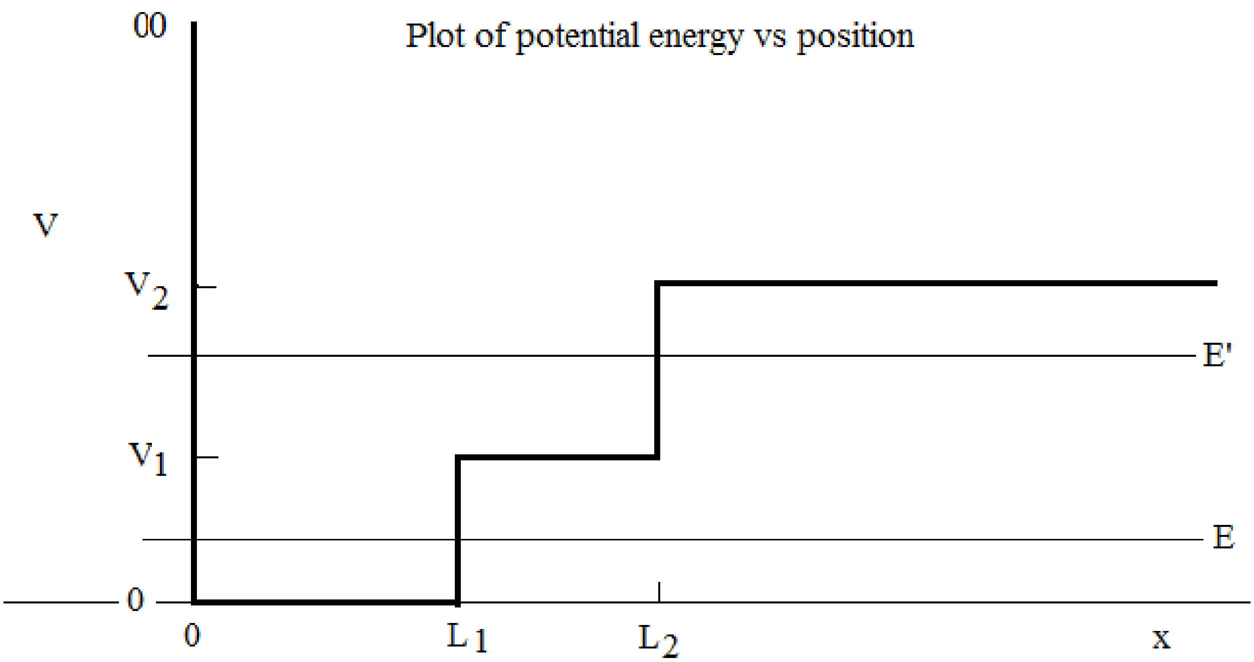
$$\mu = \frac{m_A m_B}{(m_A + m_B)} \qquad (4.2)$$

the value for B can then be used to find r_e, the equilibrium bond distance for the molecule.

Using the information below, find the value for r_e for the CN radical

B(CN) = 1.900 cm^{-1} m(^{12}C) = 12.0000 amu m(^{14}N) = 14.0031 amu

5) A plot of potential energy vs position is given below for a one dimensional system.



Sketch the following:

a) The wavefunction corresponding to an energy E, where E represents the ground state (lowest energy state) of the system.

b) The wavefunction for an excited state of the system that has two nodes and is at an energy E′.

Describe the “interesting” features of your two wavefunctions in the different potential regions.

Your sketches will be qualitative, but should be consistent with what we have discussed in class concerning wavefunctions for one dimensional systems.

Solutions.

1) a) Normalization requires that

$1 = \int_0^{2\pi} (A \sin(2\phi))^2 \, d\phi = A^2 \int_0^{2\pi} (\sin(2\phi))^2 \, d\phi$

But $\int (\sin(ax))^2 \, dx = (x/2) - (1/4a) \sin(2ax)$

And so we get

$1 = A^2 \{ (\phi/2) - (1/8) \sin(4\phi) \}_0^{2\pi} = A^2 \pi$

So $A = 1/(\pi)^{1/2}$

b) To test whether it is an eigenfunction we put the function in the eigenvalue equation

$[- (\hbar^2/2mr^2) \, d^2/d\phi^2] [A \sin(2\phi)] = [- (\hbar^2/2mr^2)] (- 4A \sin(2\phi))$

$= (2\hbar^2/mr^2) [A \sin(2\phi)]$

So yes, $A \sin(2\phi)$ is an eigenfunction of H, with eigenvalue $(2\hbar^2/mr^2)$.

c) To test whether it is an eigenfunction we put the function in the eigenvalue equation

$[(- i\hbar) \, d/d\phi] [A \sin(2\phi)] = (- i\hbar) (2) [A \cos(2\phi)]$

This is not a constant times the original function, and so $A \sin(2\phi)$ is not an eigenfunction of L_z.

2) To find the value for a commutator we can let it operate on a general function $f(\phi)$

$[\phi, L_z] f(\phi) = [\phi, - i\hbar \, d/d\phi] f(\phi)$

$= \{ \phi ((- i\hbar) \, d/d\phi) - ((- i\hbar) \, d/d\phi) \phi \} f(\phi)$

$= (- i\hbar\phi (df(\phi)/d\phi)) - [(- i\hbar \, \phi (df(\phi)/d\phi) - i\hbar f(\phi)]$

Note we used the product rule to evaluate the second term in the commutator. When we cancel out the common terms, we are left with

$= i\hbar \, f(\phi)$

Therefore the commutator is $[\phi, L_z] = i\hbar$. The two operators do not commute.

3) a) For $\ell = 3$,

$E = [(3)(4)] E_0 = 12 E_0$

$m_\ell = 3, 2, 1, 0, -1, -2, -3$ and so $g = (2\ell + 1) = 7$

b) $(- i\hbar) \, d/d\phi \, Y_{2,2}(\theta,\phi) = (- i\hbar) \, d/d\phi \, (15/32\pi)^{1/2} \sin^2\theta \exp(2i\phi)$

$= (- i\hbar) (2i) (15/32\pi)^{1/2} \sin^2\theta \exp(2i\phi) = 2\hbar \, (15/32\pi)^{1/2} \sin^2\theta \exp(2i\phi)$

So yes, $Y_{2,2}(\theta,\phi)$ is an eigenfunction of L_z, with eigenvalue $2\hbar$.

4) $B = \dfrac{h}{8\pi^2 c\mu r_e^2}$

If we solve for r_e^2 we get

$$r_e^2 = \frac{h}{8\pi^2 c\mu B}$$

$$\mu = \frac{m_C m_N}{(m_C + m_N)} = \frac{(12.0000\ \text{amu})\ (14.0031\ \text{amu})}{(12.0000 + 14.0031)\ \text{amu}} = 6.4622\ \text{amu}\ \frac{1\ \text{kg}}{6.022 \times 10^{26}\ \text{amu}} = 1.073 \times 10^{-26}\ \text{kg}$$

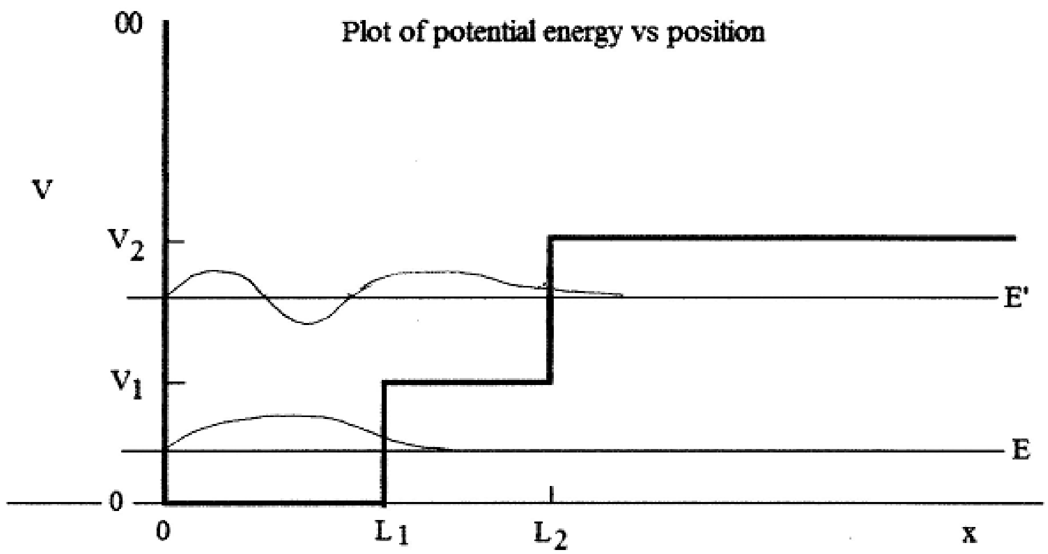
$B = 1.900\ \text{cm}^{-1}\ (100\ \text{cm/m}) = 190.0\ \text{m}^{-1}$

$$r_e^2 = \frac{(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})}{8\pi^2\ (2.998 \times 10^8\ \text{m/s})\ (1.073 \times 10^{-26}\ \text{kg})\ (190.0\ \text{m}^{-1})} = 1.373 \times 10^{-20}\ \text{m}^2$$

And so $r_e = (1.373 \times 10^{-20}\ \text{m}^2)^{1/2} = 1.172 \times 10^{-10}\ \text{m} = 0.1172\ \text{nm}$

In checking the dimensional analysis recall that $1\ \text{J} = 1\ \text{kg}\cdot\text{m}^2/\text{s}^2$

5) A sketch of the wavefunctions is given below. The important points in the sketch are as follows:



a) Since $V = \infty$, for $x < 0$, the wavefunction must be equal to zero for $x < 0$. In the region between 0 and L_1 we have $E > 0$, and so the wavefunction is oscillating. Since it it the ground state it will look similar to the ground state of a particle in a box. At $x = L_1$ the wavefunction will be slightly larger than zero (because the potential does not go to infinity, as in the particle in a box). For $x > L_1$ the wavefunction wil show an exponential decay, since $V_1 > E$.

b) As before, the wavefunction begins at zero at $x = 0$ (since $V = \infty$, for $x < 0$). Between 0 and L_2 the wavefunction will oscillate, since $E > 0$ (for) $< x < L_1$) and $E > V_1$ (for $L_1 < x < L_2$). The oscillation will be at a higher frequency in the region $0 < x < L_1$, because the difference between E and the potential energy is larger there. Two nodes have been sketch, as asked for in the problem. At $x = L_2$ the wavefunction will be slightly larger than zero (since V_2 is finite), and for $x > L_2$ the wavefunction will exponentially decay.