

NORTH CAROLINA STATE UNIVERSITY

Department of Chemistry

Name _____

CH 795T

Molecular Spectroscopy

Problem Set #2

Sept. 10, 2007

Due Date: Sept. 19, 2007

1. Show that the first three Legendre polynomials are solutions for the equation:

$$(1 - x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + \left(J(J + 1) - \frac{M^2}{1 - x^2} \right) P(x) = 0$$

You may assume the case of $M = 0$.

Legendre Polynomials

$$P_0(x) = 1$$

$$P_1(x) = x$$

$$P_2(x) = \frac{1}{2} (3x^2 - 1)$$

$$P_3(x) = \frac{1}{2} (5x^3 - 3x)$$

2. Consider two masses m_1 and m_2 in one dimension, interacting through a potential that depends only upon their relative separation ($x_1 - x_2$), so that $V(x_1, x_2) = V(x_1 - x_2)$. Given that the force acting upon the j th particle is $f_j = -(\partial V / \partial x_j)$, show that $f_1 = -f_2$. Show your work throughout this problem.

A. What law is this?

Newton's equations for m_1 and m_2 are:

$$m_1 \frac{d^2 x_1}{dt^2} = - \frac{\partial V}{\partial x_1} \quad \text{and} \quad m_2 \frac{d^2 x_2}{dt^2} = - \frac{\partial V}{\partial x_2}$$

Now introduce center-of-mass and relative coordinates by:

$$X = \frac{m_1 x_1 + m_2 x_2}{M}, \quad x = x_1 - x_2$$

where $M = m_1 + m_2$, and solve for x_1 and x_2 to obtain:

$$x_1 = X + \frac{m_2}{M} x, \quad x_2 = X - \frac{m_1}{M} x$$

Show that Newton's equations in these coordinates are:

$$m_1 \frac{d^2 X}{dt^2} + \frac{m_1 m_2}{M} \frac{d^2 x}{dt^2} = - \frac{\partial V}{\partial x}$$

and

$$m_2 \frac{d^2 X}{dt^2} - \frac{m_1 m_2}{M} \frac{d^2 x}{dt^2} = + \frac{\partial V}{\partial x}$$

Now add these equations to find

$$M \frac{d^2 X}{dt^2} = 0$$

B. Interpret this result.

Now divide the first equation by m_1 and the second by m_2 and subtract to obtain:

$$\frac{d^2 x}{dt^2} = - \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \frac{\partial V}{\partial x}$$

Or

$$\mu \frac{d^2 x}{dt^2} = - \frac{\partial V}{\partial x}$$

Give the definition of μ .

C. Interpret this result and discuss how the original two-body problem has been reduced to two one-body problems.

3. Polyenes can be treated as a particle-in-a-box problem. The longer the polyene molecule the closer the energy spacing and therefore the smaller the transition energy. This corresponds experimentally to the observation that the absorption spectra shift to lower energies (smaller wavenumber) as the length increases. Demonstrate the trend by calculating $h^2/8ma^2$ for the four polyenes shown given C-C = 154 pm and C=C = 135 pm. Note that the length of the box includes all of the bonds in the molecule plus one more C-C bond to account for the radius of carbon atoms at the end of the molecule.

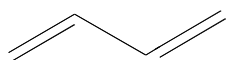
The distances are calculated as follows:

$$a(\text{butadiene}) = 2(\text{C=C}) + 2(\text{C-C}) = 2(135 \text{ pm}) + 2(154 \text{ pm}) = 578 \text{ pm}$$

$$a(\text{hexatriene}) = 3(\text{C=C}) + 3(\text{C-C}) = 3(135 \text{ pm}) + 3(154 \text{ pm}) = \dots$$

Note that in each case the number of π electrons is equal to the number of carbon atoms and further that according to the Pauli principle two electrons occupy each level of the "box".

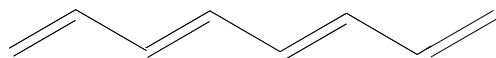
- Using this model calculate the transition energy for each of the four polyenes.
- How many nodes are predicted for the HOMO of each of these molecules based on the particle in a box wave function?



Butadiene



Hexatriene



Octatetraene



Decapentaene

4. Normalize the radial wavefunctions for the 2s and 2p orbitals of the hydrogen atom.

$$\Psi_{2s} = \left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$$

$$\Psi_{2p} = \left(\frac{r}{a_0}\right)e^{-r/2a_0}$$

5. Calculate the expectation value of $\langle r \rangle$ (i.e. the mean radius) for the normalized 2s and 2p wavefunctions. You will need to use the following integral.

$$\int_0^{\infty} r^n e^{-ar} dr = \frac{n!}{a^{n+1}}$$

6. Calculate the fraction of molecules in each of the first ten rotational states of CO at 300 K, assuming that it is a rigid rotor with a bond length of 1.13 Å.