University of Alabama
Department of Physics and Astronomy

PH 253 / LeClair Fall 2010

Problem Set 9: Molecules & Such

Instructions:

1. Answer all questions below. Show your work for full credit.
2. All problems are due Friday 12 November 2010 by the end of the day.
3. You may collaborate, but everyone must turn in their own work.

1. *Energetics of diatomic systems I.* An approximate expression for the potential energy of two ions as a function of their separation is

$$\mathsf{PE} = -\frac{\mathsf{k}e^2}{\mathsf{r}} + \frac{\mathsf{b}}{\mathsf{r}^9} \tag{1}$$

The first term is the usual Coulomb interaction, while the second term is introduced to account for the repulsive effect of the two ions at small distances. **(a)** Find b as a function of the equilibrium spacing $\mathsf{r_o}$. **(b)** For KCl, with an equilibrium spacing of $\mathsf{r_o} = 0.279\,\mathrm{nm}$, calculate the frequency of small oscillations about $\mathsf{r} = \mathsf{r_o}$. *Hint: do a Taylor expansion of the potential energy to make it look like a harmonic oscillator for small* $\mathsf{r} = \mathsf{r_o}$.

2. *Energetics of diatomic systems II.* An expression for the potential energy of two neutral atoms as a function of their separation r is given by the *Morse potential*,

$$\mathsf{PE} = \mathsf{P_o}\left[1 - e^{-\mathsf{a}(\mathsf{r}-\mathsf{r_o})}\right]^2 \tag{2}$$

(a) Find the equilibrium spacing and dissociation energy. **(b)** Calculate the force constant for small oscillations about $\mathsf{r} = \mathsf{r_o}$.

3. *Variational Principle I.* The energy of a system with wave function ψ is given by

$$\mathsf{E}[\psi] = \frac{\int \psi^* \mathsf{H}\psi \, \mathrm{d}V}{\int |\psi|^2 \, \mathrm{d}V} \tag{3}$$

where H is the energy operator. The variational principle is a method by which we guess a trial form for the wave function ψ, with adjustable parameters, and minimize the resulting energy with respect to the adjustable parameters. This essentially chooses a "best fit" wave function based on our guess. Since the energy of the system with the correct wave function will always be minimum, our guess will always lead to an energy which is slightly too high, but the variational principle

allows us to get as close as possible to the correct energy with our trial wave function.

For a hydrogen-like ion, with Z protons and a single electron, the energy operator may be written as

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Zke^2}{r} \tag{4}$$

if we presume that the wave function of such an ion in its lowest energy state is functionally the same as the hydrogen atom,

$$\psi = c_1 e^{-c_2 r} \tag{5}$$

where c_1 and c_2 are adjustable constants.

(a) Use the variational principle and normalization to find the values of c_1 and c_2 that give the minimum energy for this trial wave function.

(b) For a He^+ ion ($Z = 2$), compare the ground state energy with the values of c_1 and c_2 you determine to the second ionization energy of He, $-54.5\,\text{eV}$. *Note that since the trial function is spherically symmetric,* $dV = 4\pi r^2\,dr$ *and* $\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)$.

4. *Variational Principle II.* Pretend we didn't know the ground state wave function for hydrogen, but attempted a trial solution of

$$\psi = c_1 e^{-c_2 r^2} \tag{6}$$

How far off is the ground state energy using this trial wavefunction?

5. Consider two equal bodies (not affected by gravity), each of mass, m, attached to three springs, each with spring constant, k. They are attached in the manner depicted below. **(a)** Find the possible frequencies of stable vibrations. We can use this system as a reasonable model for several types of molecular vibrations.

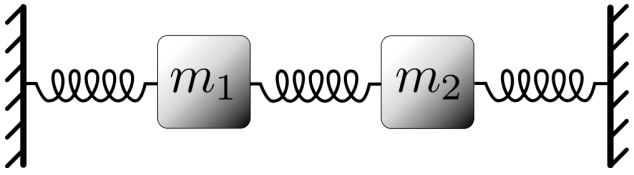

Figure 1: *From http://en.wikipedia.org/wiki/Normal_mode.*

(b) A diatomic molecule (figure (a) below) has only one mode of vibration. Find its frequency, assuming that the masses of A and B are different.

(c) A diatomic molecule adsorbed on a solid surface (figure (b) below) has more possible modes of vibration. Presuming the two springs and masses to be equivalent, find their frequencies.

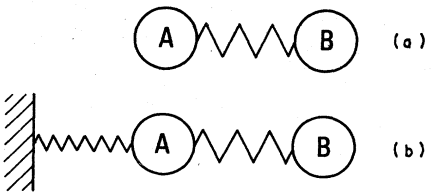

FIG. 1. (a) Classical model for vibrating free-space AB diatomic molecule; (b) same molecule adsorbed onto a surface.

Figure 2: *From http://prb.aps.org/abstract/PRB/v19/i10/p5355_1.*