Problem Set 7: Molecules

Instructions:

1. Answer all questions below. Show your work for full credit.
2. All problems are due 16 April 2013 by the end of the day.
3. You may collaborate, but everyone must turn in their own work.

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

$$E[\psi] = \frac{\int \psi^* H \psi \, dV}{\int |\psi|^2 \, dV} \tag{1}$$

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.

Pretend we don't know the ground state wave function for hydrogen, but decided to guess the following form for ψ:

$$\psi(r) = \frac{\beta}{\alpha^2 + r^2} \tag{2}$$

(a) Use the variational principle and normalization to find the values of α and β that give the minimum energy for this trial wave function. *Note that since the trial function is spherically symmetric,* $dV = 4\pi r^2 \, dr$ *and* $\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right)$.
(b) Compare this result to the correct ground state energy of hydrogen and sketch/plot your best guess for ψ with the correct ground state wave function.

2. *Variational Principle II.* The energy operator for a simple harmonic oscillator in *one dimension* is

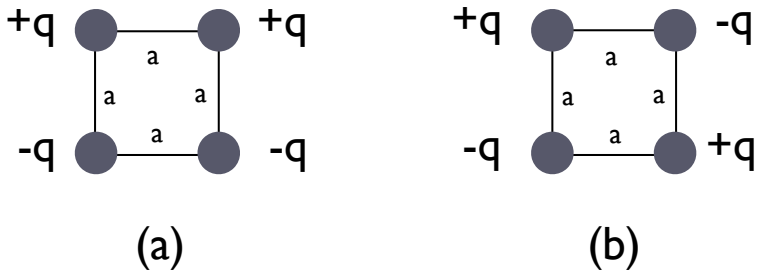
$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \tag{3}$$

Presume we don't know the proper wave function, but guessed a wave function of the form

$$\psi(r) = \frac{\beta}{\alpha^2 + x^2} \tag{4}$$

(a) Use the variational principle and normalization to find the values of α and β that give the minimum energy for this trial wave function. *Since this is a one dimensional problem, take* $dV = dx$.
(b) Compare this result to the correct ground state energy of the simple harmonic oscillator and sketch/plot your best guess for ψ with the correct ground state wave function.

3. Two positive and two negative charges are arranged on a square lattice of side a in two different ways, shown below. Calculate the electrostatic potential energy of each configuration. Which configuration of charges is more stable? Why?



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

$$PE = -\frac{ke^2}{r} + \frac{b}{r^9} \tag{5}$$

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 r_o. **(b)** For KCl, with an equilibrium spacing of $r_o = 0.279\,\text{nm}$, calculate the frequency of small oscillations about $r = r_o$. *Hint: do a Taylor expansion of the potential energy to make it look like a harmonic oscillator for small* $r = r_o$.

5. (a) A diatomic molecule has only one mode of vibration, and we may treat it as a pair of masses connected by a spring (figure (a) below). Find the vibrational frequency, assuming that the masses of A and B are different. Call them m_a and m_b, and let the spring have constant k.

(b) 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 this time, find their frequencies.

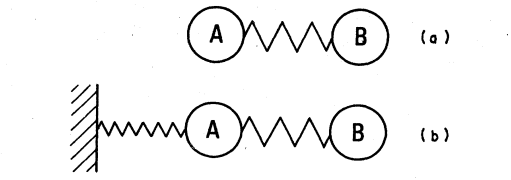


FIG. 1. (a) Classical model for vibrating free-space AB diatomic molecule; (b) same molecule adsorbed onto a surface.

Figure 1: *From http://prb.aps.org/abstract/PRB/v19/i10/p5355_1.*