Homework #8 — Phys623 — Spring 1999
Deadline: 5 p.m., Friday, April 9, 1999.
Turn in homework in the class or put in
the box on the door of Phys 2314 by 5 p.m.

Victor Yakovenko, Assistant Professor
Office: Physics 2314
Phone: (301)–405–6151
E-mail: yakovenk@physics.umd.edu

Do not forget to write your name and the homework number!
Equation numbers with the period, like (3.25), refer to the equations of Schwabl.
Equation numbers without period, like (5), refer to the equations of this homework.

Molecules (Chapter 15)

Schwabl's Problem 15.2 can be solved using the so-called elliptical coordinates (see p. 475 of the book by Baym). I do not ask you to take those integrals.

1. [**5 points**] Schwabl's Problem 15.5.

2. [**3 points**] Schwabl's Problem 15.7. This potential is called the *Lennard-Jones 6–12 potential* and is widely used in molecular physics. The power 6 represents the van der Waals attraction, and the power 12 is selected for mathematical convenience.

   Directions: Follow Ch. 15.5. Appendix D of Schwabl may be useful. The value of ε given in Schwabl is wrong. Instead do the problem for a Ne_2 molecule where $\varepsilon = 0.003$ eV and $d = 2.74$ Å. State which of the energy levels are excited and which are frozen out at the room temperature.

3. [**3 points**] The "dissociation energy" required to separate a D_2 molecule into two deuterium atoms (4.54 eV) is not the same as that of an H_2 molecule (4.46 eV), although the proton and deuteron are practically indistinguishable to the electrons. Explain why, and use the above information to compute the zero-point energy of vibration in the H_2 and D_2 molecules. (Neglect the small nuclear motion in the atoms and tiny finite nuclear size and hyperfine effects.)

4. [**3 points**] The rotational spectrum of HBr consists of a series of lines spaced equidistantly at the energy ε_0 apart. Find the internuclear distance of HBr.

5. [**5 points**] Calculate the energy of the van der Waals interaction between two hydrogen atoms in the ground states (Ch. 15.6) using the variational method. Try the following two variational functions:

$$\psi_\alpha(\mathbf{r}_1, \mathbf{r}_2) = C\psi_0(r_1)\psi_0(r_2)(1 + \alpha x_1 x_2), \tag{1}$$

   where $\psi_0(r)$ is the ground-state wave function of the hydrogen atom, C is a normalization constant, α is a variational parameter. Solution of Problem 5 of Homework 6 and the equation before Eq. (15.51) may be useful.

6. Thus far we considered molecules that consist of two atoms. Now let us consider a molecule that consists of an infinite number of atoms spaced periodically at a distance d: a crystal. Let us consider one-dimensional arrangement for simplicity. The Hamiltonian of a particle is

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \sum_{l=-\infty}^{\infty} V_l(x), \tag{2}$$

   where l is an integer, and $V_l(x) = V_0(x - ld)$ is the potential of one atom displaced to a distance ld. As a specific example, we will consider the Dirac comb:

$$\hat{H}_D = \frac{\hat{p}^2}{2\mu} - \lambda \sum_{l=-\infty}^{\infty} \delta(x - ld), \tag{3}$$

   where $\delta(x)$ is the Dirac delta-function.

Let us consider the case where the distance between the atoms, d, is substantially greater that the size of the atomic wave function a. For example, a single Dirac potential $V_0(x) = -\lambda\delta(x)$ has the wave function

$$\psi_0(x) = \sqrt{\kappa}e^{-\kappa|x|} \tag{4}$$

where $\kappa = \lambda\mu/\hbar^2$, and the energy $E_0 = -\hbar^2\kappa^2/2\mu$. We consider that case where $\kappa d \ll 1$, so the overlap of the wave functions of different atoms is exponentially small.

Let us construct the wave function in a crystal as a linear superposition of the eigenfunctions of individual atoms (the so-called *LCAO method* (linear combination of atomic orbitals) or the *tight-binding approximation*):

$$\psi(x) = \sum_n c_n\psi_n(x), \qquad \text{where} \quad \psi_n(x) = \psi_0(x - nd). \tag{5}$$

Because all wave functions $\psi_n(x)$ have the same energies within their atoms, the coefficients c_n should be determined from some sort of a secular equation. To derive this equation, let us substitute the sum (5) into the Schrödinger equation

$$\hat{H}\psi = E\psi, \tag{6}$$

and take a scalar product of (6) with $\psi_m^*(x)$.

(a) [**3 points**] Show that this generates the following equation on the coefficients c_n:

$$\sum_n \langle\psi_m|\sum_{l\neq m} V_l|\psi_n\rangle c_n = (E - E_0)[c_m + \sum_{n\neq m}\langle\psi_m|\psi_n\rangle c_n] \tag{7}$$

(b) [**5 points**] Show that $c_n^{(k)} = e^{ikn}$ is an eigenvector of Eq. (7) corresponding to the energy

$$E(k) = E_0 + \frac{\beta + \gamma(k)}{1 + \alpha(k)}, \tag{8}$$

$$\alpha(k) = \sum_{n\neq 0} e^{ikn}\langle\psi_0|\psi_n\rangle, \tag{9}$$

$$\beta = \langle\psi_0|\sum_{l\neq 0} V_l|\psi_0\rangle, \tag{10}$$

$$\gamma(k) = \sum_{n\neq 0} e^{ikn}\langle\psi_0|\sum_{l\neq 0} V_l|\psi_n\rangle. \tag{11}$$

Because the atomic wave functions typically decay exponentially (see Eq. (4)), it is sufficient to keep only the terms with $n = \pm 1$ and $l = 1$ in Eqs. (9)–(11). Further examination shows that, α and β can be dropped compared with the leading term γ. So we arrive to the following equation:

$$E(k) = E_0 + 2t\cos(k), \qquad \text{where} \quad t = \langle\psi_0|V_1|\psi_1\rangle. \tag{12}$$

The matrix element t is called the *transfer integral* between the nearest neighboring atomic sites. In this approximation, the secular equation (7) has the form:

$$Ec_m = E_0 c_m + t(c_{m+1} + c_{m-1}), \tag{13}$$

where the matrix element t "transfers" the particle from site m to the neighboring sites $m \pm 1$.

(c) [**3 points**] For the Dirac comb potential (3) in the case $\kappa d \ll 1$, check the validity of the approximations that led from Eq. (8) to Eq. (13) and calculate the transfer integral t.