PHYS 3317 Fall 2012
Homework 6 Molecules and Quantum Statistics

This is the last homework problem set in our course. Do start early with this homework and finish in time—there is no sense in dragging it over the fall break. Enjoy!
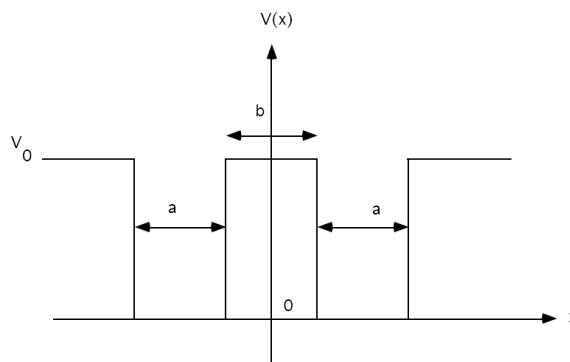
1. Hydrogen chloride

HCl molecule consists of a hydrogen atom of mass $1\,u$ bound to a chlorine atom of mass $35\,u$ (atomic mass unit $1\,u$ is equal to one twelfth of the rest mass of carbon-12 or roughly that of a single nucleon). The equilibrium separation between the atoms is $1.28\,\text{Å}$, and it requires $0.15\,\text{eV}$ of work to increase or decrease this separation by $0.1\,\text{Å}$.

(a) Calculate the four lowest rotational energies (in eV) that are possible, assuming the molecule rotates rigidly.

(b) Find the molecule's "spring constant" and its classical frequency of vibration. (Hint: recall that $U = \frac{1}{2}kx^2$.)

(c) Find the two lowest vibrational energies and the classical amplitude of oscillation corresponding to each of these energies.

(d) Determine the longest wavelength radiation that the molecule can emit in a pure rotational transition and in a pure vibrational transition.

2. Simple model of a diatomic molecule

The double square well potential can be used as a simple 1D model for the potential experienced by an electron in a diatomic molecule. The attractive forces of the nuclei on the electron are represented by the two square wells. This model ignores the internuclear repulsive force between the nuclei themselves (which can be put back "by hand").

(a) *Without doing any calculations*, sketch the ground-state wavefunction ψ_1 , and the first excited state wavefunction, ψ_2 , (i) for $b = 0$, (ii) for $b \approx a$, (iii) and for $b \gg a$.

(b) Determine *qualitatively* how the ground state energy E_1, and the first excited state energy, E_2, vary as b ranges from 0 to ∞. (Hint: Recall that, for $V = 0$, the Schrödinger equation says that the energy is proportional to the relative curvature of the wavefunction: $E_{1,2} \propto -\frac{1}{\psi_{1,2}} \frac{d^2 \psi_{1,2}}{dx^2}$.) Sketch $E_1(b)$ and $E_2(b)$ vs. b on the same graph ignoring the above mentioned internuclear repulsion.

(c) If the nuclei in the diatomic molecule (the square wells) are free to move, they will adopt the configuration of minimum energy ($b \to 0$ will generally be prevented by the neglected internuclear repulsive potential energy term of the two positively charged nuclei). In view of the results found in part **(b)**, will the electron bind the nuclei, or push them apart? (These are called *bonding* and *antibonding* orbitals in chemistry for this very reason).

(d) (Optional) Set up this potential in MATLAB (using `schrod.m`) and verify correctness of your conclusions for the first two energy states.

3. Approaching Fermi-Dirac distribution

We learned in class that Fermi-Dirac (FD) distribution approaches

$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}},$$

for a large number of indistinguishable fermions. Fermi level E_F is generally a (weak) function of temperature, though it can be treated as a constant for most practical cases. For few particles, the distribution is not exactly Fermi-Dirac though it approaches the distribution very quickly. Fig. 1, http://ecee.colorado.edu/~bart/book/book/chapter2/ch2_5.htm#2_5_2, shows an example of 20 electrons placed in the simple harmonic oscillator potential (SHO) where energy levels are given by $E_n(\text{eV}) = 0.5 + n$. The total energy of all the electrons is $106\,\text{eV}$. The author provides an Excel file which lists all possible configurations for this system, http://ecee.colorado.edu/~bart/book/book/chapter2/xls/fig2_5_3.xls. Get this file and let's play with it a bit.

(a) Inside his Excel file, you will find all possible configurations realized for this system (look under Configurations sheet). Copy these configurations into another Excel file so you can tweak things. There is one potential problem with spin-$\frac{1}{2}$ fermions when it comes to accounting for degeneracy of each configuration. E.g. consider his first configuration: $\{2, 2, 2, 2, 2, 2, 2, 2, 2, 1, 0, 0, 0, 0, 0, 1\}$ corresponding to energies 0.5 through $15.5\,\text{eV}$. Spins are anti-parallel whenever
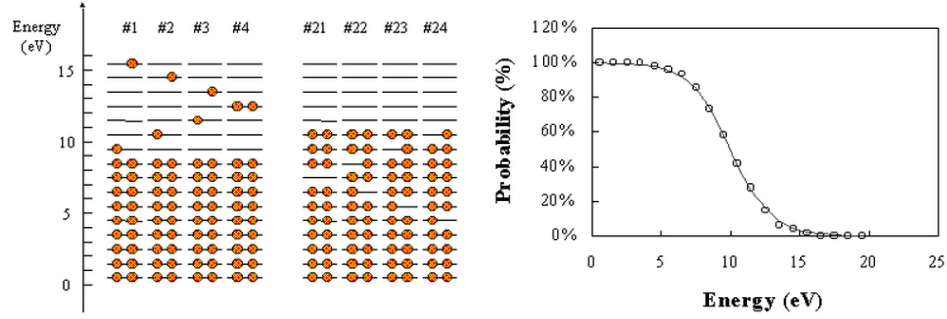
Figure 1: 20 electrons in SHO potential with 8 out of 24 possible configurations shown (on the left) and the resulting distribution plot (on the right).

there are 2 electrons sitting on each level. Such configurations (e.g. #7 in his spreadsheet) will have a degeneracy of 1 (there is only one way to realize each of these). On the other hand, two electrons each occupying *different* energy levels can have spins $\{\ldots + \ldots +\}$, $\{\ldots + \ldots -\}$, $\{\ldots - \ldots +\}$, and $\{\ldots - \ldots -\}$ (denoting spin-up state by $+$ and spin-down state by $-$). It means that having 2 unpaired electrons allows for four possible states with the same occupation numbers $\{\ldots 1 \ldots 1\}$ instead of just one. The situation here is similar to the helium atom: we saw that having two electrons occupying different energy levels results in a spin-1 triplet and a spin-0 singlet (total 4 possibilities). Generally, each unpaired electron multiplies degeneracy of the configuration by 2, i.e. k unpaired electrons in a configuration leads to $g = 2^k$ degeneracy. Since each configuration is $\times g$ as likely to get statistically realized, the occupation numbers must be adjusted by the same factor. Compute degeneracy for each configuration listed and obtain a new distribution plot.

(b) You can fit FD curve to the newly obtained points. Fitting data is a very common activity of a physicist, so let's make sure your data fitting abilities are up to snuff. In MATLAB, you can use a convenient GUI-based curve fitting tool by typing `cftool`. Then, copy and paste the numbers from Excel to MATLAB and create two 1D arrays (must be two 1D arrays), say `energy` and `prob` for the probabilities. Inside the Curve Fitting Tool window, select `energy` and `prob` as 'X data' and 'Y data' respectively. Select 'Custom Equation' to fit to and type in `1/(exp((x-Ef)/kT)+1)` (x is an independent variable, while `Ef` and `kT` are the fit parameters). Print out and submit the plot which shows both the data points and the fitted curve. Did the proper accounting of degeneracies due to unpaired spins change the result in practical terms? Also, show the location of Fermi energy, that is Fermi level at $T = 0\,\mathrm{K}$. (Hint: the total energy is no longer $106\,\mathrm{eV}$ when $T = 0\,\mathrm{K}$). Remark: Fermi level and Fermi energy are generally speaking two different things. Fermi level, also known as *chemical potential*, is defined as a point where $f(E_F(T)) = 0.5$ and it is a (weak) function

of temperature as discussed in lecture. Fermi energy is defined as Fermi level at $T = 0\,K$, and is, therefore, a constant by definition.