

## Homework # 5

### Exercise 1: The quantum harmonic oscillator

In molecules and materials, when atoms are close to their equilibrium position, they oscillate following a potential which is quadratic, as the one of the quantum harmonic oscillator. Most forces between atoms are due to interatomic potentials of the form shown in Fig.1: a repulsive part diverging when two atoms get very close, a minimum at some equilibrium distance and a tail going to zero for large distances. Very often one is interested only in a small region around the equilibrium distance, where we can approximate even complex interatomic potentials with a simple quadratic potential (i.e. a “spring”): this is the so-called *harmonic approximation*. Although the harmonic oscillator can be solved analytically, here we will adopt the variational approach.

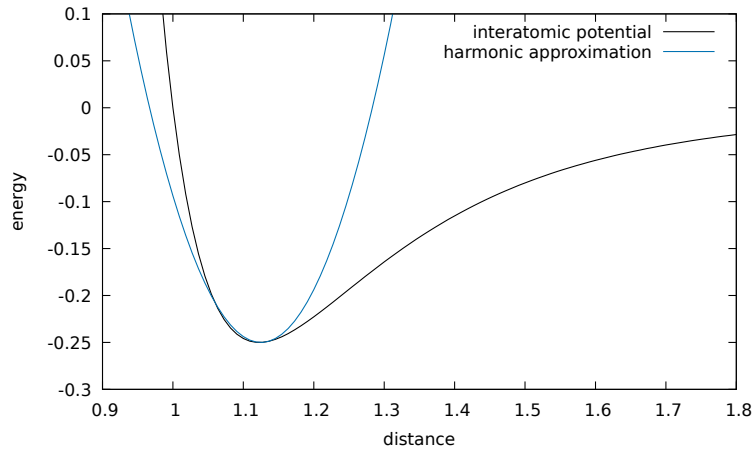


Figure 1: Typical shape of an interatomic pair potential and its harmonic approximation.

Consider a one-dimensional *quantum harmonic oscillator* described by the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2,$$

being  $\hat{p} = -i\hbar\nabla$  the quantum momentum operator, where  $\hbar = h/2\pi$ ,  $h$  is the Planck's constant,  $m$  is the mass and  $\omega$  is the frequency of oscillations.

1. Using the variational principle determine the minimum of the energy for the trial wave function:

$$\psi_\alpha(x) = A e^{-\alpha x^2}, \quad (-\infty < x < +\infty)$$

where  $\alpha$  is a real parameter, and  $A$  is the normalization constant.

(*hint*: use Gaussian integrals:)

$$\int_{-\infty}^{\infty} e^{-\gamma x^2} dx = \sqrt{\frac{\pi}{\gamma}}, \quad \int_{-\infty}^{\infty} x^2 e^{-\gamma x^2} dx = \frac{1}{2\gamma} \sqrt{\frac{\pi}{\gamma}}.$$

Determine  $A$  using the normalization condition of  $\psi_\alpha(x)$  [normalize  $\psi_\alpha(x)$  to 1]. How the evaluated minimum of energy compares with the exact ground-state energy  $E_0 = \hbar\omega/2$  (i.e. the energy of the *zero point motion*)? Is the wave function  $\psi_\alpha(x)$  the exact ground-state wave function for some value of the  $\alpha$  parameter?

2. Compute the ground state probability density of a quantum harmonic oscillator in coordinate space (i.e. find  $\rho(x)$ ), and compare it with the probability density of a classical harmonic oscillator. What are the two most striking differences?

(*Hint*: the classical probability density is proportional to  $\frac{1}{\sqrt{C-x^2}}$ , where  $C$  is a real number depending on the spring constant and  $|x| < \sqrt{C}$  ).

## Exercise 2: Uncertainty principle and the hydrogen atom

(adapted from R. Feynman, the Feynman lectures, the size of an atom)

The hydrogen atom is a bound state of an electron and a proton. The latter is three orders of magnitude heavier than the former, and can be considered at rest. Suppose we have an hydrogen atom and measure the position of the electron. We must not be able to predict exactly where the electron will be, or the momentum spread will then turn out to be infinite. Assume that the electron is at a distance " $a$ " from the proton. Every time we look at the electron, it is somewhere, but it has an amplitude to be in different places, so there is probability of it being found in different places. There is a spread in position of electron of order  $a$ .

Because of uncertainty principle, the spread in momentum of the electron is roughly  $p \sim \hbar/a$ . So if we try to measure the momentum of the electron, the momenta must be of order  $p \sim \hbar/a$ . Then the kinetic energy is  $\frac{1}{2}mv^2 = p^2/2m = \hbar^2/2ma^2$ . The potential energy is the electrostatic interaction between electron and proton. Therefore the total energy is:

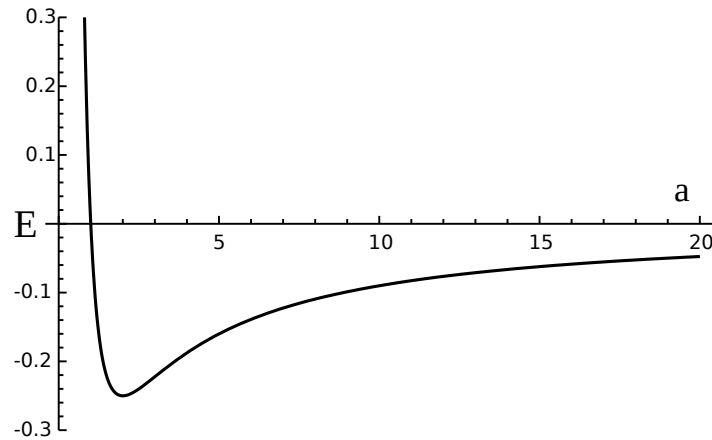
$$E(a) = \frac{\hbar^2}{2ma^2} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{a}$$

The dependence of  $E$  on  $a$  is shown in Figure 2.

1. Can the electron fall on the nucleus? Which amount of energy would this process require?
2. Determine the ground state of the hydrogen atom (*Hint: the ground state is the minimum energy state*). What is the value of  $a$  in the ground state? What is the corresponding energy in eV? And in Rydberg?
3. What is the minimal energy to remove the electron from the hydrogen atom? In which range of the electromagnetic spectrum could you find a photon with such an energy?

## Exercise 3: Ionization energies and relativistic effects for hydrogen-like atoms

*Hydrogen-like* atoms are systems consisting of a single electron bound to a nucleus with a number  $Z$  of protons. We will calculate the ionization energies of  $1s$  core electrons using the hydrogen-like

Figure 2: Schematic plot of  $E$  as a function of  $a$ .

model. The 1s or “last” ionization energy is the amount of energy required to remove the electron from the species  $X$ , during the process:



that is the energy to remove the last electron after all the other ones have been already stripped.

1. Calculate the 1s ionization energy for H, He, Li, O, Fe, Cu and compare with the experimental values (in eV, H: 13.60, He: 54.42, Li: 122.45, O: 871.41, Fe: 9277.69, Cu: 11567.62).

Suppose we want to calculate the 1s ionization energy for a *neutral atom* (i.e. the total number of electrons equals to the number of protons, hence the atom’s net charge is zero), as in the process



2. Do you expect the ionization energy to be the same, higher or lower? Why?

Now instead imagine to calculate the “first” ionization energy, that is the energy to remove the least bound electron out of a neutral atom:



3. Do you expect the first ionization energy to be larger or smaller than the last ionization energy? Why?

In the simplest approximation, we can estimate the orbital speed  $v$  of a 1s electron (in the ground state) as  $v/c = \alpha Z$ , where  $c$  is the speed of light, and  $\alpha$  is the fine-structure constant (in atomic units 1/137).

4. Estimate the orbital speed for a 1s electron in H, Fe, Au and Bi.
5. What is the minimum value of  $Z$  such that the orbital speed is at least 20% of the speed of light?

When the orbital velocity of an electron reaches a sizeable fraction of the speed of light, relativistic effects become important. For instance, the energy of a  $1s$  electron gets a correction term<sup>1</sup> proportional to  $\alpha^2 Z^2$ :

$$E_{1s} = -Z^2 \cdot 13.6\text{eV} \cdot \left(1 + \frac{Z^2 \alpha^2}{4}\right). \quad (4)$$

6. How much the relativistic correction ( $\frac{Z^2 \alpha^2}{4}$ ) affects the last ionization energy for H, Fe and Au?

---

<sup>1</sup>If you are interested in the details, have a look at Chapter 5 (pages 234-249) of *Physics of Atoms and Molecules* by Bransden and Joachin.