Solutions of homework # 5

Exercise 1: The quantum harmonic oscillator

Using the variational principle, the energy of the quantum harmonic oscillator described by the wave function $\psi_\alpha(x)$ reads:

$$E[\psi_\alpha] = \frac{\langle\psi_\alpha| H |\psi_\alpha\rangle}{\langle\psi_\alpha|\psi_\alpha\rangle} \geq E_0 \,, \tag{1}$$

where $E[\psi_\alpha]$ is the energy functional, and E_0 is the true ground-state energy. Let us compute $E[\psi_\alpha]$ using the expression for the trial wave function $\psi_\alpha(x)$.

1. The denominator of eq. (1) can be evaluated as follows:

$$\langle\psi_\alpha|\psi_\alpha\rangle = \int\limits_{-\infty}^{+\infty} \psi^*_\alpha(x)\psi_\alpha(x)\, dx = |A|^2 \int\limits_{-\infty}^{+\infty} e^{-2\alpha x^2}\, dx = |A|^2 \sqrt{\frac{\pi}{2\alpha}} \,. \tag{2}$$

Using the normalization condition we have:

$$\langle\psi_\alpha|\psi_\alpha\rangle = |A|^2 \sqrt{\frac{\pi}{2\alpha}} = 1, \tag{3}$$

$$A = \sqrt[4]{\frac{2\alpha}{\pi}}. \tag{4}$$

Now let us calculate the numerator of eq. (1):

$$\begin{aligned}
\langle\psi_\alpha| H |\psi_\alpha\rangle &= \int\limits_{-\infty}^{\infty} \psi^*_\alpha(x) \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m\omega^2}{2}x^2\right) \psi_\alpha(x)\, dx \\
&= |A|^2 \int\limits_{-\infty}^{\infty} e^{-\alpha x^2} \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m\omega^2}{2}x^2\right) e^{-\alpha x^2}\, dx \\
&= |A|^2 \int\limits_{-\infty}^{\infty} e^{-\alpha x^2} \left(\frac{\hbar^2}{2m}2\alpha(1-2\alpha x^2) + \frac{m\omega^2}{2}x^2\right) e^{-\alpha x^2}\, dx \\
&= |A|^2 \frac{\hbar^2}{2m}2\alpha \int\limits_{-\infty}^{\infty} e^{-2\alpha x^2}\, dx + |A|^2 \left(\frac{m\omega^2}{2} - \frac{2\hbar^2\alpha^2}{m}\right) \int\limits_{-\infty}^{\infty} x^2\, e^{-2\alpha x^2}\, dx \\
&= |A|^2 \frac{\hbar^2\alpha}{m}\sqrt{\frac{\pi}{2\alpha}} + |A|^2 \left(\frac{m\omega^2}{8\alpha} - \frac{\hbar^2\alpha}{2m}\right)\sqrt{\frac{\pi}{2\alpha}} \,.
\end{aligned} \tag{5}$$

Putting all together we find:

$$E[\psi_\alpha] = \frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha} \,. \tag{6}$$

The energy expectation value $E[\psi_\alpha]$ has the minimum when $dE[\psi_\alpha]/d\alpha = 0$, that is

$$\frac{dE[\psi_\alpha]}{d\alpha} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0 \quad \Longrightarrow \alpha_{\text{min}} = \pm\frac{m\omega}{2\hbar}\,. \tag{7}$$

Only α_{min} with the "+" sign has a physical meaning. The energy at the minimum is thus

$$E_{\text{min}} = E[\psi_{\alpha_{\text{min}}}] = \frac{\hbar\omega}{2} = E_0\,. \tag{8}$$

Therefore, we have found that $E[\psi_{\alpha_{\text{min}}}]$ is exactly equal to the ground-state energy E_0, which means that the wave function

$$\psi_{\alpha_{\text{min}}}(x) = \sqrt[4]{\frac{m\omega}{\hbar\pi}}e^{-\frac{m\omega}{2\hbar}x^2} \tag{9}$$

is the true exact ground-state wave function of the quantum harmonic oscillator.

2. Using Eq. (9), we can evaluate the probability density of a quantum harmonic oscillator as:

$$\rho(x) = |\psi_{\alpha_{\text{min}}}(x)|^2 = \sqrt{\frac{m\omega}{\hbar\pi}}e^{-\frac{m\omega}{\hbar}x^2}. \tag{10}$$

If we plot the classical and quantum probability density we obtain something like in Fig. 1. As you see they are very different and the two most important features are:

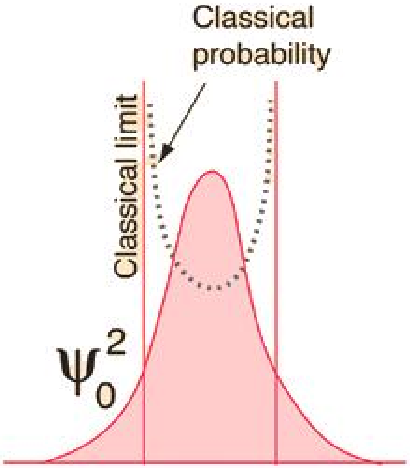


Figure 1: Comparison between the classical and quantum probability distributions for an harmonic oscillator in the ground state (source http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/hosc6.html)

- The classical probability distribution is bounded in space, simply because the kinetic energy $K = \frac{mv^2}{2}$ and potential energy $V = \frac{kx^2}{2}$ cannot be negative and the total energy $E = K + V$ must be conserved. In the quantum case the probability distribution is a Gaussian function with a tail that goes to zero at infinity, so there is non-vanishing probability of finding the particle beyond the "classical region".

- For the quantum oscillator the particle will spend most of its time near that center point, while in the classical case very little time is spent there where the particle has the maximum speed; it will spend most of its time near the end points of its oscillation where its speed is smaller.

Exercise 2: Uncertainty principle and the hydrogen atom

1. According to the text the total energy as a function of a is:

$$E(a) = \frac{\hbar^2}{2ma^2} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{a}$$

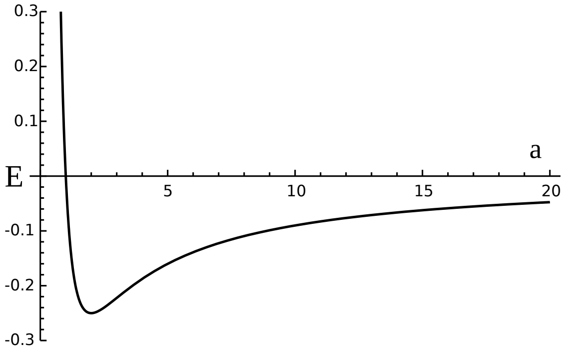


Figure 2: Schematic plot of $E(a)$ as a function of a.

From the plot in fig. 2, we can see that an infinite energy barrier is present at $a = 0$; indeed, the limit of $E(a)$ for $a \to 0$ is $+\infty$. Although there is Coulomb attraction between the electron and proton, the repulsive term is of order $1/a^2$ and is so strong that electron needs an infinite amount of energy to fall on nucleus.

2. In the opposite case, for $a \to \infty$, when electron and proton are very far apart, their interaction energy is zero: a free electron and a free proton. However, the electron wants to minimize its energy, by going to its ground state, the lowest possible energy state. We can estimate the ground state energy E_0 and the ground state distance a_0 by looking for the minimum of $E(a)$ by varying a. By taking a derivative we have:

$$0 = \left.\frac{dE(a)}{da}\right|_{a=a_0} = \left.-2\frac{\hbar^2}{2ma^3} + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{a^2}\right|_{a=a_0}$$

hence:

$$a_0 = \frac{4\pi\varepsilon_0}{e^2}\frac{\hbar^2}{m} = \frac{\varepsilon_0}{e^2}\frac{h^2}{\pi m} = \frac{8.854 \cdot 10^{-12}\,\mathrm{C^2/Nm^2}}{(1.602 \cdot 10^{-19}\,\mathrm{C})^2}\frac{\left(6.63 \cdot 1\ 0^{-34}\,\mathrm{J \cdot s}\right)^2}{\pi \cdot 9.109 \cdot 10^{-31}\,\mathrm{kg}} = 0.529\,\text{Å}$$

This is the famous Bohr radius. Now we have learned that the atomic dimensions are of order of angstroms and we have a basis to understand the size of atoms!
We can now evaluate the energy in correspondence of a_0 to obtain the minimum energy, namely the ground state:

$$E_0 \equiv E(a_0) = \frac{\hbar^2}{2ma_0^2} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{a_0} = \frac{\hbar^2}{2m}\left(\frac{me^2}{4\pi\varepsilon_0\hbar^2}\right)^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{me^2}{4\ \pi\varepsilon_0\hbar^2}\right) = -\frac{me^4}{2\hbar^2(4\pi\varepsilon_0)^2}$$

$$= -\frac{h^2}{8\pi^2 m a_0} = -\frac{\left(6.63 \cdot 10^{-34}\,\mathrm{J \cdot s}\right)^2}{8\pi^2 \cdot 9.109 \cdot 10^{-31}\,\mathrm{kg} \cdot \left(0.529 \cdot 10^{-10}\,\mathrm{m}\right)^2} = -2.17987 \cdot 10^{-18}\,\mathrm{J}.$$

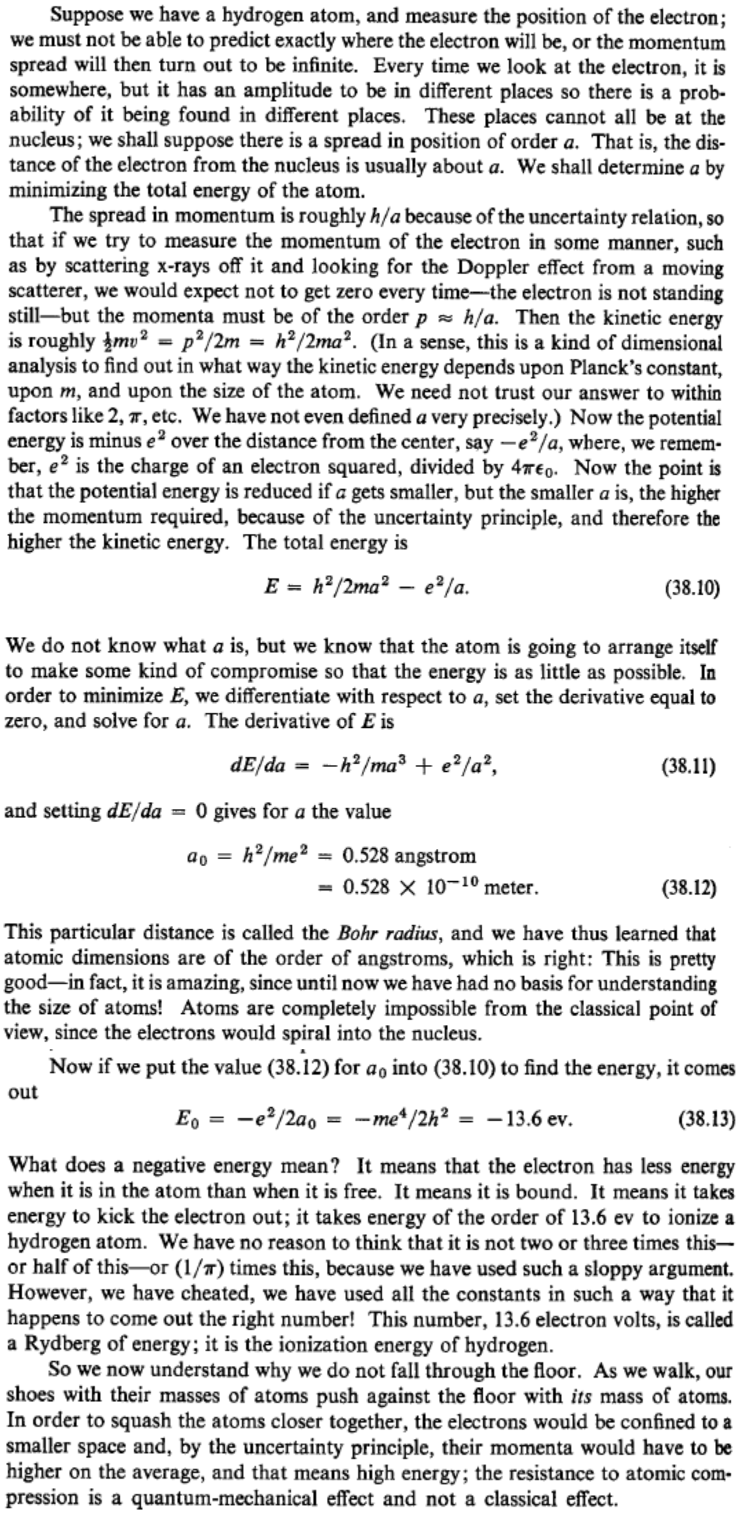
This is the energy of the ground state of the hydrogen atom in the international system of units. In atomic physics one would rather work with the electronvolt as a unit of energy. Since $1\,\mathrm{eV} = 1.602... \cdot 10^{-19}\,\mathrm{J}$, one quickly obtains:

$$E_0 = -13.605\,\mathrm{eV}$$

Note that (minus) the ground state energy of the hydrogen atom is exactly the definition of the Rydberg. Therefore:

$$E_0 = -1\,\mathrm{Ry}$$

3. If the electron is in the ground state, an energy equal to the depth of the well is needed to free the electron. Hence $E_{\mathrm{ionization}} = +13.6\,\mathrm{eV}$. From the relation $E = h\nu$, we obtain the frequency of the photon carrying that energy as $\nu = E/h = 3.29 \cdot 10^{15}\,\mathrm{Hz}$. One can also obtain its wavelength as $\lambda = \frac{hc}{E} = \frac{c}{\nu} \sim 100\,\mathrm{nm}$. This region of the electromagnetic spectrum lies in the ultraviolet and it is marks the onset of what is called *ionizing radiation*, from the far ultraviolet up to γ-rays.



Suppose we have a 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. Every time we look at the electron, it is somewhere, but it has an amplitude to be in different places so there is a probability of it being found in different places. These places cannot all be at the nucleus; we shall suppose there is a spread in position of order a. That is, the distance of the electron from the nucleus is usually about a. We shall determine a by minimizing the total energy of the atom.

The spread in momentum is roughly h/a because of the uncertainty relation, so that if we try to measure the momentum of the electron in some manner, such as by scattering x-rays off it and looking for the Doppler effect from a moving scatterer, we would expect not to get zero every time—the electron is not standing still—but the momenta must be of the order $p \approx h/a$. Then the kinetic energy is roughly $\frac{1}{2}mv^2 = p^2/2m = h^2/2ma^2$. (In a sense, this is a kind of dimensional analysis to find out in what way the kinetic energy depends upon Planck's constant, upon m, and upon the size of the atom. We need not trust our answer to within factors like 2, π, etc. We have not even defined a very precisely.) Now the potential energy is minus e^2 over the distance from the center, say $-e^2/a$, where, we remember, e^2 is the charge of an electron squared, divided by $4\pi\epsilon_0$. Now the point is that the potential energy is reduced if a gets smaller, but the smaller a is, the higher the momentum required, because of the uncertainty principle, and therefore the higher the kinetic energy. The total energy is

$$E = h^2/2ma^2 - e^2/a. \tag{38.10}$$

We do not know what a is, but we know that the atom is going to arrange itself to make some kind of compromise so that the energy is as little as possible. In order to minimize E, we differentiate with respect to a, set the derivative equal to zero, and solve for a. The derivative of E is

$$dE/da = -h^2/ma^3 + e^2/a^2, \tag{38.11}$$

and setting $dE/da = 0$ gives for a the value

$$\begin{aligned} a_0 = h^2/me^2 &= 0.528 \text{ angstrom} \\ &= 0.528 \times 10^{-10} \text{ meter}. \end{aligned} \tag{38.12}$$

This particular distance is called the *Bohr radius*, and we have thus learned that atomic dimensions are of the order of angstroms, which is right: This is pretty good—in fact, it is amazing, since until now we have had no basis for understanding the size of atoms! Atoms are completely impossible from the classical point of view, since the electrons would spiral into the nucleus.

Now if we put the value (38.12) for a_0 into (38.10) to find the energy, it comes out

$$E_0 = -e^2/2a_0 = -me^4/2h^2 = -13.6 \text{ ev}. \tag{38.13}$$

What does a negative energy mean? It means that the electron has less energy when it is in the atom than when it is free. It means it is bound. It means it takes energy to kick the electron out; it takes energy of the order of 13.6 ev to ionize a hydrogen atom. We have no reason to think that it is not two or three times this—or half of this—or $(1/\pi)$ times this, because we have used such a sloppy argument. However, we have cheated, we have used all the constants in such a way that it happens to come out the right number! This number, 13.6 electron volts, is called a Rydberg of energy; it is the ionization energy of hydrogen.

So we now understand why we do not fall through the floor. As we walk, our shoes with their masses of atoms push against the floor with *its* mass of atoms. In order to squash the atoms closer together, the electrons would be confined to a smaller space and, by the uncertainty principle, their momenta would have to be higher on the average, and that means high energy; the resistance to atomic compression is a quantum-mechanical effect and not a classical effect.

Figure 3: Feynman lectures original discussion.

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

1. The system is composed by a single electron interacting with a nucleus of charge Z, hence we can use the results for the hydrogen atom and update the atomic number:

   $$E_{1s} = -13.6\text{eV} \cdot Z^2. \tag{11}$$

   Hence, we obtain E_{1s} equal to (in eV) 13.6 for H, 54.4 eV for He, 122.5 for Li, 871 for O, 9200 for Fe and 11446 for Cu; all very close to the experimental values.

2. At variance with the first question, an electron in a neutral atom not only interacts with the nucleus but also with all the others electrons of the atom through the Coulomb force. All electrons repel each other, so the potential energy due to the electron-electron interaction is overall positive. Hence, the total energy is higher, and the ionization energy smaller.

3. The first ionization energy is the smallest, because it is the least amount of energy required to ionize a neutral atom; typically involving the removal of one of the outermost electrons (feeling a “screened” nuclear charge).

4. We use the formula $v/c = \alpha Z$ and obtain 0.0073 for H, 0.19 for Fe, 0.58 for Au and Bi 0.61. So for most elements of the periodic table, the orbital speed v of a $1s$ electron is a sizeable fraction of the speed of light.

5. We just invert the formula given in the text, $Z = 0.2/\alpha = 27.4$. Hence, it is sufficient to take Ni ($Z = 28$) to reach 20% of the speed of light for the $1s$ electron.

6. We need to evaluate the value of the relativistic correction $\frac{Z^2\alpha^2}{4}$ for H, Fe, and Au. By using the corresponding value of Z for each element, we obtain 1.3×10^{-5} for H, 9.0×10^{-3} for Fe and 8.4×10^{-2} for Au. In all these cases we obtain that $\frac{Z^2\alpha^2}{4} \ll 1$. Hence, the correction to the $1s$ electron energy is very small for H and Fe, and even for Au which is much heavier than other two elements. Stronger relativistic effects show up for other atomic orbitals (especially in heavy elements), and they are related to the so-called *spin-orbit coupling effect*, which we will not discuss in this exercise.