The ground state energy for helium atom

This article closely follows the famous textbook *Introduction to Quantum Mechanics* by David J. Griffiths. We will obtain the approximate ground state energy of helium atom using perturbation theory.

The helium atom consists of two electrons and one nucleus. Each electron has charge $-e$ and the nucleus has charge $2e$. As the nucleus is much heavier than the two electrons, we can approximate the actual situation as the nucleus is not moving, and consider the wave functions of the electrons only. Given this, it is easy to see that the Hamiltonian is given as follows:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - ke^2 \left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) \tag{1}$$

where 1 denotes the first electron and 2 denotes the second electron. You also see that the last term is the potential energy due to the Coulomb interactions between two electrons. We will treat this term as perturbation and the other terms as unperturbed Hamiltonian.

In other words, the unperturbed Hamiltonian is given as follows:

$$H_0 = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - ke^2 \left(\frac{2}{r_1} + \frac{2}{r_2} \right) \tag{2}$$

It is an easy exercise to check that the solution to Schrödinger equation for the above unperturbed Hamiltonian is given as follows:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \tag{3}$$

where ψ_1 is the solution to the Schrödinger equation for the following Hamiltonian:

$$H_1 = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2ke^2}{r_1} \tag{4}$$

And, similarly for ψ_2. (**Problem 1.** Check this.)

Also, remember that we are calculating the ground state energy, which means that ψ_1 and ψ_2 must be also the ground state ones for the respective Hamiltonians. So, what is the ground state of (4) and its energy? We already obtained the one in our earlier article "Hydrogen atom," except for the fact that there we had $-ke^2/r$ instead of $-2ke^2/r_1$. So, all we need to do is changing ke^2 for $2ke^2$.

If you correctly solved the problems in "Hydrogen atom," you must have seen that the ground state wave function for the hydrogen atom is given as follows:

$$\psi_0 = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \tag{5}$$

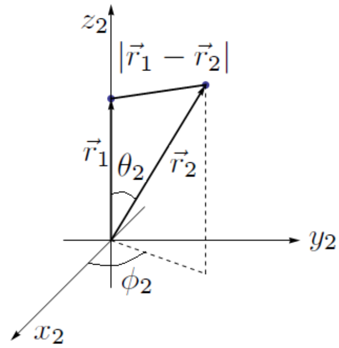

Figure 1: Coordinates for r_2

Now, from the formula for Bohr radius in that article, replacing ke^2 by $2ke^2$ is equivalent to replacing a_0 by $a_0/2$. Therefore, we have:

$$\psi_1(\vec{r}_1) = \frac{2\sqrt{2}}{\sqrt{\pi a_0^3}} e^{-r_1/a_0} \tag{6}$$

And similarly for ψ_2. Then, what would be the energy for this wave function? From the formula for the Rydberg unit energy in our earlier article "Hydrogen atom," we see that halving Bohr radius implies quadrupling the Rydberg unit of energy. This implies the energy for this wave function is -4Ry. Furthermore, as ψ_2 has the same energy, the total unperturbed energy is given by -8Ry. How about the wave function? Using (3), the unperturbed wave function is given by:

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{8}{\pi a_0^3} e^{-2(r_1+r_2)/a_0} \tag{7}$$

Remember also that the first order correction to the energy eigenvalue is given by the expectation value of the perturbed Hamiltonian in the unperturbed state. Therefore, the first order correction to the ground state energy V is given as follows:

$$\begin{aligned} V &= \int \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \psi(\vec{r}_1, \vec{r}_2) \psi^*(\vec{r}_1, \vec{r}_2)\, d^3\vec{r}_1\, d^3\vec{r}_2 \\ &= ke^2 \left(\frac{8}{\pi a_0^3} \right)^2 \int \frac{e^{-4(r_1+r_2)/a_0}}{|\vec{r}_1 - \vec{r}_2|}\, d^3\vec{r}_1\, d^3\vec{r}_2 \end{aligned} \tag{8}$$

The integration seems daunting, but it can be done by carefully choosing coordinates. See Fig.1. We will do the $\vec{r}_2$ integration first. You see that the coordinate system is chosen in such a way that $\vec{r}_1$ is pointing z axis, and θ_2 is the angle between $\vec{r}_1$ and $\vec{r}_2$. From the law of cosines, we have:

$$|\vec{r}_1 - \vec{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2} \tag{9}$$

So, we have:

$$I \equiv \int \frac{e^{-4r_2/a_0}}{|\vec{r}_1 - \vec{r}_2|}\, d^3\vec{r}_2 = \int \frac{e^{-4r_2/a_0}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}} r_2^2 \sin\theta_2\, dr_2 d\theta_2 d\phi_2 \tag{10}$$

The ϕ_2 integral is easy as the integrand doesn't depend on ϕ_2. So, it just has an effect of multiplying by 2π. The θ_2 integral gives:

$$\begin{aligned}
\int_0^\pi \frac{\sin\theta_2 d\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}} &= \frac{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta}}{r_1r_2}\Big|_0^\pi \\
&= \frac{1}{r_1r_2}\left(\sqrt{r_!^2+r_2^2+2r_1r_2}-\sqrt{r_!^2+r_2^2-2r_1r_2}\right) \\
&= \frac{1}{r_1r_2}\left[(r_1+r_2)-|r_1-r_2|\right] = \begin{cases} 2/r_1, & \text{if } r_2<r_1, \\ 2/r_2, & \text{if } r_2>r_1 \end{cases} \qquad (11)
\end{aligned}$$

Therefore, (10) becomes

$$\begin{aligned}
I &= 4\pi\left(\frac{1}{r_1}\int_0^{r_1} e^{-4r_2/a_0}r_2^2\,dr_2+\int_{r_1}^\infty e^{-4r_2/a_0}r_2\,dr_2\right) \\
&= \frac{\pi a_0^3}{8r_1}\left[1-\left(1+\frac{2r_1}{a_0}\right)e^{-4r_1/a_0}\right] \qquad (12)
\end{aligned}$$

Thus, (8) becomes:

$$V=\frac{8ke^2}{\pi a_0^3}\int\left[1-\left(1+\frac{2r_1}{a_0}\right)e^{-4r_1/a_0}\right]e^{-4r_1/a_0}r_1\sin\theta_1\,dr_1d\theta_1d\phi_1 \qquad (13)$$

At this point, if you remember our earlier article on spherical coordinate system, we have:

$$\int_{\phi_1=0}^{2\pi}\int_{\theta_1=0}^{\theta_1=\pi}\sin\theta_1\,d\theta_1d\phi_1=4\pi \qquad (14)$$

Also, the r_1 integral becomes:

$$\int_0^\infty\left[r_1e^{-4r_1/a_0}-\left(r_1+\frac{r_1^2}{a_0}\right)e^{-8r_1/a_0}\right]=\frac{5a_0^2}{128} \qquad (15)$$

Therefore,

$$V=\frac{8ke^2}{\pi a_0^3}(4\pi)\frac{5a_0^2}{128}=\frac{5ke^2}{4a_0}=\frac{5}{2}R_0 \qquad (16)$$

Therefore, for the first-order corrected ground state of Helium atom, we get:

$$E=-8\text{Ry}+\frac{5}{2}\text{Ry}=-\frac{11}{2}\text{Ry}=-75\text{eV} \qquad (17)$$

The actual value is -79 eV. Therefore, we see that the approximation is quite good.

Problem 2. Consider a system given by the following Hamiltonian.

$$H=-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2)+\frac{1}{2}m\omega^2(r_1^2+r_2^2)-\frac{\lambda}{4}m\omega^2|\vec{r}_1-\vec{r}_2|^2 \qquad (18)$$

Show that upon the following change of variables,

$$\vec{u}\equiv\frac{1}{\sqrt{2}}(\vec{r}_1+\vec{r}_2), \qquad \vec{v}\equiv\frac{1}{\sqrt{2}}(\vec{r}_1-\vec{r}_2) \qquad (19)$$

Hamiltonian can be re-written as follows:

$$H=\left[-\frac{\hbar^2}{2m}\nabla_u^2+\frac{1}{2}m\omega^2u^2\right]+\left[-\frac{\hbar^2}{2m}\nabla_v^2+\frac{1}{2}(1-\lambda)m\omega^2v^2\right] \qquad (20)$$

Problem 3. Compute the exact ground state energy for the above system assuming that $1 - \lambda > 0$.

Problem 4. Obtain the first-order corrected ground state energy by treating the term proportional to λ as a perturbation. Compare the answer obtained with the exact answer.

Summary

- We can find the approximate ground state of Helium by treating the Coulomb potential between each electron and nucleus as unperturbed Hamiltonian and the Coulomb potential between the two electrons as perturbed Hamiltonian.