

Exercise 10

Perturbation theory and variational approach

PLEASE SUBMIT YOUR SOLUTION BEFORE **THURSDAY, 2 FEBRUARY, 8.00 A.M.****1 Approximation methods applied to Helium atom (15 points)**

The Hamiltonian operator of the helium atom is

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

where the terms in the above expression represent the kinetic energy of the first electron, the electrostatic attraction between the nucleus and the first electron; the kinetic energy of the second electron, the electrostatic attraction between the nucleus and the second electron; and the electrostatic repulsion between the two electrons, respectively. If we neglect the last term, the Hamiltonian just becomes the sum of separate Hamiltonians for each electron and we would expect the wavefunction to be separable:

$$\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1)\psi(\mathbf{r}_2)$$

and the Hamiltonian would have eigenvalues

$$E = E_1 + E_2$$

If we consider the ground state, both electrons are in their lowest energy states with wavefunctions:

$$\psi_{100}(\mathbf{r}_i) = \sqrt{\frac{Z^3}{a_0^3\pi}} e^{-Z\frac{r_i}{a_0}} \quad i = 1, 2$$

with $Z = 2$. The eigenvalues of Hydrogen-like atoms are:

$$E_{0,Z} = -\frac{m_e e^4 Z^2}{32\pi^2 \epsilon_0^2 \hbar^2}$$

Then for a Helium atom the ground state is:

$$E^{(0)} = E_{0,2} + E_{0,2} = 8E_{0,1} = -4E_h$$

where $E_{0,1}$ is the ground state of the Hydrogen atom and $E_h = -\frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2}$ is the Hartree energy. This result is very different from the experimentally determined value $-2.9E_h$. This means that our initial approximation was wrong and that we cannot neglect the repulsive term between the electrons.

1.1 Perturbation theory

The Hamiltonian of the Helium atom, including the repulsive term, is not separable anymore. We can use the perturbation theory to improve our previous result, writing the ground state energy as sum of the unperturbed and repulsive term:

$$E = E^{(0)} + E^{(1)}$$

We already know the value of $E^{(0)}$, so we just need to compute the first order correction:

$$E^{(1)} = \langle \psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) | \hat{H}_{12} | \psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) \rangle = \frac{e^2}{4\pi\epsilon_0} \int_0^\infty \int_0^\infty d\mathbf{r}_1 d\mathbf{r}_2 \psi_{100}^*(\mathbf{r}_1) \psi_{100}^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) \quad (1)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$.

1. Simplify the integral (1), rewriting the term $1/r_{12}$ as an expansion in terms of spherical harmonics

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2)$$

where $r_{<}$ and $r_{>}$ are, respectively, the smaller and larger values of r_1 and r_2 . For example if $r_1 > r_2$, then $r_{<} = r_2$ and $r_{>} = r_1$. Setting correctly the integral, you should get the result

$$E^{(1)} = \frac{e^2}{4\pi\epsilon_0} \frac{16Z^6}{a_0^6} \int_0^{\infty} dr_1 r_1^2 e^{-2Zr_1/a_0} \int_0^{\infty} r_2^2 \frac{e^{-2Zr_2/a_0}}{r_{>}}$$

2. Solve the integral and show that

$$E^{(1)} = \frac{5}{8} Z \left(\frac{e^2}{4\pi\epsilon_0 a_0} \right) = \frac{5}{8} Z \left(\frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2} \right)$$

where we used $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$.

3. What is the ground state energy corrected with the perturbative term? Is the result improved?

1.2 Variational method

Another way to improve the unperturbed result $E^{(0)}$ is to use the variational method. To take into account the repulsive term, we now consider each electron interacting with the nuclear charge as if it was shielded by the other electron. This means that the "effective" nuclear charge is $Z_e < 2$. The effective charge will be our variational parameter, so our trial function is:

$$\phi_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{Z}_e) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) = \frac{Z_e^3}{a_0^3 \pi} e^{-Z_e(r_1+r_2)/a_0}$$

To find the optimal value of Z_e , it is necessary to minimize the total energy:

$$E(Z_e) = \langle \phi_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{Z}_e) | \hat{H} | \phi_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{Z}_e) \rangle$$

where \hat{H} is the Hamiltonian operator of the Helium atom.

1. Show that

$$E(Z_e) = Z_e^2 - \frac{27}{8} Z_e$$

2. What is the value of Z_e that minimizes $E(Z_e)$? What is the energy of the ground state with this approximation?

2 Linearized variational principle applied to Stark effect (10 points)

The Schrödinger equation (in atomic units) for a hydrogen atom in a uniform electric field F in the z direction is

$$\left(-\frac{1}{2} \nabla^2 - \frac{1}{r} + Fr \cos \theta \right) |\phi\rangle = (H_0 + Fr \cos \theta) |\phi\rangle = E_0(F) |\phi\rangle$$

Use the trial function

$$|\phi\rangle = c_1 |1s\rangle + c_2 |2p_z\rangle$$

where $|1s\rangle$ and $|2p_z\rangle$ are

$$|1s\rangle = \sqrt{\frac{1}{\pi}} e^{-r}$$

$$|2p_z\rangle = \sqrt{\frac{1}{32\pi}} r e^{-r/2} \cos \theta$$

to find an upper bound to $E_0(F)$. In constructing the matrix representation of H , you can avoid a lot of work by noting that

$$H_0|1s\rangle = -\frac{1}{2}|1s\rangle$$

$$H_0|2p_z\rangle = -\frac{1}{8}|2p_z\rangle$$

Using $(1+x)^{1/2} \simeq 1+x/2$, expand your answer in a Taylor series in F

$$E(F) = E(0) - \frac{1}{2}\alpha F^2$$

What is the value of α ?

Solve with pen and paper and report all important intermediate steps of your calculations. Hand in the report at the office 35.17 before next Wednesday at noon.