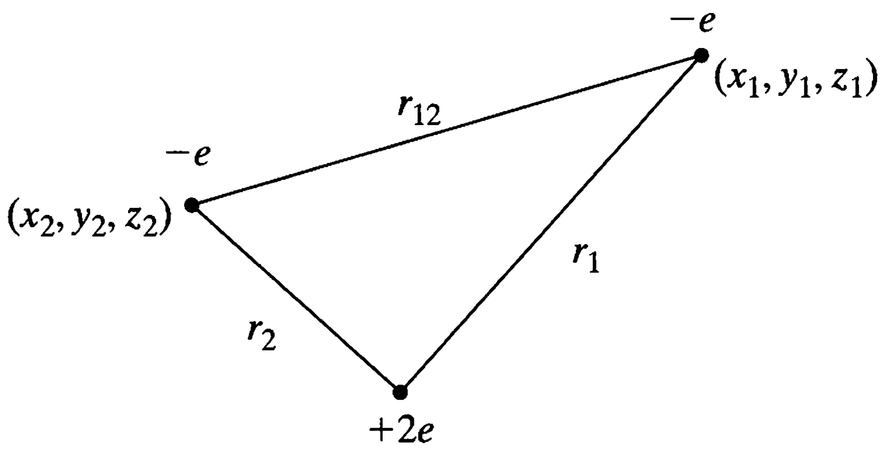
He-ATOM GROUND STATE (p. 252-253 Levine)

He atom has 2 electrons and a nucleus of charge $+2e$. We shall consider the nucleus to be at rest in the origin of the coordinate system.

The coordinates of electrons 1 and 2 are x_1, y_1, z_1 and x_2, y_2, z_2



The Hamiltonian for He is (from now on we implicitly mean $Z = 2$)

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze'^2}{r_1} - \frac{Ze'^2}{r_2} + \frac{e'^2}{r_{12}}$$

He-ATOM GROUND STATE (p. 252-253 Levine)

Because of the term containing r_{12}, the Schrödinger equation for He cannot be separated in any coordinate system, and we must use approximation methods

We can imagine to separate the Hamiltonian in the sum of 2 parts

$$\hat{H} = \hat{H}^0 + \hat{H}'$$

where

$$\begin{cases} \hat{H}^0 = -\dfrac{\hbar^2}{2m_e}\nabla_1^2 - \dfrac{Ze'^2}{r_1} - \dfrac{\hbar^2}{2m_e}\nabla_2^2 - \dfrac{Ze'^2}{r_2} \\ \hat{H}' = \dfrac{e'^2}{r_{12}} \end{cases}$$

He-ATOM GROUND STATE (p. 252-253 Levine)

The $\hat{H}^0$ term corresponds to the sum of 2 hydrogenlike Hamiltonians, one for each electron

$$\hat{H}^0 = \hat{H}_1^0 + \hat{H}_2^0$$

$$\hat{H}_1^0 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze'^2}{r_1} \qquad \hat{H}_2^0 = -\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze'^2}{r_2}$$

The wavefunction of the He atom, as well as that of a generic polielectronic atom, can be obtained through the so-called **orbital approximation**, which consists in neglecting interelectronic repulsions, namely $\hat{H}'$. In such a case, the Hamiltonian becomes $\hat{H}^0$ and we can solve the Schrödinger equation exploiting the separation of $\hat{H}^0$ in the sum of two independent operators, $\hat{H}_1^0$ and $\hat{H}_2^0$

He-ATOM GROUND STATE (p. 252-253 Levine)

In the orbital approximation, the Schrödinger equation is

$$\left(\hat{H}_1^0 + \hat{H}_2^0\right)\Psi = E\,\Psi$$

Eigenfunction

$$\Psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = \psi_a(r_1, \theta_1, \phi_1)\, \psi_b(r_2, \theta_2, \phi_2)$$

Eigenvalue

$$E = E_a + E_b$$

To find $\psi_a(r_1, \theta_1, \phi_1)$, $\psi_b(r_2, \theta_2, \phi_2)$, E_a and E_b, we must solve the following eigenvalue problems

$$\hat{H}_1^0 \psi_a(r_1, \theta_1, \phi_1) = E_a \psi_a(r_1, \theta_1, \phi_1)$$

$$\hat{H}_2^0 \psi_b(r_2, \theta_2, \phi_2) = E_b \psi_b(r_2, \theta_2, \phi_2)$$

He-ATOM GROUND STATE

(p. 252-253 Levine)

We know the solution of H-like problem. It is

$$E = -\frac{Z^2 \mu e'^4}{2n^2\hbar^2} \qquad n = 1, 2, 3, \ldots$$

$a \equiv \hbar^2/\mu e'^2$ Bohr radius

$$E_a = -\frac{Z^2 e'^2}{2an_1^2}, \quad n_1 = 1,2,3,\ldots \qquad E_b = -\frac{Z^2 e'^2}{2an_2^2}, \quad n_2 = 1,2,3,\ldots$$

Then $$E = -\frac{Z^2 e'^2}{2a}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$$

where a is the Bohr radius. Since we are looking for the lowest value of the energy, we set $n_1 = 1$ and $n_2 = 1$

$$E = -\frac{Z^2 e'^2}{a}$$

He-ATOM GROUND STATE (p. 252-253 Levine)

The wave functions ψ_a and ψ_b are

$$\psi_a(r_1, \theta_1, \phi_1) \equiv \psi_a(r_1) \equiv 1s(1) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} e^{-Zr_1/a}$$

$$\psi_b(r_2, \theta_2, \phi_2) \equiv \psi_b(r_2) \equiv 1s(2) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} e^{-Zr_2/a}$$

Denoting as $1s(1)\ 1s(2)$ the product of H-like $1s$ (normalized) functions for electrons 1 and 2, we write the wavefunction as

$$\Psi(1,2) = 1s(1)1s(2)$$

What happens if we consider Li, Be, …?

Li $\Psi(1,2,3) = 1s(1)1s(2)1s(3)$ $E = -\frac{3}{2}\frac{Z^2 e'^2}{a}$

Be $\Psi(1,2,3,4) = 1s(1)1s(2)1s(3)1s(4)$ $E = -2\frac{Z^2 e'^2}{a}$

No!

Pauli’s principle and hence electronic spin enter into play