

# Lecture 8: Radial Distribution Function, Electron Spin, Helium Atom

## 1 Radial Distribution Function

The interpretation of the square of the wavefunction is the probability density at  $r, \theta, \phi$ . This function is normalized as

$$\int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \psi_{n,l,m_l}^*(r, \theta, \phi) \psi_{n,l,m_l}(r, \theta, \phi) r^2 \sin \theta dr d\theta d\phi = 1$$

Substituting for the radial and angular parts we get

$$\int_0^{\infty} r^2 R_{n,l}^2(r) dr \int_0^{\pi} \int_0^{2\pi} Y_{l,m_l}^*(\theta, \phi) Y_{l,m_l}(\theta, \phi) \sin \theta d\theta d\phi = 1$$

If we want to find the probability of finding at a given  $r$  independent of angular distribution, it is convenient to define a quantity called the radial distribution function  $P(r)$  which is defined as

$$P(r) = r^2 R(r)^2$$

where  $R(r)$  is the radial part of the probability distribution function. The radial distribution gives the probability density at a distance  $r$  from the nucleus.

For example, we can use the 1s orbital and find out the distance  $r_{max}$  from the nucleus where the electron is most likely to be found by

$$P(r) \propto r^2 e^{-2r/a_0}$$

Using the condition for maximum as

$$\frac{dP}{dr} = 0 \quad \text{and} \quad \frac{d^2P}{dr^2} < 0$$

, we get  $r_{max} = a_0$ .

A simple extension of the Hydrogen atom is to Hydrogen-like atoms, which have a nuclear charge of  $Ze$  and one electron. For example,  $\text{He}^+$ ,  $\text{Li}^{2+}$  etc can be thought of as hydrogen-like atoms. The solutions look exactly the same with the nuclear charge replaced by  $Ze$ . The energy expression is

$$E_n = -\frac{m_e e^4 Z^2}{8h^2 \epsilon_0^2 n^2}$$

The wavefunctions are given by the same form as before with  $\rho = 2Zr/na_0$  and

$$\psi_{n,l,m_l}(r, \theta, \phi) = N_{n,l} \rho^l L_{n,l}(\rho) e^{-\rho/2} Y_{l,m_l}(\theta, \phi)$$

Thus only the radial part is affected since that is the only term that depends on the interaction.

We had briefly talked about Spin quantum number earlier. For electrons, since  $s = 1/2$ , we can have two states  $m_s = 1/2$  and  $m_s = -1/2$ . The wavefunctions corresponding to these two eigenvalues are functions of a spin variable  $s_i$  and are denoted by  $\alpha(s_i)$  and  $\beta(s_i)$  so that  $\hat{S}_z \alpha(s_i) = 1/2 \hbar \alpha(s_i)$  and  $\hat{S}_z \beta(s_i) = -1/2 \hbar \beta(s_i)$ . The total wavefunction is said to be a function of both spatial and spin coordinates and is referred to as a *spin orbital*

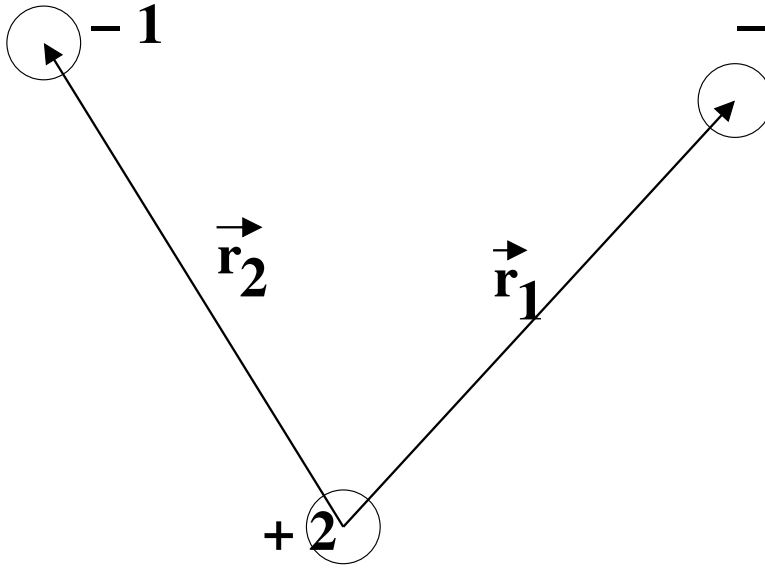
$$1s\alpha \equiv \psi_{1,0,0,1/2} \equiv \psi_{1,0,0}(r, \theta, \phi) \alpha(s_i)$$

Spin will become especially important for many-electron atoms. We will describe this when we come to the Helium atom.

## 2 Helium Atom

The Helium Atom is represented in the picture below. The Hamiltonian operator for this system can be written as

$$\hat{H}(\vec{R}, \vec{r}_1, \vec{r}_2) = -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 + \frac{e^2}{4\pi\epsilon_0} \left( -\frac{2}{|\vec{R} - \vec{r}_1|} - \frac{2}{|\vec{R} - \vec{r}_2|} + \frac{1}{|\vec{r}_2 - \vec{r}_1|} \right)$$



Assuming that the nucleus is much heavier and fixing it at the origin, we can write a simpler Hamiltonian as

$$\hat{H}(\vec{r}_1, \vec{r}_2) = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 + \frac{e^2}{4\pi\epsilon_0} \left( -\frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right)$$

where  $r_{12} = |\vec{r}_1 - \vec{r}_2|$ . The corresponding Schrödinger equation cannot be solved exactly since the Hamiltonian involves two coordinates of two particles which cannot be separated out due to the  $r_{12}$  term due to the electron-electron interactions. In fact, this interaction is the reason why all multi-electron systems cannot be solved analytically. This has resulted in development of very powerful and accurate numerical methods to treat systems which we shall not describe here. However, we will consider one very simple approximation that is related to the concept of shielding.

Suppose we assume that we can neglect the electron-electron repulsion. Then the Hamiltonian can be separated into two terms, one involving electron 1 and the other involving electron 2 and each can be solved exactly using Hydrogen-like functions with nuclear charge +2. The Schrödinger equation is now given by

$$-\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 \psi(\vec{r}_1, \vec{r}_2) + \frac{e^2}{4\pi\epsilon_0} \left( -\frac{2}{r_1} - \frac{2}{r_2} \right) \psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

which can be separated using  $\psi(\vec{r}_1, \vec{r}_2) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2)$ . This leads to two separate equations

$$\left(-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1}\right)\psi_1(\vec{r}_1) = E_1\psi_1(\vec{r}_1)$$

$$\left(-\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2}\right)\psi_2(\vec{r}_2) = E_2\psi_2(\vec{r}_2)$$

which are basically hydrogenic wavefunctions whose energies are given by

$$E_1 = -\frac{4m_e e^4}{8h^2\epsilon_0^2 n_1^2}$$

and similarly for  $E_2$ .

We can do a little better than this using the following argument. Let us assume that the effect of interelectron repulsion is to shield part of the nuclear charge from the other electron. Thus, the effective nuclear charge felt by the electrons is  $2 - \sigma$  where  $\sigma$  is a positive number less than 2, that estimates how much of the nuclear charge is shielded. Now we have the energy expression given by

$$E_1 = -\frac{(2 - \sigma)^2 m_e e^4}{8h^2\epsilon_0^2 n_1^2}$$

and similarly for  $E_2$ .

The value of  $\sigma$  can be derived from variational techniques that we do not describe here. However, we can calculate the best value of  $\sigma$  that fits experimental observations.

The wavefunction is given by

$$\psi_{n_1, l_1, m_1, n_2, l_2, m_2}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$$

$$= N_{n_1, l_1} R_{n_1, l_1}(r_1) Y_{l_1, m_1}(\theta_1, \phi_1) N_{n_2, l_2} R_{n_2, l_2}(r_2) Y_{l_2, m_2}(\theta_2, \phi_2)$$

where  $n_1, n_2 = 1, 2, 3, \dots$ , and so on. We should use a nuclear charge of  $2 - \sigma$ . The ground state wavefunction corresponds to both electrons in their  $n = 1$  states and is given by

$$\psi_{1,0,0,1,0,0}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$$

$$= 2 \left( \frac{2-\sigma}{a_0} \right)^{3/2} e^{-(2-\sigma)r_1/a_0} \left( \frac{1}{4\pi} \right)^{1/2} * 2 \left( \frac{2-\sigma}{a_0} \right)^{3/2} e^{-(2-\sigma)r_2/a_0} \left( \frac{1}{4\pi} \right)^{1/2}$$

We use this expression to explain the importance of spin and Pauli's exclusion principle. We notice that for the ground state we have

$$\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)$$

Thus we can say that the spatial part of the wavefunction is symmetric to exchange of electrons. The total wavefunction has to be antisymmetric to exchange of electrons. The total wavefunction is for each electron (spin orbital) is written as a product of the spatial part times the spin part. The spin part can be either  $\alpha$  or  $\beta$ . If the spin variables are denoted by  $s_1$  and  $s_2$ , then there are four possibilities for the total wavefunction.

$$\psi(\vec{r}_1, s_1, \vec{r}_2, s_2) = \psi_{1,0,0,1,0,0}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) \alpha(s_1) \alpha(s_2)$$

$$\psi(\vec{r}_1, s_1, \vec{r}_2, s_2) = \psi_{1,0,0,1,0,0}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) \beta(s_1) \beta(s_2)$$

$$\psi(\vec{r}_1, s_1, \vec{r}_2, s_2) = \psi_{1,0,0,1,0,0}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) \frac{1}{\sqrt{2}} (\alpha(s_1) \beta(s_2) + \beta(s_1) \alpha(s_2))$$

$$\psi(\vec{r}_1, s_1, \vec{r}_2, s_2) = \psi_{1,0,0,1,0,0}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) \frac{1}{\sqrt{2}} (\alpha(s_1) \beta(s_2) - \beta(s_1) \alpha(s_2))$$

Notice that the first 3 functions are symmetric to exchange of spin variables. The fourth one is antisymmetric. Since the spatial parts are symmetric, the spin part HAS to be antisymmetric so that the total wavefunction is antisymmetric. Thus the ground state wavefunction is given by

$$\psi(\vec{r}_1, s_1, \vec{r}_2, s_2) = \psi_{1,0,0,1,0,0}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) \frac{1}{\sqrt{2}} (\alpha(s_1) \beta(s_2) - \beta(s_1) \alpha(s_2))$$

This is a statement of Pauli's exclusion principle. If the first 3 quantum numbers ( $n, l, m_l$ ) for two electrons are identical, then the fourth one ( $m_s$ ) must necessarily be different for the two electrons.

Notice that  $\alpha(s_1) \beta(s_2)$  is not an allowed spin function since it is neither symmetric nor antisymmetric. If we have an excited states where the spatial parts are different, say  $\psi_1(\vec{r}_1)$  and  $\psi_2(\vec{r}_2)$ , then the only allowed spatial wavefunctions are

$$\frac{1}{\sqrt{2}} (\psi_1(\vec{r}_1) \psi_2(\vec{r}_2) + \psi_1(\vec{r}_2) \psi_2(\vec{r}_1))$$

and

$$\frac{1}{\sqrt{2}} (\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) - \psi_1(\vec{r}_2)\psi_2(\vec{r}_1))$$

The first one is symmetric to exchange of electrons and the second one is antisymmetric to exchange of electrons. They combine with antisymmetric and symmetric spin states respectively so that the total wavefunction is always antisymmetric to exchange of electrons.