Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 25
Nov 6th, 2013

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Objectives

- To introduce the study of Helium as a many-electron system.

- To introduce a shorthand notation of spin-orbitals.

- To introduce approximate many-electron wave-functions.

- To understand the consequence of indistinguishability of identical particles on wave-functions for many-electron system.

- To present the fact that the wave-function of many-electron systems must be antisymmetric.

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A two-electron system: The Helium atom

The helium atom consists of a nucleus and two electrons:

electron 1 r_{12} electron 2

r_1 r_2
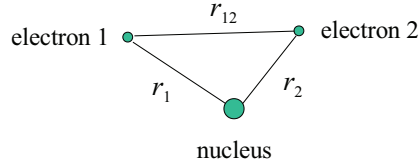
nucleus

If we are interested only in the motion of the electrons with respect to the nucleus, we can assume that the nucleus has an infinite mass and is stationary (fixed), i.e., has a zero kinetic energy. Then the Hamiltonian operator for the He atom can be written as

electron-electron repulsion

$Z = 2$ (nuclear charge)

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + \frac{1}{4\pi\varepsilon_0}\left(-\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}\right)$$

electron mass   kinetic energy of electrons 1 and 2   potential energy of electrons 1 and 2

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Shorthand notation for orbitals and spin-orbitals

Consider again the He atom. Suppose electrons 1 and 2 occupy the same 1s-like orbital and have opposite spins α and β.

Let us introduce the following simplifying notation

$$1s(1) \equiv \varphi_{1s}(\mathbf{r}_1), \quad 1s(2) \equiv \varphi_{1s}(\mathbf{r}_2)$$

$$\psi_A(1) \equiv \varphi_{1s}(\mathbf{r}_1)\alpha(1), \quad \psi_B(2) \equiv \varphi_{1s}(\mathbf{r}_2)\beta(2),$$

$$\mathbf{r}_i \equiv (x_i, y_i, z_i) \text{ or } (r_i, \theta_i, \varphi_i)$$

Then the spin-orbitals representing the states of electrons 1 and 2 may be written as

$$\psi_A(1) \quad \text{and} \quad \psi_B(2)$$

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Approximate many-electron wave-functions

The Schrödinger equation *cannot* be solved analytically for any atom or molecule with two or more electrons. For many-electron systems such as He we have to deal with *approximate* wave functions.

Consider the following candidate for the wave function of the He atom:

$$\psi(1,2) = \psi_A(1)\psi_B(2) \qquad\qquad (*)$$

The corresponding probability density:

$$\left|\psi(1,2)\right|^2 = \left|\psi_A(1)\psi_B(2)\right|^2 = \left|\psi_A(1)\right|^2\left|\psi_B(2)\right|^2$$

The motivation for choosing the product form is the multiplication rule for the joint probability of independent events:

If events A and B are independent, then

$$P(\text{A and B}) = P(\text{A})\cdot P(\text{B})$$

It turns out that the wave function $(*)$ is unacceptable.

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Indistinguishability of identical particles

Quantum particles such as electrons are not only identical to one another but also *indistinguishable*. This means that it is impossible to distinguish states of the system that differ only by the interchange of identical particles.

Consider a two-electron system. Mathematically, the requirement of indistinguishability of electrons means that the probability density $|\psi(1,2)|^2$ must not change under interchange of the electrons:

$$\left|\psi(1,2)\right|^2 = \left|\psi(2,1)\right|^2$$

Simple orbital products do not have this property. For example, for a system of two electrons we would have

$$\psi(1,2) = \psi_A(1)\psi_B(2)$$

so that

$$\left|\psi(1,2)\right|^2 = \left|\psi_A(1)\psi_B(2)\right|^2$$
$$\left|\psi(2,1)\right|^2 = \left|\psi_A(2)\psi_B(1)\right|^2 \neq \left|\psi(1,2)\right|^2$$

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Symmetric and antisymmetric functions

A functions $f(x_1,x_2)$ is said to be **symmetric** if

$$f(x_1, x_2) = f(x_2, x_1)$$

A functions $f(x_1,x_2)$ is said to be **antisymmetric** if

$$f(x_1, x_2) = -f(x_2, x_1)$$

Examples:

$f(x_1, x_2) = x_1 x_2 + 3x_1^2 x_2^2$ symmetric

$f(x_1, x_2) = e^{-x_1 - x_2}$ symmetric

$f(x_1, x_2) = x_1 - x_2$ antisymmetric

$f(x_1, x_2) = (x_1 - x_2)^2$ symmetric

$f(x_1, x_2) = x_1 x_2^3 - x_1^3 x_2 + x_1 x_2$ neither   7

Symmetric and antisymmetric spin-functions

We can write the following four spin functions for two electrons:

$\alpha(1)\alpha(2)$ symmetric

$\beta(1)\beta(2)$ symmetric

$\alpha(1)\beta(2)$ neither symmetric nor antisymmetric

$\beta(1)\alpha(2)$ neither symmetric nor antisymmetric

The last two functions are neither symmetric nor antisymmetric. However, we can remedy this by combining them (as a sum and a difference) and normalizing the result:

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right] \quad\quad \text{symmetric}$$

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \quad\quad \text{antisymmetric}$$

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Many-electron wave-functions must be antisymmetric

It is found experimentally that wave functions *of electrons* (including both spatial and spin coordinates) are <u>always</u> antisymmetric with respect to interchange of any two electrons. This fact was discovered in 1926 and is known as the **Pauli antisymmetry principle.**

Because of the antisymmetry requirement, the following wave function for the He atom is acceptable as an approximation

$$\psi(1,2) = \frac{1}{\sqrt{2}}\left[\psi_A(1)\psi_B(2) - \psi_B(1)\psi_A(2)\right]$$

normalization factor

but approximations such as

$$\psi(1,2) = \psi_A(1)\psi_B(2)$$

$$\psi(1,2) = \frac{1}{\sqrt{2}}\left[\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)\right]$$

are not acceptable.

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