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Approximate Method IV

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M.Sc. 2nd Semester
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SYMMETRIC AND ANTISYMMETRIC WAVE FUNCTION

ψ remains unchanged, the wave function is said to be symmetric with respect to interchange; if sign changes, the function is antisymmetric. Let us consider a system of N particles described by the wave function $\psi(1,2,3,1\ldots r\ldots s\ldots N)$ where 1 stands for all coordinates (position and spin) of particle 1 and similarly for 2 ... r ... s and N

The eigenvalues of $\hat{P}$ in turn lead to the following representation.

$$\psi(1,2,3\ldots r\ldots s\ldots N) = \pm\,\psi(1,2,3\ldots r\ldots s\ldots N)$$

Now we define symmetric and antisymmetric wave function, A wave function is said to be symmetric if the interchange of any pair of particles leaves the wavefunction unchanged (with eigen-value +1 of the operator $\hat{P}$)

i.e the eigenvalue of the operator $\hat{P}$ are $\pm$).

The function is antisymmetric if the interchange of any pair of particles changes the sign of ψ. It is however, an experimentally established fact that all the eigen functions of a given type of particles show the same exchange symmetry.

As an example, let us consider the case of the two electron system. If $\psi(1,2)$ represents the wave function corresponding to to the electron 1, 2 and $\psi_a(1)$ and $\psi_b(2)$ be the wave functions representing the states of individual electrons, then we can write

$$\psi_{(1,2)} = \psi_a(1)\,\psi_b(2) \quad -①$$

Where each wavefunction on the right-hand side is completly independent of the other, since the electrons are indistinguishable particles, we cannot specify the position of the electrons exactly. Therefore, an equally good wave function will be

$$\psi_{(2,1)} = \psi_a(2)\,\psi_b(1) \quad - (II)$$

As a particles are identical there should not be any difference in the Probability $|\psi|^2$ of the System when electrons are interchanged, i.e.

$$|\psi(1,2)|^2 = |\psi(2,1)|^2$$
$$\psi_{(1,2)} = \psi_{(2,1)} \quad \ldots\ (III)$$

When $\psi(1,2) = \psi(2,1)$, the Wave function is Symmetric. A wave function is said to be Symmetric if the interchange of a pair of particles leaves the sign of the wave function unchanged.

When $\psi_{(1,2)} = -\psi(2,1)$ the wavefunction is antisymmetric. The function is antisymmetric if the interchange of a pair of particles changes the sign of ψ.

NOW, taking into account the indistinguishability of the electron, the best representation for two electrons can be attained by taking the linear combination of equation I & II

$$\psi = \psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1)$$

Now, the symmetric wave function $\psi_{(S)}$ will be given by

$$\psi_S = \psi_a(1)\psi_b(2) + \psi_a(2)\cdot\psi_b(1) \quad \text{—(IV)}$$

and the antisymmetric wave funtion (ψ_A) by

$$\psi_A = \psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1) \quad \text{—(V)}$$

if electrons 1 and 2 are interchanged in these functions, it is obvious that ψ_S is unaltered but ψ_A' changes its sign.

$$\psi_A' = \psi_a(2)\psi_b(1) - \psi_a(1)\psi_b(2) - [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)]$$

When the two electrons have the same set of orbital quantum numbers n, l, m, e.g, the ground state helium atom $(1s^2)$, then $\psi_a = \psi_b$ so that $\psi_{(1,2)} = \psi_{1s}(1)\psi_{1s}(2)$. If the electrons are interchanged, the functions $\psi_{(1,2)}$ will be symmetric and will represent the same state of the system, i.e

$$\psi_{1s}(1)\psi_{1s}(2) = \psi_{1s}(2)\psi_{1s}(1) \quad \text{—(VI)}$$

So, only one spatial state is possible in the case of the ground state helium atom. Till now we have considered only the orbital wave function but electrons do posses spin as well. So, the complete wavefunction for an electron will be the product of the orbital wave-function and the spin function $\alpha(S)$ or $\beta(S)$

$$\psi = \psi_{orb.}\,\alpha(s) \text{ or } \psi_{orb}\,\beta(s) \quad -(VII)$$

where s is the spin quantum number, having either $+\frac{1}{2}$ or $-\frac{1}{2}$ value, so symmetric or antisymmetric character of a wavefunction must be on the basis of the equation (VII) - can be written as

$$\alpha(1)\,\alpha(2),\ \beta(1)\,\beta(2),\ \alpha(1)\,\beta(2)\cdot\alpha(2)\,\beta(1) \quad -(VIII)$$

Out of these four spin function, the last two are not acceptable because they distinguish - between the electron. Electrons are identical to one another and there is no way of experimentally determining which electron has spin $+\frac{1}{2}$ and which has spin $-\frac{1}{2}$, Hence, the third and fourth spin functions are replaced by their linear combinations, and are given by

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\,\beta(2) \pm \alpha(2)\,\beta(1)\right. \quad -(IX)$$

where $\frac{1}{\sqrt{2}}$ is the normalization const. The two electron system become.

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

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

The first three spin funtion are symmetric and the last one is antisymmetric with respect to interchange of electrons.

The antisymmetric character of the electronic wave function can be best represented by the use of a determinant form, called Slater determinant. Thus, the ground state helium atom may be represented by

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s}(1)\,\alpha(1) & \psi_{1s}(1)\,\beta(1) \\ \psi_{1s}(2)\,\alpha(2) & \psi_{1s}(2)\,\beta(2) \end{vmatrix} \quad \text{—(XI)}$$

If we expand this determinant, we get -

$$\frac{1}{\sqrt{2}} \left[\psi_{1s}(1)\,\alpha(1)\,\psi_{1s}(2)\,\beta(2) - \psi_{1s}(1)\,\beta(1)\,\psi_{1s}(2)\,\alpha(2) \right.$$

$$= \frac{1}{\sqrt{2}} \left[\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1) \right] \psi_{1s}(1)\,\psi_{1s}(2)$$

Which is same as equation — (IX)