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WAVE FUNCTIONS OF MANY-ELECTRON SYSTEMS

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A general form has been derived for a wave function which is an eigenfunction of S^2 and S_z and satisfies the Pauli principle. An expression is given for the Schrödinger wave function of the system constructed from one-electron functions.

1. INTRODUCTION

In many problems in the quantum mechanics of many-electron systems one can in first approximation neglect the spin dependence of the Hamiltonian. Then the determination of the wave function consists in the approximate solution of the Schrödinger equation containing only spatial coordinates. However, the symmetry properties of the Schrödinger wave function depend on the total spin of the system. Fock[1] derived the symmetry conditions which the Schrödinger wave function has to satisfy in order for the total wave function of the system to be an eigenfunction of S^2 (**S** is the total spin operator) and to satisfy the Pauli principle. Fock showed that these conditions are satisfied by a product of determinants consisting of one-electron functions, if the same coordinate function is taken for every pair of electrons with opposite spins. However, there exist methods of solving the Schrödinger equation which do not introduce only one-electron functions (the method of partial separation of variables, the adiabatic method, etc.). On the other hand, even in the approximation that uses one-electron functions we cannot use the simple product of determinants in those cases when two electrons with opposite spins are known to be in different states (e.g., the case of the singlets of the alkaline-earth elements).

In these cases it is often difficult to construct from the approximate solution of the Schrödinger equation a Schrödinger function which satisfies the Fock conditions, or a total wave function of the system. The method of the Young scheme[2] and the method of Abarenkov[3] have the disadvantage that they do not give sufficiently convenient expressions for the total and the Schrödinger wave function of the system.

We shall show below that the Schrödinger and the total wave functions are most conveniently constructed from a given approximate solution of the Schrödinger equation with the help of operators transforming an arbitrary function into an eigenfunction of J^2 and J_z (**J** is the spin, orbital, or total angular momentum of the system in units of $\hbar$). We shall call them the characteristic operators for J^2 and J_z.

2. THE CHARACTERISTIC OPERATORS FOR J^2 AND J_z AND THEIR PROPERTIES

We introduce the operator A^j_{pq}, which operates on the function $g(x_1, \ldots, x_n)$ according to

$$A^j_{pq} g = \int\limits_0^{2\pi} d\varphi \int\limits_0^{2\pi} d\psi \int\limits_0^{\pi} \sin\vartheta \, d\vartheta \cdot \overline{f^j_{pq}}(\varphi, \vartheta, \psi) P_{\varphi,\vartheta,\psi} g. \quad (1)$$

Here $x_1, \ldots, x_n$ are the coordinates of the particles of the system (both spin and spatial), $P_{\varphi,\vartheta,\psi}$ is the rotation operator of the coordinate system given by the Eulerian angles φ, ϑ, ψ. It operates either on the spin or on the spatial coordinates, or on both, depending on the character of the angular momentum J. Also,

$$f^j_{pq} = (2\pi)^{-2} e^{ip\varphi} e^{iq\psi} F^j_{pq}(\vartheta); \quad (2a)$$

$$F^j_{pq} = M^{ab}_n \left(\cos\frac{\vartheta}{2}\right)^b \left(i \sin\frac{\vartheta}{2}\right)^a G^{ab}_n(\cos\vartheta); \quad (2b)$$

$$G^{ab}_n(x) = \frac{(-1)^n}{n!\,2^n}(1-x)^{-a}(1+x)^{-b}\frac{d^n}{dx^n} \times (1-x)^{a+n}(1+x)^{b+n}; \quad (2c)$$

$$M^{ab}_n = \frac{a+b+2n+1}{2}\sqrt{\frac{n!\,(a+b+n)!}{(a+n)!\,(b+n)!}}; \quad (2d)$$

$$a = |p-q|; \; b = |p+q|; \qquad j = n + \frac{a+b}{2}; \; n = 0, 1, 2\ldots \quad (2e)$$

Each of the numbers p and q may thus take any value from −j to j in steps of unity, $G^{ab}_n(x)$ is the Jacobi polynomial.[4] The functions $f^j_{p,q}$ are, up to a numerical factor, the matrix elements of the irreducible representation of the rotation group.[5] In fact,

$$f^j_{pq}(\varphi, \vartheta, \psi) = \frac{2j+1}{8\pi^2} D^j(P_{\varphi, \vartheta, \psi})_{pq}.$$

We shall in the following assume that the function g may be expanded into a series in terms of eigenfunctions of J^2 and J_z, corresponding to either only integer or only half odd-integer values j. Group theory[5,6] yields the following fundamental property of the operators A^j_{pq}.

If $g^{j'}_m$ is an eigenfunction of J^2 and J_z with eigenvalues $j'(j'+1)$ and m, respectively, then

$$A^j_{pq} g^{j'}_m = \delta_{jj'} \delta_{qm} g^j_p. \tag{3}$$

From this we derive the following properties:

$$J^2 A^j_{pq} = A^j_{pq} J^2 = j(j+1) A^j_{pq}, \tag{4}$$

$$J_z A^j_{pq} = p A^j_{pq}, \tag{5}$$

$$A^j_{pq} J_z = q A^j_{pq}, \tag{6}$$

$$(J_x \pm iJ_y) A^j_{pq} = \sqrt{(j \mp p)(j \pm p + 1)}\, A^j_{p \pm 1, q}, \tag{7}$$

$$A^j_{pq}(J_x \pm iJ_y) = \sqrt{(j \pm q)(j \mp q + 1)}\, A^j_{p, q \mp 1}, \tag{8}$$

$$A_{pt} A^{j'}_{t'q} = \delta_{jj'} \delta_{tt'} A^j_{pq}, \tag{9}$$

$$\sum_{j, p} A^j_{pp} = 1, \tag{10}$$

$$A^{j+}_{pq} = A^j_{qp}. \tag{11}$$

In the last formula, A^{j+}_{pq} is the hermitian conjugate operator to A^j_{pq}. In formulas (3) to (11) the values j, j' can be either all integers, or all odd half-integers.

If the Hamiltonian of the system H is invariant under the rotations $P_{\varphi\vartheta\psi}$, then clearly

$$H A^j_{pq} = A^j_{pq} H. \tag{12}$$

In this case the operators A^j_{pq} have the following extremal property. Let g_m be an approximate solution of the Schrödinger equation which is not an eigenfunction of J^2, but which is an eigenfunction of J_z with eigenvalues m. We can construct new functions from g_m by a rotation of the coordinate system. All functions obtained in this way give the same expectation value for the energy.

We form

$$u = \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_0^{\pi} \sin\vartheta\, d\vartheta \cdot f(\varphi, \vartheta, \psi)\, P_{\varphi\vartheta\psi} g_m \tag{13}$$

and take $f(\varphi, \vartheta, \psi)$ such that the functional

$$I = (u, Hu) \text{ with the condition } (u, u) = 1 \tag{14}$$

has an extremal value. For this purpose we expand $f(\varphi, \vartheta, \psi)$ in a series of the functions f^j_{pq}:

$$f = \sum_{j, p, q} a^j_{pq} f^j_{pq}(\varphi, \vartheta, \psi),$$

from where we get

$$u = \sum_{j, p} a^j_{pm} A^j_{pm} g_m.$$

Taking a^j_{pm} as the variation parameters and using the properties of the operators A^j_{pm}, we can easily show that the functional (14) has an extremal value for the functions

$$u^j_{pm} = A^j_{pm} g_m / (A^j_{mm} g_m, g_m), \tag{15}$$

and the corresponding energy values are given by the expression

$$E_{jm} = (A^j_{mm} g_m, H g_m) / (A^j_{mm} g_m, g_m), \tag{16}$$

where, according to (22), $j = |m| + n$, $n = 0, 1, 2, \ldots$ This property of the operators A^j_{pq} was recently used in the theory of the nucleus.[7]

3. THE SCHRÖDINGER WAVE FUNCTION FOR THE MANY-ELECTRON SYSTEM

In this section A^s_{pq} denotes the characteristic operator for S^2 and S_z. ($\mathbf{S}$ is the vector of the spin angular momentum of the system of N electrons in units of $\hbar$).

We introduce two functions of the z component of the spin of electron i (we call this component $\frac{1}{2}\sigma_i$):

$$u_i = \begin{matrix} 1 & \text{for } \sigma_i = -1 \\ 0 & \text{for } \sigma_i = 1 \end{matrix}, \quad v_i = \begin{matrix} 0 & \text{for } \sigma_i = -1 \\ 1 & \text{for } \sigma_i = 1 \end{matrix}. \tag{17}$$

We use the notation

$$e_{\alpha_1} \ldots \alpha_k = u_1 \ldots u_k v_{k+1} \ldots v_N. \tag{18}$$

This is an eigenfunction of S_z with eigenvalues s, if $k = N/2 - s$.

An arbitrary function of the spin variables with a given value for the projection of the total spin can be expanded in terms of the functions $e_{\alpha_1 \ldots \alpha_k}$ with various sets $\alpha_1, \ldots, \alpha_k$. Hence, because of the properties of the operator A^s_{pq}, an arbitrary function of the spin coordinates which is an eigenfunction of S^2 and S_z with eigenvalues $s(s+1)$ and m, respectively, can be represented as a linear combination of functions $A^s_{ms} e_{\alpha_1 \ldots \alpha_k}$.

Let now $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ be an approximate solution of the Schrödinger equation which is independent of spin. The problem is now to use this solution in order to construct the total wave function for the system satisfying the Pauli principle and being an eigenfunction of S^2 and S_z (we shall in the following call a function satisfying these three conditions, a "correct" function). It follows that the most general "correct" function which can be constructed from Ψ is an arbitrary linear combination of terms

$$A^s_{ms} A \Psi(\mathbf{r}_1 \ldots \mathbf{r}_N)\, e_{\alpha_1 \ldots \alpha_k} \tag{19}$$

with various sets $\alpha_1 \ldots \alpha_k$ (A is the antisymmetrization operator). We may take the numbers $\alpha_1 \ldots \alpha_k$ to give the places in the function Ψ corresponding to a negative spin projection. The remaining places correspond to positive spin projection. Thus the most general "correct" function derivable from Ψ is an arbitrary linear combination of expressions obtained from

$$A^s_{ms} A\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) e_{1\ldots k} \tag{20}$$

by interchanging the numbers designating the places corresponding to the negative spin projection in the function Ψ.

We now consider the principal case, when Ψ is expressed as a product of one-electron functions:

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \Psi_1(\mathbf{r}_1)\Psi_2(\mathbf{r}_2)\ldots\Psi_N(\mathbf{r}_N). \tag{21}$$

In this case the position number of the argument coincides with the number of the one-electron function. The first k functions in (20) correspond to negative spin projection; the remaining functions, to positive spin projection. Furthermore, $h_k = A\Psi_1(r_1)\ldots\Psi_N(r_N)e_{1\ldots k}$ is simply the Slater determinant:

$$h_k = \begin{vmatrix} \Psi_1(\mathbf{r}_1)u_1 & \ldots & \Psi_1(\mathbf{r}_N)u_N \\ \ldots & \ldots & \ldots \\ \Psi_k(\mathbf{r}_1)u_1 & \ldots & \Psi_k(\mathbf{r}_N)u_N \\ \Psi_{k+1}(\mathbf{r}_1)v_1 & \ldots & \Psi_{k+1}(\mathbf{r}_N)v_N \\ \ldots & \ldots & \ldots \\ \Psi_N(\mathbf{r}_1)v_1 & \ldots & \Psi_N(\mathbf{r}_N)v_N \end{vmatrix}. \tag{22}$$

We note that

$$P_{\varphi\vartheta\psi}u_i = \beta v_i + \delta u_i; \quad P_{\varphi\vartheta\psi}v_i = \alpha v_i + \gamma u_i,$$

where α, β, γ, δ are the Cayley-Klein parameters:

$$\begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix} = \begin{pmatrix} \cos\frac{\vartheta}{2} e^{i(\varphi+\psi)/2} & i\sin\frac{\vartheta}{2} e^{i(\varphi-\psi)/2} \\ i\sin\frac{\vartheta}{2} e^{i(\psi-\varphi)/2} & \cos\frac{\vartheta}{2} e^{-i(\varphi+\psi)/2} \end{pmatrix}. \tag{23}$$

Using the properties of the operator A^s_{pq}, we easily obtain

$$A^s_{ms}h_k = \sqrt{\frac{(s+m)!}{(s-m)!\,(2s)!}}\,(S_x - iS_y)^{s-m} A^s_{ss}h_k, \tag{24}$$

$$A^s_{ss}h_k = \sum_{(\alpha)} \Phi^s_{\alpha_1\ldots\alpha_k} e_{\alpha_1\ldots\alpha_k}, \tag{25}$$

where we sum over all possible sets $\alpha_1 \ldots \alpha_k$, and

$$\Phi^s_{1,2\ldots k} = \frac{2s+1}{2}\int_0^\pi \left(\cos\frac{\vartheta}{2}\right)^{2s} \sin\vartheta\, d\vartheta \begin{vmatrix} \Psi_1(\mathbf{r}_1)\cos\frac{\vartheta}{2} \ldots \Psi_1(\mathbf{r}_k)\cos\frac{\vartheta}{2} & \Psi_1(\mathbf{r}_{k+1})\, i\sin\frac{\vartheta}{2} \ldots \Psi_1(\mathbf{r}_N)\, i\sin\frac{\vartheta}{2} \\ \ldots & \ldots \\ \Psi_k(\mathbf{r}_1)\cos\frac{\vartheta}{2} \ldots \Psi_k(\mathbf{r}_k)\cos\frac{\vartheta}{2} & \Psi_k(\mathbf{r}_{k+1})\, i\sin\frac{\vartheta}{2} \ldots \Psi_k(\mathbf{r}_N)\, i\sin\frac{\vartheta}{2} \\ \Psi_{k+1}(\mathbf{r}_1)\, i\sin\frac{\vartheta}{2} \ldots \Psi_{k+1}(\mathbf{r}_k)\, i\sin\frac{\vartheta}{2} & \Psi_{k+1}(\mathbf{r}_{k+1})\cos\frac{\vartheta}{2} \ldots \Psi_{k+1}(\mathbf{r}_N)\cos\frac{\vartheta}{2} \\ \ldots & \ldots \\ \Psi_N(\mathbf{r}_1)\, i\sin\frac{\vartheta}{2} \ldots \Psi_N(\mathbf{r}_k)\, i\sin\frac{\vartheta}{2} & \Psi_N(\mathbf{r}_{k+1})\cos\frac{\vartheta}{2} \ldots \Psi_N(\mathbf{r}_N)\cos\frac{\vartheta}{2} \end{vmatrix} \tag{26}$$

$\Phi^s_{\alpha_1\ldots\alpha_k}$ differs from (26) in that $\cos(\vartheta/2)$ appears in those elements of the determinant which stand at the intersection of the columns with numbers $\alpha_1 \ldots \alpha_k$ and the first k rows, and also in the elements remaining after these columns and rows are crossed out. All other elements contain $i\sin(\vartheta/2)$.

Formula (26) gives an expression for the Schrödinger function corresponding to the "correct" function (24) (by Schrödinger function we mean the function of spatial coordinates which may be substituted for the total wave function in the calculation of the matrix elements of symmetric, spin-independent operators).

If the first k one-electron functions are linear combinations of the remaining N-k functions the right hand side of (26) reduces to the usual product of determinants. In the general case the right hand side of (26) may easily be written in the form of a linear combination of products of determinants, by expanding the determinant under the integral according to the minors constructed from the first k rows.

We introduce a general formula for the result of operating on the Slater determinant with the operator A^s_{pq}:

$$A^s_{pq}h_l = \sum_{(\alpha)} \Phi^{spq}_{\alpha_1\ldots\alpha_m} e_{\alpha_1\ldots\alpha_m}; \quad l = \frac{N}{2} - q; \quad m = \frac{N}{2} - p, \tag{25a}$$

$$\Phi^{spq}_{\alpha_1\ldots\alpha_m} = \int_0^\pi \overline{F^s_{pq}}(\vartheta)\, \Delta^l_{\alpha_1\ldots\alpha_m} \sin\vartheta\, d\vartheta, \tag{26a}$$

where F^s_{pq} is given by (26), and $\Delta^l_{\alpha_1\ldots\alpha_m}$ is a determinant differing from the determinant in (26) only in that $\cos(\vartheta/2)$ appears in the elements standing at the intersection of the columns with numbers $\alpha_1 \ldots \alpha_m$ and the first l rows, and also in the elements remaining after these columns and rows are crossed out. The other elements contain i sin ($\vartheta/2$). $\Phi^{spq}_{\alpha_1\ldots\alpha_m}$ is the Schrödinger function for the "correct" function (25a).

$A^s_{pq}h_l$ can also be expressed as a linear combination of Slater determinants $h_{\alpha_1\ldots\alpha_m}$, which differ from h_l only in that here the spin factors u appear in the elements of the rows with numbers $\alpha_1\ldots\alpha_m$, while the elements of the remaining rows contain the spin factors v:

$$A^s_{pq}h_l = \sum_{(\alpha)} C^{st_\alpha}_{pq} h_{\alpha_1\ldots\alpha_m}, \tag{27}$$

where we sum over all sets $\alpha_1\ldots\alpha_m$. Here

$$C^{st_\alpha}_{pq} = \int_0^\pi \overline{F^s_{pq}(\vartheta)} \left(\cos\frac{\vartheta}{2}\right)^{p+q+2t_\alpha} \left(i\sin\frac{\vartheta}{2}\right)^{N-p-q-2t_\alpha} \sin\vartheta\, d\vartheta; \tag{28}$$

t_α is the number of common elements in the sets $1, 2, \ldots, l$ and $\alpha_1, \ldots, \alpha_m$; l and m are related to p and q through (25a). A special case of the expansion (27) is formula (15) in Loewdin's paper.[8] We note that his projection operators ${}^{2l+1}\Theta$ are related to the operators A^s_{pq} in the following way:

$$ {}^{(2s+1)}\Theta = \sum_{p=-s}^{s} A^s_{pp}. \tag{29}$$

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