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Group-theoretical Methods in Quantum-chemical Calculations

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Group-theoretical methods used in quantum chemistry have been reviewed. The method for constructing the basis functions of the irreducible representations of finite groups by means of projection operators has been examined in detail. Particular attention has been paid to the use of the theory of permutation groups for constructing the eigenfunctions of the operator of the square of the total spin S^2 and obtaining closed equations for the matrix elements of the Hamiltonian in a state having a definite value of S. A method has been described for finding the allowed molecular states and the orders of the secular equations obtained in variation quantum-chemical calculations. The use of the mathematical apparatus of continuous groups in quantum-chemical calculations has been discussed.
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I. INTRODUCTION

The methods of group theory are at present being widely used in chemistry. The application of the abstract apparatus of group theory to specific problems of the structure of molecules is based on the symmetry properties of the systems studied. Two types of symmetry can be distinguished: a) symmetry with respect to spatial transformations, and b) symmetry with respect to the permutation of identical particles. Both types of symmetry emerge from the properties of the Schrödinger equation for many-electron systems.

In addition to the symmetry with respect to the transformation of the coordinates of real three-dimensional space, for a number of problems the Schrödinger equation may exhibit symmetry with respect to the transformation of variables in a fictitious n-dimensional space. In these cases, the term latent or dynamic symmetry is used. A widely studied example is the symmetry, discovered by Fock, of the Schrödinger equation for the hydrogen atom, written in the momentum representation, in a four-dimensional space of dynamic variables.

Many familiar concepts used in quantum chemistry are based on the group-theoretical properties of many-electron systems. Thus Pauli's principle for many-electron systems is related to the forbidden character of all irreducible representations of the permutation group of the electrons except the antisymmetric. The conservation with time of various quantities characterising the state of a molecule, such as the spin, momentum, and orbital angular momentum of an isolated molecule, is related to the fact that these quantities are characterised by the irreducible representations of groups whose operations leave the Hamiltonian of the system invariant.

The introduction of the apparatus of group theory makes it possible to explain qualitatively a number of properties of the systems being considered without resorting to numerical calculations, for example to determine the degree of degeneracy and symmetry of the allowed states and the probability of quantum transitions (selection rules). At the same time, group theory simplifies the quantitative calculation considerably, since it makes it possible to obtain effective equations for calculating the matrix elements of the physical quantities being sought.

In the present review, attention is paid to both aspects of the application of the apparatus of group theory. The construction of the basis functions of irreducible representations by means of projection operators is examined in detail. This method makes it possible to standardise this procedure completely, and does not require the solution of systems of equations or the introduction of intuitive considerations for the selection of independent functions, as is often suggested in many quantum-chemical handbooks.

Particular attention is paid in the present review to the construction of the eigenfunctions of the operator of the square of the total spin S^2. In the case where spin is preserved, the antisymmetric total wavefunction, which is an eigenfunction of the operator S^2, can be represented as a linear combination of the products of coordinate and spin functions, transforming as the conjugate irreducible representations of the permutation group. This makes it possible to develop effective methods for classifying the molecular states obtained in a specific quantum-chemical calculation, that is to find the allowed types of point symmetry and the corresponding values of the electron spin (see Section V). The secular equation of the variational problem breaks down into secular equations for each molecular multiplet.

For calculating the properties of a molecule which are independent of spin interactions, it is sufficient to know only the coordinate wavefunction, the permutation symmetry of which is related unambiguously to the value of the total electron spin. This approach was proposed by the author of the present review[1-3] (the method of coordinate wavefunctions) and independently by Matsen[4,5] (spin-free quantum chemistry). The use of coordinate wavefunctions instead of Slater determinants makes it possible to obtain closed equations for the matrix elements of the Hamiltonian in states with a definite value of the spin S.

Section VI of the present review gives these expressions for the case of the configuration of non-orthogonal orbitals. The equations for the configurations of orthogonal orbitals are obtained as particular cases of the general equations. These equations are subsequently used (Section VII) to derive self-consistent field spin-projected equations for the case of an arbitrary molecular configuration containing both closed and open shells.

In addition to the traditional point groups, and also permutation groups, in recent years use has been made of unitary groups[6-9]. The final section of the present review describes an approach to the calculation for many-electron systems based on the use of the apparatus of unitary groups, and discusses its possibilities.

II. SYMMETRY GROUP OF THE SCHRÖDINGER EQUATION. CONSTRUCTION OF THE BASIS FUNCTIONS OF IRREDUCIBLE REPRESENTATIONS

All applications of group theory in quantum mechanics are based on the result obtained by Wigner[10] in 1927, often called Wigner's theorem: the wavefunctions belonging to a given energy level transform as a representation of the symmetry group of the Schrödinger equation, that is as a representation of the group whose operations leave the Schrödinger equation invariant.

The Schrödinger equation of an isolated quantum-mechanical system is invariant with respect to the operations of the following groups:

a) the group of displacements in space of the system as a whole; the irreducible representations of this group are characterised by the value of the momentum of the system,

b) the group of orthogonal transformations in three-dimensional space, consisting of rotations about any axis passing through the centre of gravity of the system, taken as the origin of coordinates, and inversion with respect to the origin of coordinates; the irreducible representations of this group are characterised by the values of the angular momentum of the system and the parity of the basis functions,

c) the group of permutations of identical particles; the characteristics of the irreducible representations of a permutation group will be discussed below.

If the system is placed in an external potential field, the symmetry groups of the Schrödinger equation are as follows:

a) the symmetry group of the external field,

b) the group of the permutations of identical particles.

In the adiabatic approximation, the motion of the electrons in a molecule can be regarded as taking place in the external field of stationary nuclei situated in equilibrium positions†. The potential field in this case exhibits the symmetry of the point group of the molecule. Thus according to Wigner's theorem, the electronic wave-functions of the molecule belonging to a given energy level should transform as the irreducible representations of the symmetry point group of the molecule and the permutation group of the electrons. There are no restrictions on possible irreducible representations of the point group, but of the irreducible representations of the permutation group of the electons, only the antisymmetric is realised. This last restriction is usually called the Pauli principle.

To find the basis function of the representation $\Gamma^{(\alpha)}$ of a given point group G of order g it is sufficient to apply the operator

$$\varepsilon_{ik}^{(\alpha)} = \frac{f_\alpha}{g} \sum_R \Gamma_{ik}^{(\alpha)}(R)^* R \tag{1}$$

to an arbitrary function ψ_0,

$$\psi_{ik}^{(\alpha)} = \varepsilon_{ik}^{(\alpha)} \psi_0 = \frac{f_\alpha}{g} \sum_R \Gamma_{ik}^{(\alpha)}(R)^* R\psi_0. \tag{2}$$

In Eqn. (2), $\Gamma_{ik}^{(\alpha)}(R)$ denotes the matrix element of the representation $\Gamma^{(\alpha)}(R)$ corresponding to the operation $R \in G$; the summation is carried out over all elements k of the group; f_α gives the dimension of the representation.

It can readily be shown[14] that for an arbitrary operation $Q \in G$

$$Q\psi_{ik}^{(\alpha)} = \sum_l \Gamma_{li}^{(\alpha)}(Q^{-1})^* \psi_{lk}^{(\alpha)}. \tag{3}$$

For unitary representations

$$Q\psi_{ik}^{(\alpha)} = \sum_l \Gamma_{li}^{(\alpha)}(Q)\, \psi_{lk}^{(\alpha)}, \tag{4}$$

that is the functions $\psi_{ik}^{(\alpha)}$ are transformed by the operations of the group according to the ith column of the irreducible representation $\Gamma^{(\alpha)}$, and the set of f_α functions $\psi_{ik}^{(\alpha)}$ with fixed index k forms the basis of the irreducible representation $\Gamma^{(\alpha)}$. Thus by changing the values of the index k it is possible to form f_α independent bases. This is realised if ψ_0 does not exhibit symmetry properties with respect to the operations of the group G. Otherwise, the result of the application of the operator $\epsilon_{ik}^{(\alpha)}$ to it may give zero. The operator $\epsilon_{ii}^{(\alpha)}$ converts the function $\psi_{ik}^{(\alpha)}$ into itself. The operators exhibiting this property are called projection operators. For these, the following operator equation is applicable:

$$\varepsilon_{ii}^{(\alpha)} \varepsilon_{ii}^{(\alpha)} = \varepsilon_{ii}^{(\alpha)}. \tag{5}$$

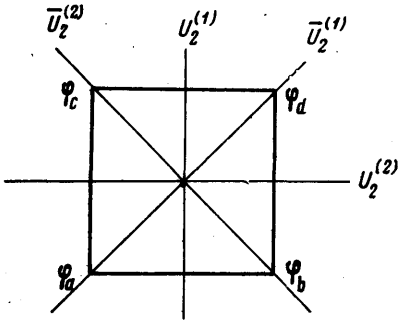
The procedure for constructing the bases of irreducible representations by means of characters[15,16], usually employed in quantum chemistry, does not make it possible to distinguish the basis functions in the case of multiple irreducible representations. Eyring, Walter, and Kimball[15] put forward a method for separating independent basis functions by solving a system of equations. Streitwieser[16] states that it is necessary to use intuition to solve this problem. The method using the projection operators (1), however, makes it possible to standardise completely the procedure for finding the bases of irreducible representations, and intuition is not required.

The effect of the operation R on the original non-symmetrised bases is found from simple geometric considerations. The original basis is broken down into separate sets in such a way that the functions belonging to a given set are transformed only into one another by the operations of the group G. These representations obviously cannot

† In a degenerate electronic state, the adiabatic approximation becomes inapplicable. Symmetrical arrangements of the nuclei now do not correspond to an energy minimum (Jahn–Teller theorem). As a consequence of electronic-vibrational interaction, instead of one minimum for a symmetrical configuration of the nuclei, there appear several minima for unsymmetrical configurations of the nuclei. The potential surface becomes multi-sheeted, and the nuclei undergo a complex motion over this surface (see Refs. 11–13 for more details).

be broader than the regular one, so that the number of times it contains an irreducible representation $\Gamma^{(\alpha)}$ is not greater than its dimension f_α. This feature makes the procedure for constructing the basis using the operators $\epsilon_{ik}^{(\alpha)}$ unambiguous, since there are f_α independent sets of operators $\epsilon_{ik}^{(\alpha)}$ differing in the value of the index k. The matrices of the irreducible representations of all the point groups and permutation groups π_3–π_6 required in order to use Eqn. (2) in specific calculations are given in a book by the author of the present review[14], which also gives examples of the construction of basis functions.

The procedure for constructing basis functions, based on the method of projection operators, can be examined for the simple example of a system of four equivalent atoms situated at the corners of a square *a*, *b*, *c*, *d*. It is assumed that an orbital of the same type is given on each atom:



This atomic configuration is invariant with respect to the operations of the point group D_4. The four orbitals φ_a, φ_b, φ_c, φ_d form the basis of a four-dimensional reducible representation Γ of the group D_4. The characters $\chi^{\Gamma}(R)$ of this representation are equal to the number of orbitals remaining invariant on application of the corresponding operation R of the group D_4:

R	E	C_2	$2C_4$	$2U_2$	$2\bar{U}_2$
$\chi^{\Gamma}(R)$	4	0	0	0	2

The representation Γ is readily broken down into the irreducible representations of the group D_4 using the character tables of the irreducible representations $\Gamma^{(\alpha)}$ of the group D_4. According to the theory of representations, the number of times the representation $\Gamma^{(\alpha)}$ appears in the breakdown of the representation Γ is given by the equation

$$a^{(\alpha)} = \frac{1}{g}\sum_R \chi^{\Gamma}(R)\,\chi^{(\alpha)}(R)^*. \qquad (6)$$

This gives‡

$$\Gamma \doteq A_1 + B_2 + E. \qquad (7)$$

The basis functions of the irreducible representations appearing in the breakdown (7) are constructed by applying the appropriate operators $\epsilon_{ik}^{(\alpha)}$ to any of the orbitals. To be specific, the orbital φ_a can be taken. The following are the orbitals into which the orbital φ_a is transformed by the eight operations of the group D_4:

R	E	C_4	C_2	C_4^3	$U_2^{(1)}$	$U_2^{(2)}$	$\bar{U}_2^{(1)}$	$\bar{U}_2^{(2)}$
$R\varphi_a$	φ_a	φ_b	φ_d	φ_c	φ_b	φ_c	φ_a	φ_d

Character tables are sufficient for constructing the basis functions of the one-dimensional representations A_1 and B_2. To construct the basis of the two-dimensional irreducible representation E it is necessary to know its matrix elements. The matrix elements for the irreducible representations of the group D_4 are given below:

	E	C_4	C_2	C_4^3	$U_2^{(1)}$	$U_2^{(2)}$	$\bar{U}_2^{(1)}$	$\bar{U}_2^{(2)}$
A_1	1	1	1	1	1	1	1	1
B_2	1	−1	1	−1	1	1	−1	−1
E	$\begin{pmatrix}1&\\&1\end{pmatrix}$	$\begin{pmatrix}&1\\-1&\end{pmatrix}$	$\begin{pmatrix}-1&\\&-1\end{pmatrix}$	$\begin{pmatrix}&-1\\1&\end{pmatrix}$	$\begin{pmatrix}&-1\\-1&\end{pmatrix}$	$\begin{pmatrix}1&\\&1\end{pmatrix}$	$\begin{pmatrix}1&\\&-1\end{pmatrix}$	$\begin{pmatrix}-1&\\&1\end{pmatrix}$

Since each representation $\Gamma^{(\alpha)}$ appears once in the breakdown (7), in this example multiple representations do not appear. To construct the basis of the representation E, it is sufficient to use either of the two sets of projection operators: $(\epsilon_{11}^{E}, \epsilon_{21}^{E})$ or $(\epsilon_{12}^{E}, \epsilon_{22}^{E})$. This gives the following normalised functions:

$$\sigma^{A_1} = \frac{1}{2}(\varphi_a + \varphi_b + \varphi_c + \varphi_d),$$

$$\sigma^{B_2} = \frac{1}{2}(\varphi_a - \varphi_b - \varphi_c + \varphi_d),$$

$$\begin{cases}\sigma_1^{E} = \dfrac{1}{\sqrt{2}}(\varphi_a - \varphi_d),\\ \sigma_2^{E} = \dfrac{1}{\sqrt{2}}(-\varphi_b + \varphi_c).\end{cases}$$

Because of the importance of permutational symmetry in the quantum theory of many-electron systems, it will be considered separately.

III. PERMUTATIONAL SYMMETRY

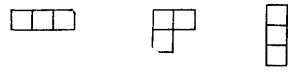
In the theory of the permutation group[14,17,18], it is shown that each irreducible representation of the permutation group of N objects, denoted π_N, can be associated with one of the partitions of the number N into integral positive terms (partition numbers). These terms are arranged in descending order:

$$\lambda^{(1)} + \lambda^{(2)} + \ldots + \lambda^{(m)} = N,\ \lambda^{(1)} \geqslant \lambda^{(2)} \geqslant \ldots \geqslant \lambda^{(m)}. \qquad (8)$$

The number of non-equivalent irreducible representations of the group π_N is equal to the number of such partitions. For example, for $N = 3$ there are three partitions:

$$3,\ 2+1,\ 1+1+1. \qquad (9)$$

The partitions (8) and (9) are represented effectively by so-called Young diagrams, in which each number $\lambda^{(i)}$ is associated with a row consisting of a number of squares equal to $\lambda^{(i)}$. Thus for $N = 3$, in accordance with Eqn.(9), three Young diagrams are possible:



The Young diagrams will subsequently be denoted by the symbol $[\lambda] \equiv [\lambda^{(1)}\lambda^{(2)}\ldots\lambda^{(m)}]$; the existence of several rows $\lambda^{(i)}$ of identical magnitude, for brevity, will be denoted by the power of $\lambda^{(i)}$. Thus the Young diagrams

‡ The point above the equality symbol indicates that this is not a literal algebraic equation; the representations in the right hand side of Eqn. (7) are contained in the representation Γ.

represented above are denoted by the following symbols: [3], [21], [1^3].

The Young diagrams characterise the symmetry of the basis functions with respect to permutation of the arguments. A Young diagram consisting of one row corresponds to a function symmetrical with respect to all its arguments; a Young diagram consisting of one column corresponds to a function antisymmetric with respect to all arguments. All other Young diagrams characterise intermediate symmetry types. There are rules which make it possible to find the matrices of the irreducible representations of the group π_N using only Young diagrams. These rules are particularly simple in the case of the so-called standard orthogonal representation§ (the Young–Yamanouchi representation[14,17]). The matrices of the standard representation for $N = 3$ are given below. In this case there are three irreducible representations, two of which are one-dimensional; $\Gamma^{[3]}(P) = 1$, and $\Gamma^{[1^3]}(P) = (-1)^p$, where p is the parity of the permutation. The representation $\Gamma^{[21]}$ is two-dimensional, and is given by the following matrices:

$$1 \quad P_{12} \quad P_{23} \quad P_{13} \quad P_{123} \quad P_{132}$$
$$\begin{pmatrix}1\\&1\end{pmatrix}\begin{pmatrix}1\\&-1\end{pmatrix}\begin{pmatrix}-\frac{1}{2}&\frac{\sqrt{3}}{2}\\\frac{\sqrt{3}}{2}&\frac{1}{2}\end{pmatrix}\begin{pmatrix}-\frac{1}{2}&-\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&\frac{1}{2}\end{pmatrix}\begin{pmatrix}-\frac{1}{2}&\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix}\begin{pmatrix}-\frac{1}{2}&-\frac{\sqrt{3}}{2}\\\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix}.$$

The basis functions of the irreducible representations $\Gamma^{[\lambda]}$ are found by applying the projection operators (1) to the non-symmetrised function Φ_0, which can be taken in the form of a product of orbitals or geminals, or in any other cluster form. In the case of a permutation group, it is more convenient to use, instead of the operator (1), the so-called Young operator¶

$$\omega_{rt}^{[\lambda]} = \sqrt{\frac{f_\lambda}{N!}} \sum_P \Gamma_{rt}^{[\lambda]}(P)\, P, \tag{11}$$

where f_λ is the dimension of the representation $\Gamma^{[\lambda]}$. The right hand side of Eqn. (11) differs from the right hand side of Eqn. (1) by a factor which is chosen in such a way that the action of $\omega_{rt}^{[\lambda]}$ on the orthonormalised product Φ_0 of one-particle functions gives a normalised function.

For representations characterised by single-row $[N]$ or single-column $[1^N]$ Young diagrams, the operator (11) is the ordinary symmetrisation or antisymmetrisation operator:

$$\omega^{[N]} = \frac{1}{\sqrt{N!}} \sum_P P, \tag{12}$$

$$\omega^{[1^N]} = \frac{1}{\sqrt{N!}} \sum_P (-1)^p P. \tag{13}$$

It is possible to find basis functions

$$\Phi_{rt}^{[\lambda]} = \omega_{rt}^{[\lambda]}\Phi_0 = \sqrt{\frac{f_\lambda}{N!}} \sum_P \Gamma_{rt}^{[\lambda]}(P)\, P\Phi_0 \tag{14}$$

for the irreducible representations of the group π_3 in the case where Φ_0 is a product of orbitals. For the representation $\Gamma^{[21]}$ it is possible to construct two independent basis sets. This is due to the fact that the 3! functions $P\Phi_0$ in this case form the basis of a regular representation of the group π_3, and in the breakdown of the regular representation, the number of times each irreducible representation appears is equal to its dimension. Use of the explicit form of the matrix elements $\Gamma_{rt}^{[21]}$ gives:

$$\Phi^{[3]} = \frac{1}{\sqrt{6}}\{\varphi_a(1)\varphi_b(2)\varphi_c(3) + \varphi_a(2)\varphi_b(1)\varphi_c(3) +$$
$$+ \varphi_a(3)\varphi_b(2)\varphi_c(1) + \varphi_a(1)\varphi_b(3)\varphi_c(2) + \varphi_a(2)\varphi_b(3)\varphi_c(1) + \varphi_a(3)\varphi_b(1)\varphi_c(2)\}$$

$$\Phi^{[1^3]} = \frac{1}{\sqrt{6}}\{\varphi_a(1)\varphi_b(2)\varphi_c(3) - \varphi_a(2)\varphi_b(1)\varphi_c(3) -$$
$$- \varphi_a(3)\varphi_b(2)\varphi_c(1) - \varphi_a(1)\varphi_b(3)\varphi_c(2) + \varphi_a(2)\varphi_b(3)\varphi_c(1) + \varphi_a(3)\varphi_b(1)\varphi_c(2)\},$$

$$\begin{cases}\Phi_{11}^{[21]} = \frac{1}{\sqrt{12}}\{2\varphi_a(1)\varphi_b(2)\varphi_c(3) + 2\varphi_a(2)\varphi_b(1)\varphi_c(3) - \\ \quad - \varphi_a(3)\varphi_b(2)\varphi_c(1) - \varphi_a(1)\varphi_b(3)\varphi_c(2) - \\ \quad - \varphi_a(2)\varphi_b(3)\varphi_c(1) - \varphi_a(3)\varphi_b(1)\varphi_c(2)\} \\ \Phi_{21}^{[21]} = \frac{1}{2}\{-\varphi_a(3)\varphi_b(2)\varphi_c(1) + \varphi_a(1)\varphi_b(3)\varphi_c(2) - \\ \quad - \varphi_a(2)\varphi_b(3)\varphi_c(1) + \varphi_a(3)\varphi_b(1)\varphi_c(2)\},\end{cases}$$

$$\begin{cases}\Phi_{12}^{[21]} = \frac{1}{2}\{-\varphi_a(3)\varphi_b(2)\varphi_c(1) + \varphi_a(1)\varphi_b(3)\varphi_c(2) + \\ \quad + \varphi_a(2)\varphi_b(3)\varphi_c(1) - \varphi_a(3)\varphi_b(1)\varphi_c(2)\} \\ \Phi_{22}^{[21]} = \frac{1}{\sqrt{12}}\{2\varphi_a(1)\varphi_b(2)\varphi_c(3) - 2\varphi_a(2)\varphi_b(1)\varphi_c(3) + \\ \quad + \varphi_a(3)\varphi_b(2)\varphi_c(1) + \varphi_a(1)\varphi_b(3)\varphi_c(2) - \\ \quad - \varphi_a(2)\varphi_b(3)\varphi_c(1) - \varphi_a(3)\varphi_b(1)\varphi_c(2)\}.\end{cases}$$

IV. CONSTRUCTION OF ANTISYMMETRIC WAVE-FUNCTIONS WHICH ARE EIGENFUNCTIONS OF S^2. "SPIN-FREE QUANTUM CHEMISTRY"

Although the introduction of the concept of spin has made it possible to explain the chemical bond, electron spins do not take direct part in chemical bond formation; the interactions responsible for chemical bonding are purely electrostatic in character. The coordinate and spin variables in the electronic wavefunction are separated, and the function can be represented as the product of coordinate and spin wavefunctions. The fact that the energy of a system of electrons depends on the value of their total spin S is due to the existence of a unique correspondence between the permutational symmetry of the coordinate wavefunction and the value of the spin $\mathbf{S}$.

The electronic wavefunction of a molecule should satisfy three symmetry conditions:

1) the exclusion principle, that is it should be antisymmetric with respect to permutation of the electrons;

2) it should belong to one of the irreducible representations of the group of rotations in spin space, that is it should be an eigenfunction of the operator $\hat{S}^2$;

3) it should belong to one of the irreducible representations Γ^α of the symmetry point group of the molecule.

States of a molecule characterised by definite S and Γ^α are usually called electronic molecular multiplets, and denoted ${}^{2S+1}\Gamma^{(\alpha)}$.

To find a function satisfying the third condition, it is sufficient to use the operator $\epsilon_{ik}^{(\alpha)}$ defined by Eqn. (1). For the first two conditions to be fulfilled, instead of using the cumbersome procedure involving the construction of appropriate linear combinations of Slater determinants, it is convenient to use the apparatus of the permutation group. The representation of the complete wavefunction in the form of the product of coordinate and spin wavefunctions,

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§ The matrices of the orthogonal representation satisfy the condition:

$$\Gamma_{rt}(P^{-1}) = \Gamma_{tr}(P)\ . \tag{10}$$

¶ The operator (11) should not be confused with the operator of symmetrisation with respect to the rows and antisymmetrisation with respect to the columns of the Young diagram, which is also often called the Young operator[17,18].

symmetrised with respect to the irreducible representations $\Gamma^{[\lambda]}$ of the permutation group, makes it possible to satisfy the first two conditions automatically. For this purpose, the coordinate and spin Young diagrams should be dual with respect to one another, that is one should be obtained from the other by interchanging rows and columns.

The representation $\Gamma^{[\tilde{\lambda}]}$ ($[\lambda]$ is the Young diagram dual with respect to the diagram $[\lambda]$) is conjugate with respect to the representation $\Gamma^{[\lambda]}$, and this means that their matrix elements are related by the expression

$$\Gamma^{[\tilde{\lambda}]}_{rt}(P) = (-1)^p \Gamma^{[\lambda]}_{rt}(P), \tag{15}$$

where p is the parity of the permutation P.

It will be shown that the function

$$\Psi^{[1^N]} = \frac{1}{\sqrt{f_\lambda}} \sum_r \Phi^{[\lambda]}_r \Omega^{[\tilde{\lambda}]}_{\tilde{r}}, \tag{16}$$

where $\Phi^{[\lambda]}_r$ is a many-electron coordinate function, and $\Omega^{[\tilde{\lambda}]}_{\tilde{r}}$ is a spin function, is antisymmetric with respect to the simultaneous permutation of the space and spin variables. An arbitrary permutation $P \in \pi_N$ is applied to Eqn. (16). From Eqn. (4) it follows that

$$P\Psi^{[1^N]} = \frac{1}{\sqrt{f_\lambda}} \sum_{u,v} \sum_r \Gamma^{[\lambda]}_{ur}(P)\, \Gamma^{[\tilde{\lambda}]}_{\tilde{v}\tilde{r}}(P)\, \Phi^{[\lambda]}_u \Omega^{[\tilde{\lambda}]}_{\tilde{v}}. \tag{17}$$

From the definition of the conjugate representation (15) and the properties of orthogonality of the matrices of the representation $\Gamma^{[\lambda]}$, it follows that

$$P\Psi^{[1^N]} = \frac{1}{\sqrt{f_\lambda}} \sum_{u,v} \left[\sum_r \Gamma^{[\lambda]}_{ur}(P)\, \Gamma^{[\lambda]}_{vr}(P) \right] (-1)^p \Phi^{[\lambda]}_u \Omega^{[\tilde{\lambda}]}_{\tilde{v}} =$$

$$= \frac{1}{\sqrt{f_\lambda}} \sum_u (-1)^p \Phi^{[\lambda]}_u \Omega^{[\tilde{\lambda}]}_{\tilde{u}} = (-1)^p \Psi^{[1^N]},$$

which it was required to prove.

The symmetrised coordinate function $\Phi^{[\lambda]}_r$ is constructed, as described in the previous section, using Young operators. For a non-symmetrised function Φ_0 consisting of the product of N different orbitals, it is possible to obtain f_λ^2 independent functions $\Phi^{[\lambda]}_{rt}$ which break down into f_λ basis sets, corresponding to different values of the index t.

The spin function $\Omega^{[\tilde{\lambda}]}_{\tilde{r}}$ is obtained analogously by applying the Young operator $\omega^{[\tilde{\lambda}]}_{\tilde{r}\tilde{t}}$ to the product of the one-electron two-component spin functions χ_σ, which are spinors[19]:

$$\Omega_{\sigma_1,\ldots,\sigma_N} = \chi_{\sigma_1}(1)\, \chi_{\sigma_2}(2) \ldots \chi_{\sigma_N}(N). \tag{18}$$

The set of 2^N quantities $\Omega_{\sigma_1 \ldots \sigma_N}$ form a tensor of rank N in two-dimensional spinor space. On rotation of the system of coordinates, a 2^N-dimensional representation of the group of the rotations is induced in the components of Eqn. (18). This is broken down into irreducible parts by the application of the Young operators to the function (18) (see section 4-2 in Ref. 14). The spin functions obtained

$$\Omega^{[\tilde{\lambda}]}_{r,\sigma_1,\ldots\sigma_N} = \omega^{[\tilde{\lambda}]}_{\tilde{r}\tilde{t}} \Omega_{\sigma_1 \ldots \sigma_N} \tag{19}$$

for a fixed set $\sigma_1 \ldots \sigma_N$, transform as an irreducible representation of the permutation group $\Gamma^{[\tilde{\lambda}]}$, and for a fixed $\tilde{r}$ they transform as an irreducible representation $D^{(S)}$ of the group of three-dimensional rotations, that is the number of independent functions (19) with a fixed $\tilde{r}$ is equal to $2S + 1$ (this explains the absence of the index $\tilde{t}$ from the left hand side of Eqn. (19); to find one of the f_λ basis sets corresponding to the representation D^S, it is sufficient to select any fixed $\tilde{t}$ for which the application of $\omega^{[\tilde{\lambda}]}$ to $\Omega\sigma_1 \ldots \sigma_N$ does not give zero).

The spin variables for an electron take only two values. Since an antisymmetric function becomes zero when the variables coincide, the spin Young diagrams for electrons cannot contain more than two squares in a column, that is the spin diagram $[\tilde{\lambda}]$ contains not more than two rows. If the projection of the spin of the electron in one square of a column of the spin Young diagram is 1/2, the projection of the spin of the electron in the other square should be equal to −1/2, that is the spins of these electrons are paired. It is obvious that a contribution to the total spin of the system will be made only by unpaired spins, the number of which is determined as the difference in the rows of the Young diagram $(\tilde{\lambda}^{(1)} - \tilde{\lambda}^{(2)})$. Thus the value of the total spin corresponding to the function (19) is defined unambiguously by the spin Young diagram $[\tilde{\lambda}]$ and is equal to†:

$$S = \frac{1}{2}(\tilde{\lambda}^{(1)} - \tilde{\lambda}^{(2)}), \tag{20}$$

where $\tilde{\lambda}^{(i)}$ is the length of the ith row, and the value of the projection of the spin is determined from the equation

$$M_S = \sum_{i=1}^{N} \sigma_i. \tag{21}$$

Thus for example for three electrons, two independent spin functions, transforming as the representation $\Gamma^{[21]}$ of the group π_3 and describing the state with $S = 1/2$ and $M_S = 1/2$, are found by applying the Young operator $\omega^{[21]}_{\tilde{r}\tilde{t}}$ to $\Omega_{\frac{1}{2},\frac{1}{2},-\frac{1}{2}} \equiv \alpha(1)\alpha(2)\beta(3)$. Since the matrices of the representation $\Gamma^{[21]}$ are related to the matrices of the representation $\Gamma^{[21]}$ (Russian page 1033) by Eqn. (15), it follows that

$$\Omega^{[21]}_{1,\alpha\alpha\beta} = \frac{1}{\sqrt{2}} [-\alpha(1)\beta(2)\alpha(3) + \beta(1)\alpha(2)\alpha(3)],$$

$$\Omega^{[21]}_{2,\alpha\alpha\beta} = \frac{1}{\sqrt{6}} [2\alpha(1)\alpha(2)\beta(3) - \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3)].$$

In quantum chemistry, the term covalent structure is used to describe a configuration of atoms with one valency electron on each atom, characterised by a definite way of combining the spins of the valency electrons to give the total spin S. The number of such ways determines the number of independent covalent structures with spin S. In classical textbooks of quantum chemistry, it is determined by the so-called Rumer rule[15]. Since a configuration of valency electrons is in fact a configuration of singly-filled orbitals, the wavefunction describing it can be written in the form

$$\Psi^{[1^N]}_t = \frac{1}{\sqrt{f_\lambda}} \sum_r \Phi^{[\lambda]}_{rt} \Omega^{[\tilde{\lambda}]}_{\tilde{r}}, \tag{22}$$

† This unique correspondence between the Young diagram and the total spin applies only to particles having a spin of 1/2. For particles having $s > 1/2$, several values of S may correspond to the permutational symmetry of the given Young diagram. Thus if the spin of the particle $s = 1$, the diagram[31] corresponds to values of the total spin $S = 1, 2, 3$.[14]

where the subscript t numbers the independent states, the number of which is equal to the dimension f_λ of the irreducible representation $\Gamma^{[\lambda]}$. The expression for f_λ is written in terms of N and S [14]:

$$n(N, S) \equiv f_\lambda = \frac{N!\,(2S+1)}{\left(\frac{N}{2}+S+1\right)!\left(\frac{N}{2}-S\right)!}. \qquad (23)$$

This is also the equation for the number of covalent structures. For example, in the case of the singlet state for the six π-electrons of the benzene molecule, there are five covalent structures (corresponding to the three Kekule structures and the two Dewar structures); for the triplet state, $n(6,1) = 9$.

In problems not involving spin interactions, it is sufficient, for a complete description of the system, to give only the coordinate wavefunction. The "memory" of spin is preserved, since it is contained in the permutational symmetry of the coordinate wavefunction. Thus for a description of covalent structures it is sufficient to give the coordinate functions $\Phi_{rt}^{[\lambda]}$ found from Eqn. (14). The use of coordinate wavefunctions is also convenient in more complex cases (see subsequent sections). This "spin-free quantum chemistry", as already noted in the Introduction, was first proposed in papers by the author of the present review[1-3] and Matsen[4,5]. This approach has been widely used in recent years[20-28].

It should be noted that calculations using the complete wavefunction in the form (16) are equally convenient in those cases where characteristics of the molecule associated with spin are being dealt with. This applies particularly to the calculation of spin density[29,30]. In the case of the calculation of spin-orbital interactions, since in non-relativistic theory these calculations are carried out using perturbation theory, it is again convenient to take the wavefunctions of the zeroth approximation in the form (16).

V. QUASI-DIAGONALISATION OF THE SECULAR EQUATION. DETERMINATION OF ALLOWED MOLECULAR MULTIPLETS

Most procedures in present-day quantum-chemical calculations are based on the one-electron approximation. In calculations taking account of the possible realisation of different orbital configurations in the system, the problem of solving secular equations of very high order arises (the order of the equations is determined by the number of many-electron states considered). The total number of states in an N-electron system with allowance for all configurations in a basis of k orbitals is equal to[14]

$$n(k, N) = \binom{2k}{N} = \frac{(2k)!}{(2k-N)!\,N!}. \qquad (24)$$

Thus the order of the secular equation obtained is very large, even for small systems. Thus for six electrons and six orbitals, $n(6,6) = 924$.

If however the states of the system are described by wavefunctions belonging to bases of irreducible representations of the symmetry group of the Hamiltonian, the secular equation is quasi-diagonalised. It follows from the Wigner–Eckart theorem[14] that if the function $\psi_{ik}^{(\alpha)}$ belongs to the kth basis of the representation $\Gamma^{(\alpha)}$ of the symmetry group of the Hamiltonian $\mathcal{H}$, then

$$\langle \psi_{ik}^{(\alpha)} | \mathcal{H} | \psi_{i'k'}^{(\alpha')} \rangle = \delta_{\alpha\alpha'}\delta_{ii'} \langle k \| \mathcal{H} \| k' \rangle^{(\alpha)}, \qquad (25)$$

where δ_{ik} is the Kronecker symbol ($\delta_{ii} = 1$, $\delta_{ik} = 0$ for $i \neq k$). The diagonal terms relating to the same irreducible representation are equal. All the non-diagonal terms become zero, except the matrix elements with functions from different bases, transforming according to the same column i; the double bar in the matrix element indicates that it is independent of the number i of the basis function.

Thus the original secular equation breaks down into equations relating to separate irreducible representations. The order of the secular equation corresponding to the representation $\Gamma^{(\alpha)}$ is equal to the total number of times $\Gamma^{(\alpha)}$ appears in the breakdown of the reducible representation induced by the original set of variation functions.

Since the Hamiltonian of a molecule is invariant with respect to permutation of the electrons, in the construction of the wavefunction from Eqn. (16) the secular equation breaks down into blocks, each of which corresponds to a definite irreducible representation $\Gamma^{[\lambda]}$ of the permutation group. As shown in the previous section, the representation $\Gamma^{[\lambda]}$ is related unambiguously to the value of the total electron spin of the system S.

Further diagonalisation of the secular equation takes place in the construction, from functions corresponding to a definite value of S, of linear combinations transforming as the irreducible representations $\Gamma^{(\alpha)}$ of the symmetry group of the Hamiltonian, that is in the construction of the eigenfunctions of the molecular multiplets $^{2S+1}\Gamma^{(\alpha)}$. This is achieved by applying the operators $\epsilon_{ik}^{(\alpha)}$ to the functions $\Phi_{rt}^{[\lambda]}$. The variation problem reduces to the solution of the secular equation for each multiplet.

Thus before carrying out the variation calculation it is appropriate to find all possible molecular multiplets for the given problem and the orders of the corresponding secular equations. This problem can be examined for the case of a system of N equivalent atoms, on each of which one degenerate orbital $\varphi_{m,a}^{(l)}$ is given, where a is the number of the atom, and l and m the orbital angular moment and its projection on the z axis respectively. It is assumed that the number of electrons is equal to N. The total number of non-symmetrised coordinate states, described by functions of the type

$$\Phi_{m_1 \ldots m_N}^{(l)} = \varphi_{m_i a}^{(l)}(1)\,\varphi_{m_j b}^{(l)}(2) \ldots \varphi_{m_{N_q}}^{(l)}(N). \qquad (26)$$

is obviously equal to $(2l+1)^N$. The construction, from the functions (26), of the basis of the representation unambiguously related to the spin S is carried out by applying the Young operators $\omega_{rt}^{[\lambda]}$ to $\Phi_{m_i \ldots m_N}^{(l)}$. The order of the reducible representation induced in these functions is $f_\lambda (2l+1)^N$. To find the characters of this representation, the operation of the symmetry point group (this operation, given at the origin of coordinates, is denoted $\mathfrak{R}$) is applied to the function $\omega_{rt}^{[\lambda]} \Phi_{m_i \ldots m_N}^{(l)}$. The application of $\mathfrak{R}$ to the configuration of localised orbitals reduces to the permutation P of the centres of the orbitals and the operations of the point symmetry R in the atomic system of coordinates. For the operation $\mathfrak{R}$, this corresponds to the permutation P with the cyclic structure $\{1^{\nu_1} 2^{\nu_2} \ldots k^{\nu_k}\}$, where ν_i is the number of cycles of length i, the equation for the character being sought can be written in the form[31]:

$$X^{[\lambda]}(\mathfrak{R}) = \chi^{[\lambda]}(P)\,[\chi^{(l)}(R)]^{\nu_1}\,[\chi^{(l)}(R^2)]^{\nu_2} \ldots [\chi^{(l)}(R^k)]^{\nu_k}, \qquad (27)$$

where $\chi^{(l)}(R)$ is the character of the irreducible representation $D^{(l)}(R)$ of the group of orthogonal transformations of three-dimensional space corresponding to the operation of the point symmetry R.

When orbitals of different types are given on the atoms, it is possible to have several covalent configurations, differing in the permutations of orbitals between identical atoms. A contribution to the character is made only by those configurations which are transformed into themselves by the operation $\mathfrak{R}$. The number of such configurations will be noted $\tau(\mathfrak{R})$. The equation for the character has the following form:

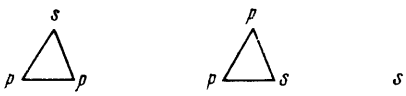
$$X^{[\lambda]}(\mathfrak{R}) = \chi^{[\lambda]}(P)\,[\chi^{(l_1)}(R)]^{\nu_1}\,[\chi^{(l_2)}(R^2)]^{\nu_2} \ldots [\chi^{(l_k)}(R^k)]^{\nu_k}\tau(\mathfrak{R}). \quad (28)$$

The orbital momenta l_i for the atoms appearing in a given cycle should coincide, otherwise the character becomes zero. If all the atoms are equivalent, and l_i are identical, it follows that $\tau(\mathfrak{R}) = 1$, and Eqn. (28) becomes Eqn. (27).

The breakdown of the representation with the characters (28) into irreducible representations $\Gamma^{(\alpha)}$ gives the allowed types of point symmetry. The corresponding values of the electron spin S, according to Eqn. (20), are determined unambiguously by the form of the spin Young diagram $[\widetilde{\lambda}]$, dual with respect to the coordinate Young diagram $[\lambda]$. This is a consequence of the fact that a unique correspondence exists between the irreducible representations $U_2^{[\widetilde{\lambda}]}$ of the unitary group $\mathbf{U}_2$, induced in the spin functions $\Omega^{[\widetilde{\lambda}]}$, and the irreducible representations $D^{(S)}$ of the group of rotations $\mathbf{R}_3$.[14] The method for finding the allowed molecular multiplets can be represented schematically as follows:

$$\begin{array}{ccc} U^{[\lambda]}_{l_1 l_2 \ldots l_k} & \leftrightarrow & U_2^{[\widetilde{\lambda}]} \\ \downarrow & & \downarrow \\ \Gamma^{(\alpha)} & \longleftrightarrow & D^{(S)} \end{array} \quad . \quad (29)$$

An example is provided by a system of three equivalent atoms, with point symmetry $\mathbf{C}_{3v}$, where p orbitals are given on two of the atoms, and an s orbital is given on the other:



Three covalent configurations are possible. The state of the system with $S = 3/2$ can be considered. This corresponds to the spin Young diagram $[\widetilde{\lambda}] = [3]$. The permutational symmetry of the coordinate wavefunction in this state is characterised by the Young diagram $[1^3]$. The group $\mathbf{C}_{3v}$ contains three classes of operation. For the identity class E, all three configurations make a contribution to the character, that is $\tau(E) = 3$. Each of the operations of the class σ_v leaves one of the configurations invariant, so that $\tau(\sigma_v) = 1$. On application of the operation C_3, the configurations are converted into one another, that is $\tau(C_3) = 0$. The permutations corresponding to the operations of the point group have the following cyclic structure:

$$\begin{array}{ccc} E & C_3 & \sigma_v \\ \{1^3\} & \{3\} & \{12\} \end{array} \quad .$$

From Eqn. (28) and the equality $\tau(C_3) = 0$, it follows that

$$X^{[1^3]}(E) = \chi^{[1^3]}(\{1^3\})\,\chi^0(E)\,[\chi^{(1)}(E)]^3\,\tau(E),$$

$$X^{[1^3]}(C_3) = 0,$$

$$X^{[1^3]}(\sigma_v) = \chi^{[1^3]}(\{12\})\,\chi^{(0)}(\sigma_v)\,\chi^{(1)}(\sigma_v^2 \equiv E)\,\tau(\sigma_v).$$

Since moreover $\chi^{(0)}(E) = \chi^{(0)}(\sigma_v) = 1$, $\chi^{(1)}(E) = 3$, and $\chi^{[1^3]}(\{12\}) = -1$, the characters of the reducible representation are:

$$\begin{array}{ccc} E & 2C_3 & 3\sigma_v \\ 27 & 0 & -3 \end{array} \quad .$$

Breakdown of this representation into the irreducible representations of the group $\mathbf{C}_{3v}$ gives the allowed quartets and their multiplicity 3^4A_1, 6^4A_2, 9^4E. The maximum order of the secular equation corresponds to the term ^4E and is equal to nine.

The use of the methods of group theory also makes it possible to solve a more general problem, namely to find the allowed molecular states which can be formed from given atomic states. The solution of this problem was first given by Kotani[32] and was subsequently generalised for the case of complexes of impurity ions in a crystal[33,34]. Kotani's method, however, requires the tedious calculation of the spin factor. The present author[35,36] showed that the determination of the allowed states of a system is simplified considerably by breaking down the complete wavefunction into coordinate and spin functions (16). This approach was used as a basis for the development of general methods for classifying the states of many-electron systems for given states of the sub-systems[31,37]. In these methods, the permutations of the sub-systems reduce to the permutations of particles between the sub-systems. For systems in which the number of particles $N \geqslant 10$, this is no longer effective. Since in the given problem the internal structure of the sub-system is not important, it is more natural to regard each sub-system as a single whole. This approach was developed in Refs. 38–41. The essential features of the method proposed in Ref. 39 will be described briefly.

A many-particle system consisting of n many-particle sub-systems, which may be atoms, ions, combinations of ions (ligands), etc., can be considered. From the viewpoint of the transformational properties of the wavefunction of the system of interest, each of the sub-systems can be regarded as a single particle having spin S_a. Depending on whether S_a is integral or half-integral, the sub-systems obey Bose–Einstein or Fermi–Dirac statistics, and the total wavefunction of the system is symmetric or antisymmetric with respect to permutations of the sub-systems. The wavefunction of the system, which exhibits regular permutational symmetry, can be represented in the form

$$\Psi = \frac{1}{\sqrt{f_\lambda}} \sum_r \Phi_r^{[\lambda]} \Omega_r^{[\widetilde{\lambda}]}, \quad (30)$$

where

$$[\widetilde{\lambda}] = \begin{cases} [\lambda] & \text{for boson sub-systems,} \\ [\widetilde{\lambda}] & \text{for fermion sub-systems,} \end{cases}$$

$[\widetilde{\lambda}]$, as in Eqn. (16), is the Young diagram dual with respect to the diagram $[\lambda]$.

The coordinate function with symmetry corresponding to the Young diagram $[\lambda]$ is constructed by means of the Young operators from the coordinate functions of the sub-systems, each of which belongs to a given irreducible representation $\Gamma^{(\alpha_a)}$ of the local symmetry group of the sub-system $\mathbf{G}_a$. The group $\mathbf{G}_a$ may be either the group of orthogonal transformations in three-dimensional space $\mathbf{O}_3 = \mathbf{R}_3 \times C_i$ (the sub-systems are assumed to be free) or a symmetry point group (the sub-systems are considered in an external field, usually a crystal field). The expression for the character of the reducible representation

$U^{[\lambda]}_{\alpha_1 \ldots \alpha_k}$ induced in the coordinate functions of the entire system, is analogous to Eqn. (28):

$$X^{[\lambda]}(\Re) = \chi^{[\lambda]}(P)\,[\chi^{(\alpha_1)}(R)]^{\nu_1}\,[\chi^{(\alpha_2)}(R^2)]^{\nu_2} \ldots [\chi^{(\alpha_k)}(R^k)]^{\nu_k} \tau(\Re). \quad (31)$$

The breakdown of the representation (31) into irreducible representations gives the allowed types of point symmetry. To determine the corresponding values of the total electron spin of the system S, it is necessary to break down the representation $U^{[\tilde{\lambda}]}_{^2S_a+1}$ of the unitary group $U_{^2S_a+1}$, induced in $(2S_a + 1)$-dimensional spin space in the functions $\Omega^{[\tilde{\lambda}]}_{\tilde{r}}$, into the irreducible representations of the group R_3. In contrast to the case where $S_a = 1/2$, when there is a unique correspondence of the representations $U^{[\tilde{\lambda}]}_2$ and $D^{(S)}$, in the case where $S_a > 1$ a single Young diagram can correspond to several different values of the total spin S. Tables of these quantities are given in Appendix 3 of Ref. 14.

Thus the procedure for finding the allowed multiplets can be represented schematically in the form

$$\begin{array}{ccc} U^{[\lambda]}_{\alpha_1 \ldots \alpha_k} & \leftrightarrow & U^{[\tilde{\lambda}]}_{^2S_a+1} \\ \downarrow & & \downarrow \\ \Gamma^{(\alpha)} & \longleftrightarrow & D^{(S)} \end{array} . \quad (32)$$

Since with the exception of the case where $S_a = 1/2$ the Young diagram $[\tilde{\lambda}]$ can correspond to several values of S, the procedure (32) is carried out systematically for all allowed Young diagrams of n squares, after which the sums of identical terms are taken.

An expression can readily be obtained for the characters of the reducible representation containing all terms of a given multiplicity. As shown in Refs. 38–41, the equations for the characters can be derived in terms of the coefficients of the plethysm of the unitary groups introduced by Littlewood[42]. On the other hand, the same equations are expressed in terms of the $3nj$ symbols of the group of three-dimensional rotations. As a result, it is possible to obtain a relationship between the coefficients of the plethysm and the $3nj$ symbols[39–41].

This method has been generalised for the case of spin-orbit coupling, and examples have been given for various specific systems[39–41].

VI. CALCULATION OF THE MATRIX ELEMENTS OF THE HAMILTONIAN IN A STATE HAVING A DEFINITE TOTAL SPIN

The representation of the eigenfunctions of the operator $\hat{S}^2$ in the closed form (16), instead of the linear combinations of Salter determinants, makes it possible to obtain equations for the matrix elements of a Hamiltonian not depending on spin[43] for the case of an arbitrary configuration of non-orthogonal orbitals. The coefficients in these equations include explicitly the dependence on spin, since they contain the matrix elements of the irreducible representation $\Gamma^{[\lambda]}$, unambiguously related to S. The expressions for the configurations of orthogonal orbitals usually employed are obtained as particular cases.

It is possible to give the corresponding equations for the configuration of singly-filled non-orthogonal orbitals‡:

$$K: \varphi_1 \varphi_2 \ldots \varphi_N, \ \langle \varphi_a | \varphi_b \rangle = s_{ab} \neq 0, \quad (33)$$

used in the spin-projected method of "different orbitals for different spins". The non-symmetrised coordinate function of this configuration can be denoted Φ_0:

$$\Phi_0(K) = \varphi_1(1)\,\varphi_2(2) \ldots \varphi_N(N).$$

As a consequence of the non-orthogonality of the orbitals, the symmetrised coordinate function $\Phi^{[\lambda]}_{rt}$, obtained by applying $\omega^{[\lambda]}_{rt}$ to Φ_0, must be normalised:

$$\Phi^{[\lambda]}_{rt} = N^{[\lambda]}_t(K)\,\omega^{[\lambda]}_{rt}\Phi_0(K). \quad (34)$$

It can readily be shown[44] that the normalisation factor $N^{[\lambda]}_t(K)$ is given by the following equation:

$$[N^{[\lambda]}_t(K)]^{-2} = \sum_P \Gamma^{[\lambda]}_{tt}(P)\,\langle \Phi_0(K) | P\Phi_0(K)\rangle = \\ = 1 + \sum_{P_{ab}} \Gamma^{[\lambda]}_{tt}(P_{ab})\,s^2_{ab} + \sum_{P_{abc}} \Gamma^{[\lambda]}_{tt}(P_{abc})\,s_{ac}s_{ba}s_{cb} + \ldots \quad (35)$$

The index t numbers the different states, differing in the way in which the spins of the individual electrons are combined to give the total spin S. The number of such states is equal to f_λ. The average value of the Hamiltonian for the configuration (33) and a particular choice of ways of combining the electron spins was obtained by Goddard[20] using the apparatus of the permutation group. The equations in Goddard's paper are very complex, however. Gerratt[23] (see also Ref. 44) obtained much more compact expressions for an arbitrary way of combining the spins. Since the Hamiltonian of a molecule is the sum of one-electron and two-electron operators

$$\mathcal{H} = F + G = \sum_{i=1}^{N} f_i + \sum_{i<j}^{N} g_{ij}, \quad (36)$$

expressions can be given for the matrix elements of the operators F and G. These matrix elements can be represented as follows:

$$\langle Kt | F | K\tilde{t}\rangle^{[\lambda]} = N^{[\lambda]}_t(K)\,N^{[\lambda]}_{\tilde{t}}(K) \sum_{a,b} N^{[\lambda]}_{t\tilde{t}}(K_a, K_b)\,f_{ab}, \quad (37)$$

$$N^{[\lambda]}_{t\tilde{t}}(K_a, K_b) = \sum_{P'} \Gamma^{[\lambda]}_{t\tilde{t}}(P'P^{i_a}_b)\,\langle \Phi_0(K_a) | P'\Phi_0(K_b)\rangle, \quad (38)$$

where K_a is the configuration obtained from the configuration K by removing the orbital φ_a; the permutation $P^{i_a}_b$ moves the electron of the orbital φ_a into the orbital φ_b in the function $\Phi_0(K)$; the permutations P' belong to the group π_{N-1}, obtained from π_N by removing the electron i_a; and $f_{ab} = \langle \varphi_a | f | \varphi_b \rangle$ is the one-electron matrix element.

$$\langle Kt | G | K\tilde{t}\rangle^{[\lambda]} = \frac{1}{2} N^{[\lambda]}_t(K)\,N^{[\lambda]}_{\tilde{t}}(K) \times \\ \times \sum_{a,b} \sum_{c,d} \gamma_{ac}\gamma_{bd} N^{[\lambda]}_{t\tilde{t}}(K_{ac}, K_{bd})\,g_{ac,bd}, \quad (39)$$

$$N^{[\lambda]}_{t\tilde{t}}(K_{ac}, K_{bd}) = \sum_{P} \Gamma^{[\lambda]}_{t\tilde{t}}(P''P^{i_a i_c}_{bd})\,\langle \Phi_0(K_{ac}) | P''\Phi_0(K_{bd})\rangle. \quad (40)$$

‡ To avoid confusion, it should be emphasised that the subscripts a and b number the orbitals, and are not related to the numbering of the atoms, that is the orbital φ_a may denote either an atomic (if the valency scheme method is used) or a molecular orbital, including contributions from all the atoms.

In Eqn. (39), $\gamma_{ac} = 1 - \delta_{ac}$, which corresponds to the single filling of the orbitals of the configuration K. The permutation $P^{i_a i_c}_{bd}$ moves the electrons from the orbital φ_a to φ_b and from φ_c to φ_d; the permutations P'' belong to the group π_{N-2}, obtained from π_N by removing the electrons i_a and i_c. The two-electron matrix element is $g_{ac,bd} = \langle \varphi_a(i)\varphi_c(j)|g_{ij}|\varphi_b(i)\varphi_d(j)\rangle$.

For antisymmetric coordinate states with $[\lambda] = [1^N]$, corresponding to the maximum value of the spin, it can readily be shown that Eqns. (37) and (39) become Löwdin's familiar equations[45] for the one-determinant wavefunction constructed on non-orthogonal spin-orbitals:

$$\langle K|F|K\rangle^{[1^N]} = \frac{1}{\det|s_{mn}|}\sum_{a,b}(-1)^{i_a-i_b}\det|s_{mn}|_{ab}f_{ab}, \quad (41)$$

$$\langle K|G|K\rangle^{[1^N]} = \frac{1}{\det|s_{mn}|}\sum_{a<c}\sum_{b<d}(-1)^{i_a+i_b+i_c+i_d}\det|s_{mn}|_{ac,bd}(g_{ac,bd}-g_{ac,db}), \quad (42)$$

where $\det|s_{mn}|_{ab}$ is the minor of the determinant $\det|s_{mn}|$ obtained by deleting the ath row and the bth column.

Equations as simple as Eqns. (41) and (42) are obtained only for the case of maximum spin or for a one-determinant wavefunction, not corresponding in general to a definite value of S. For an arbitrary spin, it is necessary to use Eqns. (37)–(40). The calculation of the non-orthogonality coefficients $N^{[\lambda]}_{tt}(K_a, K_b)$ and $N^{[\lambda]}_{tt}(K_{ac}, K_{bd})$ is most complex. These coefficients are related to one another by the simple expression

$$N^{[\lambda]}_{\bar{t}\bar{t}}(K_a, K_b) = \sum_d \gamma_{ac}\gamma_{bd}N^{[\lambda]}_{\bar{t}\bar{t}}(K_{ac}, K_{bd})\,s_{cd}, \quad (43)$$

which is fulfilled for any $c \neq a$. The following equation, analogous to Eqn. (43),

$$N^{[\lambda]}_{\bar{t}\bar{t}}(K_{ac}, K_{bd}) = \sum_f \gamma_{ace}\gamma_{bdf}N^{[\lambda]}_{\bar{t}\bar{t}}(K_{ace}, K_{bdf})\,s_{ef}, \quad (44)$$

is fulfilled for any $e \neq a, c$. The symbol $\gamma_{abc} = (1-\delta_{ab})(1-\delta_{ac})(1-\delta_{bc})$. The quantities $N^{[\lambda]}_{tt}(K_{ace}, K_{bfd})$ are determined from equations analogous to Eqns. (38) and (40):

$$N^{[\lambda]}_{\bar{t}\bar{t}}(K_{ace}, K_{bdf}) = \sum_{P'''}\Gamma^{[\lambda]}_{\bar{t}\bar{t}}(P'''P^{i_a i_c i_e}_{bdf})\langle\Phi_0(K_{ace})|P'''\Phi_0(K_{bdf})\rangle. \quad (45)$$

Analogous quantities can be determined for the configuration with four "separated" orbitals, etc., including the limiting case corresponding to the "separation" of all N orbitals of the configuration:

$$N^{[\lambda]}_{\bar{t}\bar{t}}(K_{ace\ldots q}, K_{bdf\ldots r}) = \Gamma^{[\lambda]}_{\bar{t}\bar{t}}(P^{i_a i_c i_e\ldots i_q}_{bdf\ldots r}). \quad (46)$$

It is convenient to use the chain of recurrence equations (43)–(46) for the computer calculation of $N^{[\lambda]}_{tt}$. For this it is sufficient to give the matrix of the overlap integrals and the matrices of the transpositions $\Gamma^{[\lambda]}(P_{i,i+1})$, since all other permutations are expressed in terms of the products of transpositions of this type. Here it is necessary to take account of the fact that the form of the coefficients $N^{[\lambda]}_{tt}$ remains unchanged for identical permutations of the indices in the two configurations appearing in the argument.

In the case of a configuration of orthogonal orbitals, the expressions for the matrix elements are simplified considerably. An arbitrary configuration of orthogonal orbitals

$$K: \varphi_a^{n_a}\varphi_b^{n_b}\ldots\varphi_q^{n_q},\ \sum_a n_a = N,\ \langle\varphi_a|\varphi_b\rangle = \delta_{ab}. \quad (47)$$

can be considered. Expressions can be obtained for the matrix elements, diagonal with respect to configuration, of the operators F and G. The matrix element of the operator F is independent of the symmetry of the state

$$\langle Kt|F|K\bar{t}\rangle^{[\lambda]} = \delta_{\bar{t}\bar{t}}\sum_a n_a f_{aa}. \quad (48)$$

For the operator G, an elegant result is obtained: the entire dependence on spin is included in the coefficient of the exchange integral:

$$\langle Kt|G|K\bar{t}\rangle^{[\lambda]} = \delta^{\lambda}_{\bar{t}\bar{t}}\sum_a{}' g_{aa,aa} + \sum_{a<b} n_a n_b[\delta_{\bar{t}\bar{t}}g_{ab,ab} + \Gamma^{[\lambda]}_{\bar{t}\bar{t}}(P_{ab})\,g_{ab,ba}]. \quad (49)$$

The prime of the sum over a denotes that the sum is taken only over doubly-filled orbitals. The coefficients of the exchange integrals are equal to the matrix elements of the transposition P_{ab} between the orbitals. If the orbitals φ_a and φ_b are doubly filled, it is possible to take as P_{ab} any permutation of the electrons between the orbitals φ_a and φ_b, since for these permutations, $\Gamma^{[\lambda]}_{tt}(P_{ab})$ are identical.

For brevity, the following symbols are introduced:

$$g_{ab,ab} = \alpha_{ab},\ g_{ab,ba} = \beta_{ab}.$$

Eqns. (48) and (49) make it possible to represent the matrix elements of the Hamiltonian $\mathcal{H} = F + G$ as a sum of two terms. The first contains the one-electron and Coulomb integrals, and the second is the sum of only exchange integrals:

$$\langle Kt|\mathcal{H}|Kt\rangle^{[\lambda]} = \delta_{\bar{t}\bar{t}}Q + J^{[\lambda]}_{\bar{t}\bar{t}}, \quad (50)$$

where

$$Q = \sum_a n_a f_{aa} + \sum_a{}'\alpha_{aa} + \sum_{a<b} n_a n_b \alpha_{ab}, \quad (51)$$

$$J^{[\lambda]}_{\bar{t}\bar{t}} = \sum_{a<b} n_a n_b \Gamma^{[\lambda]}_{\bar{t}\bar{t}}(P_{ab})\,\beta_{ab}. \quad (52)$$

The non-diagonal elements of the energy matrix contain only the exchange integrals with coefficients which depend on the spin of the state. Since a contribution to the spin is made only by unpaired electrons, the coefficients of the exchange integrals can be determined in the group of the permutations of not all but only the unpaired electrons. For this purpose, the configuration K must be represented in the form K_0K_1, putting the doubly filled orbitals first (configuration K_0), and then the singly filled orbitals (configuration K_1). The Young diagram characterising the symmetry of the configuration K_1 is obtained from the Young diagram $[\lambda]$ by removing the m upper rows (m is the number of doubly filled orbitals), and is denoted $[\lambda^{(m)}]$. In the equation given below, the letters a and b are used to denote the orbitals of the configuration K_0 and the letters c and d the orbitals of the configuration K_1. Thus by making use of the properties of the standard representation of the group of permutations[14] for the spin-dependent non-diagonal elements of the Hamiltonian (52), it is possible to obtain the following expression:

$$J^{[\lambda]}_{\bar{t}\bar{t}} = -\sum_{a<b} 2\beta_{ab} - \sum_{a,c}\beta_{ac} + \sum_{c<d}\Gamma^{[\lambda^m]}_{i_c i_c}(P_{cd})\,\beta_{cd}. \quad (53)$$

In molecular calculations, the number of singly filled molecular orbitals is usually small. The matrices $\Gamma^{[\lambda]}(P_{ab})$ for all transpositions of the groups π_3–π_4 and the transpositions of the type $P_{i,i+1}$ of the groups π_5–π_6 are given in the Appendix to Ref. 14, and the matrices of all the transpositions of the groups π_3–π_6 are given in the expanded edition of the book by the present author[46].

VII. SPIN-PROJECTED SELF-CONSISTENT FIELD EQUATIONS

In the valence bond method and in the simple molecular orbital method, the one-electron functions are assumed to be known. It is possible, however, in the one-particle approximation, to formulate the many-electron problem without imposing previous restrictions on the one-electron functions. This approach, first proposed and developed for the atom by Hartree[47] and Fock[48] (see also Slater's paper[49]), is usually called the Hartree–Fock or self-consistent field (SCF) method.

The derivation of the equations which must be satisfied by the one-electron functions being sought is based on the variation principle

$$\bar{E} = \int \Psi^* \mathcal{H} \Psi \, \mathrm{d}V = \min \tag{54}$$

with the additional condition

$$\int \Psi^* \Psi \, \mathrm{d}V = 1, \tag{55}$$

but only the determinants of the one-electron functions are allowed as competing functions. Since for arbitrary Ψ the variation principle (54) and (55) leads to the Schrödinger equation (see for example Ref. 19), the best function of this type is found by solving the variation problem with a determinantal wavefunction.

In molecular calculations, the term Hartree–Fock equation is usually employed to describe the SCF equations obtained in the description of the system by a single determinant with doubly filled orbitals. This determinant corresponds to the spin $S = 0$, and describes the ground state of most molecules. The derivation of the Hartree–Fock equations can also be carried out without relating it to the determinantal representation of the wavefunction. As noted above, all the properties of a molecule which are independent of spin interactions are described by giving only the coordinate wavefunction. In fact, the derivation of the SCF equations requires only an expression for the average value of the energy in the state being considered. By partitioning the total wavefunction into coordinate and spin functions, expressions of this kind were obtained in the previous section for an arbitrary configuration in a state with a definite value of the spin S. This makes it possible to derive the SCF equations in the general case and to obtain all particular cases from them, without deriving these equations separately for each state being considered, as has to be done when operating with wavefunctions in the form of linear combinations of determinants.

With allowance for Eqns. (48) and (49), an expression can be written for the average energy in a form symmetrical with respect to the indices a and b:

$$\bar{E} = \mathcal{H}_{tt}^{[\lambda]}(K) = \sum_a n_a f_{aa} + \frac{1}{2}\sum_{a,b} \beta(n_a, n_b)\,[\alpha_{ab} + \Gamma_{tt}^{[\lambda]}(P_{ab})\,\beta_{ab}],$$
$$\beta(n_a, n_b) = \begin{cases} n_a n_b & a \neq b, \\ 1 & a = b. \end{cases} \tag{56}$$

For $a = b$, $\Gamma_{tt}^{[\lambda]}(P_{ab}) = 1$. Following Roothaan[50], it is possible to introduce Coulomb $\hat{\alpha}_b$ and exchange $\hat{\beta}_b$ operators, defined by the relationships

$$\hat{\alpha}_b(i)\,\varphi_a(i) = \left[\int \varphi_b^*(j)\,\varphi_b(j)\,g_{ij}\,\mathrm{d}V_j\right]\varphi_a(i),$$
$$\hat{\beta}_b(i)\,\varphi_a(i) = \left[\int \varphi_b^*(j)\,\varphi_a(j)\,g_{ij}\,\mathrm{d}V_j\right]\varphi_b(i). \tag{57}$$

It can readily be verified that the operators $\hat{\alpha}_b$ and $\hat{\beta}_b$ are Hermitian, that is they satisfy the relationships§

$$\langle \psi | \hat{\alpha}_b | \varphi \rangle = \langle \varphi^* | \hat{\alpha}_b^* | \psi^* \rangle,$$
$$\langle \psi | \hat{\beta}_b | \varphi \rangle = \langle \varphi^* | \hat{\beta}_b^* | \psi^* \rangle. \tag{58}$$

The operators (57) make it possible to write the Coulomb and exchange integrals as one-electron integrals:

$$\alpha_{ab} = \langle \varphi_a | \hat{\alpha}_b | \varphi_a \rangle = \langle \varphi_b | \hat{\alpha}_a | \varphi_b \rangle,$$
$$\beta_{ab} = \langle \varphi_a | \hat{\beta}_b | \varphi_a \rangle = \langle \varphi_b | \hat{\beta}_a | \varphi_b \rangle. \tag{59}$$

The following expression is obtained for the average energy E (56) with allowance for Eqns. (59):

$$\bar{E} = \sum n_a \langle \varphi_a | \hat{f} | \varphi_a \rangle + \frac{1}{2}\sum_{a,b} \beta(n_a, n_b)\,\langle \varphi_a | \hat{\alpha}_b + \Gamma_{tt}^{[\lambda]}(P_{ab})\,\hat{\beta}_b | \varphi_a \rangle. \tag{60}$$

Thus the solution of the variation problem (54) and (55) involves the determination of the set of orbitals φ_a minimising the energy (60), with fulfilment of the conditions for orthonormalisation of the orbitals

$$\langle \varphi_a | \varphi_b \rangle = \delta_{ab}. \tag{61}$$

This problem can be solved by the Lagrange method, and reduces to the determination of the unconditional extremal value of the function

$$J = \sum_a \left\langle \varphi_a \left| n_a \hat{f} + \frac{1}{2}\sum_b \beta(n_a, n_b)\,[\hat{\alpha}_b + \Gamma_{tt}^{[\lambda]}(P_{ab})\,\hat{\beta}_b] \right| \varphi_a \right\rangle - \sum_{ab} \varepsilon_{ba} \langle \varphi_a | \varphi_b \rangle, \tag{62}$$

where ϵ_{ab} represents the Lagrange factors. For this it is necessary to find the first variation of the functional J. When taking the variation with respect to φ_b^* and φ_b, it is convenient to use the equivalence of the two forms in which the Coulomb and exchange integrals (59) can be written. Allowance for the Hermitian character of the operators $\hat{f}$, $\hat{\alpha}_b$, and $\hat{\beta}_b$ makes it possible to represent the variation in the form

$$\delta J = \sum_a \left\langle \delta\varphi_a \left| n_a \hat{f} + \sum_b \beta(n_a, n_b)\,[\hat{\alpha}_b + \Gamma_{tt}^{[\lambda]}(P_{ab})\,\hat{\beta}_b] \right| \varphi_a \right\rangle - \sum_{a,b} \langle \delta\varphi_a | \varepsilon_{ba} \varphi_b \rangle +$$
$$+ \sum_a \left\langle \delta\varphi_a^* \left| n_a \hat{f} + \sum_b \beta(n_a, n_b)\,[\hat{\alpha}_b^* + \Gamma_{tt}^{[\lambda]}(P_{ab})\,\hat{\beta}_b^*] \right| \varphi_a^* \right\rangle - \sum_{a,b} \langle \delta\varphi_a^* | \varepsilon_{ab} \varphi_b^* \rangle. \tag{63}$$

By equating δJ to zero and making allowance for the independence of the variations $\delta\varphi_a$ and $\delta\varphi_a^*$, it is possible to obtain two complex-conjugate systems of equations, which are equivalent if the matrix of the Lagrange coefficients is Hermitian:

$$\varepsilon_{ba} = \varepsilon_{ab}^*. \tag{64}$$

The required set of minimising orbitals should be a solution of the integro-differential equations

$$\hat{\mathcal{H}}_a \varphi_a = \sum_b \varepsilon_{ba} \varphi_b, \quad a = 1, 2, \ldots N - m \tag{65}$$

with the one-electron Hamiltonian

$$\hat{\mathcal{H}}_a = n_a \hat{f} + \sum_b \beta(n_a, n_b)\,[\hat{\alpha}_b + \Gamma_{tt}^{[\lambda]}(P_{ab})\,\hat{\beta}_b]. \tag{66}$$

The system of $(N - m)$ equations (65) and (66) contains $(N - m)$ unknown functions φ_a (for the configuration of singly filled orbitals there are N functions, and for the configuration K_0 with all doubly filled orbitals there are $N/2$ functions) and $(N - m)^2$ unknown Lagrange factors ϵ_{ba}.

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§ It may be remembered that $\langle \psi | \hat{\alpha}_b | \varphi \rangle \equiv \int \psi^* \hat{\alpha}_b \varphi \, \mathrm{d}V$.

It must therefore be supplemented by an additional $(N-m)^2$ equations. Multiplication of Eqn. (65) by φ_b^* and integration with respect to the whole of space give

$$\varepsilon_{ba} = \langle \varphi_b | \hat{\mathcal{H}}_a | \varphi_a \rangle. \quad (67)$$

In practice, it is more convenient to use the more symmetrical form of writing the Lagrange factors:

$$\varepsilon_{ba} = \frac{1}{2}\langle \varphi_b | \hat{\mathcal{H}}_a + \hat{\mathcal{H}}_b | \varphi_a \rangle. \quad (68)$$

Eqns. (65) describe the state of an arbitrary molecular configuration with value of the total spin S. In this general case, each orbital φ_a has its own Hamiltonian $\hat{\mathcal{H}}_a$; the coefficients ϵ_{ba} do not have a definite physical significance.

For a closed electron level, when all the orbitals are doubly filled, Eqns. (65) are simplified. This state corresponds to the spin $S = 0$, and the orbital Young diagram $[\lambda] = [2^m]$. Since $\Gamma^{[2^m]}(P_{ab}) = -1/2$ (see Ref. 14), $n_a = n_b = 2$, and $\hat{\alpha}_b$ and $\hat{\beta}_b$ are equivalent for $a = b$, it is found that all orbitals of the configuration K_0 satisfy the single equation

$$\hat{\mathcal{H}}_0 \varphi_a = \sum_b \varepsilon_{ba} \varphi_b, \quad (69)$$

$$\hat{\mathcal{H}}_0 = 2\hat{f} + 2\sum_b (2\hat{\alpha}_b - \hat{\beta}_b). \quad (70)$$

It can readily be shown (see Ref. 50) that the operator (70) is invariant with respect to an arbitrary unitary transformation of the orbitals. If the transformation which diagonalises the Hermitian matrix of the Lagrange factors (68) is used as unitary transformation, Eqns. (69) can be transformed to a problem in the eigenvalues of the operator $\hat{\mathcal{H}}_0$.

$$\hat{\mathcal{H}}_0 \varphi_a = 2\varepsilon_a \varphi_a. \quad (71)$$

The factor 2 in front of ϵ_a is introduced so that ϵ_a has the significance of the energy of the electron in the orbital φ_a¶. By separating the analogous factor from the operator $\hat{\ }_0$ (70), it is possible to obtain the familiar Hartree–Fock equation for a closed level

$$\hat{\mathcal{H}}_0 \varphi_a = \varepsilon_a \varphi_a, \quad (72)$$

$$\hat{\mathcal{H}}_0 = \hat{f} + \sum_b (2\hat{\alpha}_b - \hat{\beta}_b). \quad (73)$$

The orbitals satisfying the Hartree–Fock equations (72) are eigenfunctions of the same Hamiltonian. From this it follows immediately that: a) the self-consistent orbitals corresponding to different eigenvalues of Eqn. (72) are orthogonal to one another; and b) the orbitals corresponding to a given eigenvalue transform as the irreducible representations of the symmetry group of the Hamiltonian (if there is no accidental degeneracy). The operator $\hat{\mathcal{H}}_0$ consists of the one-electron operator $\hat{f}$, the symmetry of which is determined by the equilibrium configuration of the nuclei, that is it coincides with the symmetry of the molecule, and the sum of the Coulomb and exchange operators, which depends on the orbitals. The last sum, as noted above, is scalar with respect to the operations of the unitary group, and hence to the operations of its point sub-group. Thus the symmetry of the Hamiltonian coincides with the symmetry of the operator $\hat{f}$, and the solutions of the Hartree–Fock equation should transform as the irreducible representations of the symmetry point group of the molecule.

It is obvious that

$$\varepsilon_a = \langle \varphi_a | \mathcal{H}_0 | \varphi_a \rangle = f_{aa} + \sum_b (2\alpha_{ab} - \beta_{ab}). \quad (74)$$

If the sum of the energies ϵ_a over all electrons, is now taken, it is found that

$$2\sum_a \varepsilon_a = 2\sum_a f_{aa} + 2\sum_{a,b} (2\alpha_{ab} - \beta_{ab}). \quad (75)$$

On the other hand, the total energy of the electrons for the configuration K_0 being considered, according to Eqn. (50), is

$$E_0 = 2\sum_a f_{aa} + \sum_{a,b} (2\alpha_{ab} - \beta_{ab}), \quad (76)$$

that is the sum of the one-electron energies is greater than the total energy of this system by an amount corresponding to the energy of interaction of the electrons. This is related to the fact that in the summation with respect to all the electrons, the interaction of each pair of electrons was included twice. It may be noted that it is because the total energy is not equal to the sum of the one-electron energies that the filling of the orbital states does not always take place in order of increasing ϵ_a, since the term containing the interaction

$$\sum_{a,b} (2\alpha_{ab} - \beta_{ab})$$

may compensate the loss in energy, obtained by the "irregular" filling of the orbitals.

The expression for the total energy (76) can also be written in the additive form:

$$E_0 = \sum_a \left(2f_{aa} + \sum_b (2\alpha_{ab} - \beta_{ab})\right) = \sum_a \varepsilon'_a, \quad (77)$$

$$\varepsilon'_a = 2\varepsilon_a - \sum_b (2\alpha_{ab} - \beta_{ab}), \quad (78)$$

that is the electronic energy can be represented as the sum of appropriately renormalised one-electron energies. This explains why, with an appropriate selection of parameters in some semi-empirical calculations, it is possible not to take explicit account of electron interactions (for example in the Hückel method).

VIII. THE USE OF THE APPARATUS OF CONTINUOUS GROUPS IN QUANTUM-CHEMICAL CALCULATIONS

The mathematical apparatus of unitary groups can be used not only for the classification of states[38–41,51] but also directly in the calculation of the matrix of the Hamiltonian[6–9,59,60]. Its application is based on the following features.

A many-electron wavefunction can always be expanded in a series with respect to products of orthonormalised one-electron functions (spin-orbitals). This expansion is accurate when account is taken of all configurations in the complete (infinite) set of one-electron functions. Practical

¶ The need to introduce the factor 2 for the interpretation of φ_a as the one-electron energy is related to the fact that when taking account of the bonding conditions by means of the Lagrange factor in Eqn. (62), the summation was carried out only with respect to the orbitals, without allowance for the multiplicity of the filling. Thus in the SCF equations, represented in the form of the eigenvalue problem of the one-electron operator $\mathcal{H}_a(i)$, ϵ_a characterises the total energy of all the electrons in the orbital φ_a, that is, for doubly filled orbitals, the energy of two electrons.

calculations are naturally based on a finite set; its order is denoted $2q$. These $2q$ orthonormalised spin-orbitals can be regarded as the basis unit vectors of a $2q$-dimensional vector space. The complete many-electron wavefunction is constructed from the products of N vectors of this space, and is an antisymmetric tensor of rank N in the space of $2q$ measurements. In the original one-electron basis it is possible to construct a model Hamiltonian for which a given many-electron function is not an approximate but an exact eigenfunction. In the representation of secondary quantisation, the model Hamiltonian has the following form:

$$\mathcal{H} = \sum_{k,l}^{2q} f_{kl} a_k^+ a_l + \frac{1}{2} \sum_{kl,m,n} g_{km,ln} a_k^+ a_m^+ a_n a_l, \qquad (79)$$

where the operators for the generation a_k^+ and annihilation a_k of an electron in the state $k = \varphi_a \chi_{\sigma_k}$ satisfy the fermion commutation relationships:

$$[a_k, a_l^+]_+ = \delta_{kl}, \quad [a_k^+, a_l^+]_+ = [a_k, a_l]_+ = 0. \qquad (80)$$

For the operators f_{ij} and g_{ij}, which do not depend on spin, the matrix elements are

$$f_{kl} = \delta_{\sigma_k \sigma_l} f_{ab}, \quad g_{km,ln} = \delta_{\sigma_k \sigma_l} \delta_{\sigma_m \sigma_n} g_{ab,cd}, \qquad (81)$$

when the one-electron and two-electron matrix elements f_{ab} and $g_{ab,cd}$ are defined in the orbitals φ_a, and not in the spin-orbitals k.

If the matrix elements (81) are not calculated, but are found from the comparison with experimental data, Eqn. (79) is a semi-empirical model Hamiltonian. Thus in the Pariser–Parr–Pople Hamiltonian

$$g_{ab,cd} = \delta_{ac} \delta_{bd} I_{ab}, \qquad (82)$$

and in the Hubbard Hamiltonian

$$g_{ab,cd} = \delta_{ac} \delta_{bd} \delta_{ab} I. \qquad (83)$$

Using the anticommutation relationships (80), it can readily be shown that the commutator

$$[a_k^+ a_l, a_m^+ a_n]_- = \delta_{lm} a_k^+ a_n - \delta_{kn} a_m^+ a_l. \qquad (84)$$

Eqns. (84) coincide with the commutation relationships for the infinitesimal generators of the unitary group, defining the structural constants of the corresponding Lie algebra[6,17]:

$$[E_{kl}, E_{mn}]_- = \delta_{lm} E_{kn} - \delta_{kn} E_{ml}. \qquad (85)$$

Thus the operators a_k^+ and a_l are algebraically equivalent to the infinitesimal generators E_{kl} of the unitary group, and can be identified with them.

Since

$$a_k^+ a_m^+ a_n a_l = a_k^+ a_l a_m^+ a_n - \delta_{ln} a_k^+ a_m, \qquad (86)$$

the Hamiltonian (79) can be expressed in terms of the generators E_{kl}. Thus

$$\mathcal{H} = \sum_{k,l}^{2q} f_{kl} E_{kl} + \frac{1}{2} \sum_{k,l,m,n} g_{km,ln} [E_{kl} E_{mn} - \delta_{lm} E_{kn}]. \qquad (87)$$

As noted above, a many-electron wavefunction is an antisymmetric tensor of rank N in the space of $2q$ measurements. Since the Hamiltonian is assumed to be independent of the spin variables, the total wavefunction can be broken down into coordinate and spin functions, and the coordinate wavefunction is defined in the space of q measurements. For unitary transformations of space, the coordinate wavefunction transforms as the tensor representation of the group U_q. The representation breaks down into the irreducible representations $U_q^{[\lambda]}$ on symmetrisation of the tensor in accordance with a Young diagram of N squares[14,52]. As early as 1950, Gel'fand and Tseitlin[53,54] determined the canonical basis for the irreducible representations of the unitary group, in which there are simple equations for the matrix elements of the infinitesimal generators of the unitary group, Since the Hamiltonian (87) is a polynomial of second degree in the generators E_{kl}, the problem of calculating the matrix elements using the Gel'fand–Tseitlin basis becomes very simple.

A similar approach was proposed by Matsen[6], and realised by Paldus[8] for computer calculation in the approximation of the configuration interaction method. The program compiled is very efficient. Thus for a six-electron problem and the Pariser–Parr–Pople Hamiltonian, the time required on an IBM 360/75 computer for calculating the complete matrix of the configuration interaction for singlet states (order of the matrix 175×175) or triplet states (order of the matrix 198×198) is less than 1 s.[8]

The use of an anlogous approach for calculating atomic states was proposed by Patera[55] and Harter[9,56]. In a central field for an orbital momentum of the electron $l \geqslant 2$, the problem of the additional quantum numbers identifying the state arises, since the same value of the total orbital momentum L may be encountered several times in a configuration[14,57]. For the one-level configuration l^N, the space of the orthogonal orbitals has the dimension $2l + 1$. In unitary transformations of this space, the many-electron coordinate function transforms as the tensor representation of the group of unitary transformations U_{2l+1}. The Gel'fand–Tseitlin basis separates the irreducible representations $U_{2l+1}^{[\lambda]}$ and corresponds to the reduction in the chain of groups $U_{2l+1} \subset U_{2l} \supset U_{2l-1} \supset \ldots \supset U_1$. This reduction ensures that a complete set of quantum numbers is obtained for all many-electron states.

However, although the wavefunctions in the Gel'fand–Tseitlin basis are eigenfunctions of the operators $\hat{S}^2$, $\hat{S}_z$, and L_z, they do not correspond to a definite value of the orbital momentum L. This leads to large orders of the secular equations. This is not a problem for modern fast computers, but for carrying out analytical calculations, the generally accepted procedure for calculations using the Racah technique appears much more convenient. There therefore does not seem to be sufficient basis for the opinion, put forward by Harter and Patterson[9], that the method of calculation using the apparatus of unitary groups should completely replace the Racah method. A more detailed comparison of the two methods is given in a review[58] of the book by Harter and Patterson[9].

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