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New Developments in Molecular Orbital Theory*†

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INTRODUCTION

FOR dealing with the problems of molecular quantum mechanics, two methods of approximation have been developed which are capable of handling many-electron systems. The Heitler-London-Pauling-Slater or valence bond (*VB*) method¹⁻³ originated from a chemical point of view. The atoms are considered as the material from which the molecule is built; accordingly, the molecular wave function is constructed from the wave functions of the individual atoms. The Hund-Mulliken or molecular orbital (*MO*) method⁴ is an extension of the Bohr theory of electron configurations from atoms to molecules. Each electron is assigned to a one-electron wave function or molecular orbital, which is the quantum-mechanical analog of an electron orbit. Each of the two fundamentally so different approaches has its merits; so that chemical valence finds a more natural place in the *VB* method, whereas the *MO* method is simpler in describing the processes of excitation and ionization. However, when the two methods are carried through to their ultimately possible refinements, they lead to the same molecular wave function; from a mathematical point of view, they differ only in taking a different starting point as a first approximation.

It is the purpose of this paper to build a rigorous mathematical framework for the *MO* method. Much attention has been devoted to developing an unambiguous and consistent notation system, and to keeping it as simple as possible. We shall be concerned only with

the electronic part of the molecular wave functions. For the processes of excitation and ionization the nuclei are considered to be kept in fixed positions; our calculations therefore apply to vertical excitation and ionization. The magnetic effects due to the spins and the orbital motions of the electrons will be neglected throughout this paper.

I. GENERAL CONSIDERATIONS

The basic concept of the *MO* method is to find approximate electronic wave functions for a molecule by assigning to each electron a one-electron wave function which in general extends over the whole molecule.

The simplest procedure is as follows: give each electron a wave function depending on the space coordinates of that electron only, called a *molecular orbital* (*MO*):

$$\varphi_i^\mu = \varphi_i(x^\mu, y^\mu, z^\mu), \quad (1)$$

where x^μ, y^μ, z^μ , or simply the superscript μ , stands for the coordinates of the μ th electron; the subscript i labels the different *MO*'s.

The total N -electron wave function is now built up as a product of such *MO*'s; it has, however, to be borne in mind that the Pauli principle allows each *MO* to be occupied by not more than two electrons, that is, a particular *MO* φ_i may occur not more than twice in the product wave function.

The more refined procedure requires that we give each electron a wave function which in addition to the space coordinates also contains the spin coordinates of that electron, and which will be called a *molecular spinorbital* (*MSO*). Since we shall neglect magnetic effects, each *MSO* factors into a *MO* and a spin function:

$$\begin{aligned} \psi_{i\kappa}^\mu &= \psi_\kappa(x^\mu, y^\mu, z^\mu, s^\mu) \\ &= \varphi_{i(\kappa)}(x^\mu, y^\mu, z^\mu) \eta_\kappa(s^\mu) = \varphi_{i(\kappa)}^\mu \eta_\kappa^\mu, \quad (2) \end{aligned}$$

where the superscript μ again stands for the (in this case space and spin) coordinates of the μ th electron; and the subscripts κ and i label the different *MSO*'s and

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¹ W. Heitler and F. London, *Z. Physik* **44**, 455 (1927).

² L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), pp. 340-380.

³ Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944), Chapters XII and XIII.

⁴ F. Hund, *Z. Physik* **51**, 759 (1928); **73**, 1 (1931); etc.; R. S. Mulliken, *Phys. Rev.* **32**, 186 (1928); **32**, 761 (1928); **41**, 49 (1932); etc.

MO's, respectively. Since the same *MO*, when connected with different spin factors, may occur in different *MSO*'s, the labelings κ and i can in general not be identified. The spin factors can usually be taken to be

$$\eta_{\kappa}^{\mu} = \begin{cases} \alpha^{\mu} \\ \beta^{\mu} \end{cases}, \quad (3)$$

although occasionally it may be useful to use more general spin functions of the type

$$\eta_{\kappa}^{\mu} = c_{\kappa\alpha}\alpha^{\mu} + c_{\kappa\beta}\beta^{\mu}, \quad (4)$$

with

$$\bar{c}_{\kappa\alpha}c_{\kappa\alpha} + \bar{c}_{\kappa\beta}c_{\kappa\beta} = 1. \quad (5)$$

The total N -electron wave function is now built up as an *antisymmetrized product of MSO's (AP)*:^{5,6}

$$\Phi = (N!)^{\frac{1}{2}} \psi_1^{i_1} \psi_2^{i_2} \cdots \psi_N^{i_N} = (N!)^{-\frac{1}{2}} \begin{vmatrix} \psi_1^{i_1} \psi_2^{i_2} \cdots \psi_N^{i_1} \\ \psi_1^{i_2} \psi_2^{i_2} \cdots \psi_N^{i_2} \\ \dots \dots \dots \\ \psi_1^{i_N} \psi_2^{i_N} \cdots \psi_N^{i_N} \end{vmatrix}. \quad (6)$$

The operation of "alternation,"⁷ indicated by $[1\ 2 \cdots N]$, is defined by: take all the permutations of the sequence $1\ 2 \cdots N$, give the even ones a plus sign, the odd ones a minus sign, add them together and divide by their total number, $N!$.

We mention now two important rules which the operation of "alternation" obeys. The first one states that for an *AP* it makes no difference whether the alternation is carried out over the superscripts, the subscripts, or both:

$$\psi_1^{i_1} \psi_2^{i_2} \cdots \psi_N^{i_N} = \psi_{[1]}^{i_1} \psi_2^{i_2} \cdots \psi_{[N]}^{i_N} = \psi_{[1]}^{i_1} \psi_2^{i_2} \cdots \psi_{[N]}^{i_N}. \quad (7)$$

The proof of Eq. (7) is elementary, and will be omitted here. The second rule states that when \mathfrak{M} is any operator which acts symmetrically on the superscripts of an *AP* (that is, which acts symmetrically on all the N electrons), then

$$\begin{aligned} & \int \bar{\psi}'_1^{i_1} \bar{\psi}'_2^{i_2} \cdots \bar{\psi}'_N^{i_N} \mathfrak{M} \psi_1^{i_1} \psi_2^{i_2} \cdots \psi_N^{i_N} d\tau \\ &= \int \bar{\psi}'_1^{i_1} \bar{\psi}'_2^{i_2} \cdots \bar{\psi}'_N^{i_N} \mathfrak{M} \psi_1^{i_1} \psi_2^{i_2} \cdots \psi_N^{i_N} d\tau \\ &= \int \bar{\psi}'_1^{i_1} \bar{\psi}'_2^{i_2} \cdots \bar{\psi}'_N^{i_N} \mathfrak{M} \psi_1^{i_1} \psi_2^{i_2} \cdots \psi_N^{i_N} d\tau, \quad (8) \end{aligned}$$

⁵ M. Goepfert-Mayer and A. L. Sklar, *J. Chem. Phys.* **6**, 645 (1938).

⁶ M. Goepfert-Mayer and A. L. Sklar wrote down that part of the benzene wave function involving the six carbon π -electrons only, and antisymmetrized it. In the present paper we consider antisymmetrized wave functions involving *all* the electrons of the molecule.

⁷ J. A. Schouten and D. Struik, *Einführung in die neueren Methoden der Differentialgeometrie* (P. Noordhoff, Groningen, 1935), Vol. I, p. 15.

where $d\tau$ is the volume element of all configuration space, including the spins; $\psi_1, \psi_2, \dots, \psi_N$ and $\psi'_1, \psi'_2, \dots, \psi'_N$ can be any two sets of *MSO*'s. The proof of Eq. (8) can be found in most textbooks on quantum mechanics.⁸

A wave function of the type (6) has several interesting properties. We note first that all the *MSO*'s must be linearly independent, since otherwise the determinant vanishes identically. In particular, no two *MSO*'s can be the same; or, only two *MO*'s can be the same, namely, when the corresponding *MSO*'s have opposite spins. Therefore, the Pauli principle in the form given above is automatically satisfied.

It is often useful to collect the set of *MSO*'s ψ_{κ} in a row vector ψ :⁹

$$\psi = (\psi_1 \psi_2 \cdots \psi_N). \quad (9)$$

Let us subject the *MSO*'s ψ_{κ} to a linear transformation

$$\psi'_{\kappa} = \sum_{\lambda} \psi_{\lambda} A_{\lambda\kappa}, \quad (10)$$

or

$$\psi' = \psi \mathbf{A}, \quad (10')$$

where \mathbf{A} is a nonsingular $N \times N$ matrix. If we designate the *AP*'s built from ψ and ψ' by Φ and Φ' , respectively, then

$$\Phi' = \Phi \text{Det}(\mathbf{A}). \quad (11)$$

The proof of Eq. (11) is elementary and will be omitted here.

From Eq. (11) it is obvious that Φ' represents the same physical situation as Φ . Since the *MSO*'s ψ_{κ} are linearly independent, we can always choose the transformation matrix \mathbf{A} such that the transformed *MSO*'s ψ'_{κ} form an orthonormal set (one way of achieving this is Schmidt's orthogonalization process).¹⁰ Hence we may as well assume that our initial *MSO*'s are orthonormal, that is

$$\int \bar{\psi}_{\kappa} \psi_{\lambda} d\tau = \delta_{\kappa\lambda}, \quad (12)$$

where $d\tau$ is the one-electron volume element including spin. We shall assume throughout this paper that Eq. (12) holds.

⁸ See, for instance, reference 3, p. 144.

⁹ The reason for writing the set of *MSO*'s in a row vector rather than a column vector is the following. The wave functions ψ_{κ} are geometrical objects, which, under transformations, have the same properties as base vectors; e.g., the $2px, 2py, 2pz$ functions for an atom behave like the unit vectors $\mathbf{i}, \mathbf{j}, \mathbf{k}$. Since it is customary to write the components v_1, v_2, v_3 of an arbitrary vector \mathbf{v} as a column vector, it follows that $\mathbf{i}, \mathbf{j}, \mathbf{k}$ should be written as a row vector, so that

$$\mathbf{v} = i v_1 + j v_2 + k v_3 = (\mathbf{i} \ \mathbf{j} \ \mathbf{k}) \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}.$$

¹⁰ Schmidt's orthogonalization process is usually formulated for real functions. See for instance R. Courant and D. Hilbert, *Methoden der mathematischen Physik* (1931), Vol. I, p. 41. The generalization to the case of complex functions causes hardly any complication.

It follows then that in a given AP the M SO's are determined except for a *unitary* transformation among themselves; for orthonormality of the M SO's is preserved under a linear transformation if and only if the transformation is unitary. The transformation of the AP , Eq. (11), now reduces to multiplication by a phase factor, since the determinant of a unitary matrix is a number of modulus unity. The freedom which here still remains in the choice of the M SO's will be used later (Secs. II and III).

Equation (12) also has the important implication that the AP given by (6) is now normalized, that is,

$$\int \bar{\Phi} \Phi d\tau = 1. \quad (13)$$

Equation (13) is easily proved by use of Eqs. (7) and (8). The totally symmetrical operator \mathfrak{H} of Eq. (8) is here the identity operator. We have

$$\begin{aligned} \int \bar{\Phi} \Phi d\tau &= N! \int \bar{\psi}_1^{N-1} \bar{\psi}_2^{N-1} \cdots \bar{\psi}_N^{N-1} \psi_1^{N-1} \psi_2^{N-1} \cdots \psi_N^{N-1} d\tau \\ &= N! \int \bar{\psi}_1^{N-1} \bar{\psi}_2^{N-1} \cdots \bar{\psi}_N^{N-1} \psi_1^{N-1} \psi_2^{N-1} \cdots \psi_N^{N-1} d\tau. \end{aligned}$$

In the last expression, only the first permutation, which leaves all the subscripts unchanged, gives a contribution; the other terms vanish because of Eq. (12). The first permutation appears with a factor $1/N!$, so that

$$\int \bar{\Phi} \Phi d\tau = \int \bar{\psi}_1^{N-1} \psi_1^{N-1} d\tau^1 \int \bar{\psi}_2^{N-1} \psi_2^{N-1} d\tau^2 \cdots \int \bar{\psi}_N^{N-1} \psi_N^{N-1} d\tau^N = 1,$$

each integral being unity because of Eq. (12).

When an electronic state is represented by the normalized wave function Φ , its electronic energy is given by

$$E = \int \bar{\Phi} \mathfrak{H} \Phi d\tau, \quad (14)$$

where the *total hamiltonian operator* \mathfrak{H} is defined by

$$\mathfrak{H} = \sum_{\mu} H^{\mu} + \frac{1}{2} e^2 \sum_{\mu \neq \nu} \frac{1}{r^{\mu\nu}}, \quad (15)$$

H^{μ} is the hamiltonian operator for the μ th electron moving in the field of the nuclei alone; this operator is linear and hermitian;¹¹ $r^{\mu\nu}$ is the distance between the μ th and the ν th electron.

¹¹ The summation over μ runs from 1 to N ; in the double summation, μ and ν run from 1 to N independently, except for the restriction $\mu \neq \nu$.

¹² An operator M is linear if

$$M(c\varphi + c'\varphi') = cM\varphi + c'M\varphi',$$

where φ and φ' are any two functions, and c and c' any two con-

An important concept in molecular orbital theory, as in the theory of atomic structure, is that of *electron shells*. An electron shell is defined as a set of M SO's, in which (1) every MO occurs twice, namely, once with either spin, and (2) if there is degeneracy on account of the molecular symmetry, the MO 's in the shell form a complete degenerate set. Accordingly, a *closed-shell structure* refers to an AP which is made up of complete electron shells. Unlike atoms, most molecules in the MO method have a closed-shell structure in the ground state, the most notable exception being O_2 ; that is, there exists an AP of closed-shell type which is a reasonably good approximation to the exact wave function of the ground state; but only in so far as this approximation is reasonably good does it make sense to speak of a closed-shell structure. A more detailed discussion of electron-shells and closed-shell structure will be given in Sec. V.

For a closed-shell structure, the M SO's are given by

$$\psi_{2i-1} = \varphi_i \alpha, \quad \psi_{2i} = \varphi_i \beta, \quad (16)$$

where the MO 's may be grouped in complete degenerate sets. We introduce for the MO 's and spin functions also a matrix notation:

$$\left. \begin{aligned} \phi &= (\varphi_1 \varphi_2 \cdots \varphi_n), \\ \mathbf{n} &= (\alpha \beta), \end{aligned} \right\} \quad (17)$$

so that we may write the row vector ψ representing the set of closed-shell M SO's as the direct product¹³ of ϕ and \mathbf{n} :

$$\psi = \phi \times \mathbf{n}. \quad (16')$$

If we apply Eq. (12) to the M SO's ψ_{2i} and ψ_{2j} (or ψ_{2i-1} and ψ_{2j-1}), we can integrate over the spin factors, and obtain

$$\int \bar{\varphi}_i \varphi_j d\nu = \delta_{ij}, \quad (18)$$

so that the MO 's which make up a closed shell also form an orthonormal set.

The $2n$ -electron AP for the closed-shell is now given by

$$\Phi = [(2n)!]^{1/2} (\varphi_1 \alpha)^{n-1} (\varphi_1 \beta)^{n-1} \cdots (\varphi_n \alpha)^{2n-1} (\varphi_n \beta)^{2n-1}. \quad (19)$$

Substituting this wave function into the expression for the energy (14), and using methods similar to those used for the proof of Eq. (13), we find for the energy of a

stants. The operator M is hermitian if

$$\int \bar{\varphi} M \varphi d\nu = \int \varphi \bar{M} \bar{\varphi} d\nu,$$

for any function φ . This is equivalent to the requirement

$$\int \bar{\varphi}' M \varphi d\nu = \int \varphi \bar{M}' \bar{\varphi}' d\nu,$$

for any two functions φ and φ' .

¹³ For the definition and properties of the direct product of matrices, see E. Wigner, *Gruppentheorie und ihre Anwendungen auf die Atompektren* (Friedrich Vieweg and Sohn, Braunschweig, 1931), p. 19.

closed-shell AP

$$E = 2 \sum_i H_i + \sum_{ij} (2J_{ij} - K_{ij}),^{14} \quad (20)$$

where the *nuclear-field orbital energies* H_i , the *coulomb integrals* J_{ij} , and the *exchange integrals* K_{ij} are defined by

$$H_i = \bar{H}_i = \int \bar{\varphi}_i H \varphi_i dv, \quad (21)$$

$$\left. \begin{aligned} J_{ij} = J_{ji} = \bar{J}_{ij} = \bar{J}_{ji} &= e^2 \int \frac{\bar{\varphi}_i^\mu \bar{\varphi}_j^\nu \varphi_i^\mu \varphi_j^\nu}{r^{\mu\nu}} dv^{\mu\nu}, \\ K_{ij} = K_{ji} = \bar{K}_{ij} = \bar{K}_{ji} &= e^2 \int \frac{\bar{\varphi}_i^\mu \bar{\varphi}_j^\nu \varphi_j^\mu \varphi_i^\nu}{r^{\mu\nu}} dv^{\mu\nu}. \end{aligned} \right\} \quad (22)$$

From Eqs. (22) it is clear that

$$K_{ii} = J_{ii}. \quad (23)$$

For later purposes it is useful to define the *coulomb operator* J_i and the *exchange operator* K_i by means of

$$\left. \begin{aligned} J_i^\mu \varphi^\mu &= e^2 \left(\int \frac{\bar{\varphi}_i^\nu \varphi_i^\nu}{r^{\mu\nu}} dv^\nu \right) \varphi^\mu, \\ K_i^\mu \varphi^\mu &= e^2 \left(\int \frac{\bar{\varphi}_i^\nu \varphi_i^\nu}{r^{\mu\nu}} dv^\nu \right) \varphi_i^\mu. \end{aligned} \right\} \quad (24)$$

These operators are linear and hermitian.¹² J_i is just the potential energy operator which would arise from an electron distributed in space with a density $|\varphi_i|^2$; K_i , however, has no classical analog.

The coulomb and exchange integrals J_{ij} and K_{ij} can be expressed as one-electron integrals, making use of the coulomb and exchange operators J_i and K_i , namely:

$$\left. \begin{aligned} J_{ij} &= \int \bar{\varphi}_i J_j \varphi_i dv = \int \bar{\varphi}_j J_i \varphi_j dv, \\ K_{ij} &= \int \bar{\varphi}_i K_j \varphi_i dv = \int \bar{\varphi}_j K_i \varphi_j dv. \end{aligned} \right\} \quad (25)$$

In Appendix I the following useful relation is proved:

$$0 \leq K_{ij} \leq J_{ij} \leq \frac{1}{2}(J_{ii} + J_{jj}); \quad (26)$$

¹⁴ The summations have to be taken over all the MO 's of the closed-shell ground state, that is, from 1 to n ; in the double sum, the two summations have to be carried out independently. It is well known that Eq. (20) permits the following physical interpretation. The first sum represents the energy of all the electrons in the field of the nuclei alone (each MO is doubly occupied, hence the factor 2). The second sum represents the electronic interactions. The repulsion energy which one would expect classically between the four electrons in φ_i and φ_j , with probability densities $|\varphi_i|^2$ and $|\varphi_j|^2$, is $4J_{ij} + J_{ii} + J_{jj}$. This explains all the coulomb integrals in Eq. (20) except one J_{ii} for every i ; but these cancel against the K_{ii} 's according to Eq. (23). The remaining exchange integrals K_{ij} for $i \neq j$ have no classical analog; they represent additional interactions between all the pairs of electrons with parallel spins.

the first equality sign holds if and only if φ_i and φ_j do not penetrate each other; the second one if and only if $\varphi_i = \varphi_j$; the third one if and only if $|\varphi_i| = |\varphi_j|$.

Equations (20), (21), and (22) will be the starting point for the theory to be developed in the next two sections. It is to be noted that the expression for the total electronic energy in terms of integrals over MO 's, Eq. (20), was derived on the basis that the MO 's form an orthonormal set. If non-orthonormal MO 's were used, a much more complicated expression for the total electronic energy would result; and a physical interpretation along the lines of footnote 14 would not apply in that case.

II. THE HARTREE-FOCK SELF-CONSISTENT FIELD METHOD FOR A CLOSED-SHELL GROUND-STATE¹⁵

We consider an AP which represents a closed-shell ground state; this AP is built up from n MO 's each of which may extend over the whole molecule. When looking for a good set of MO 's, one may of course find that there are a number among them each of which is concentrated mainly around a particular atom; such orbitals form the *inner shells* of the molecule, and do not play an essential role in the chemical binding. It is to be expected that these inner-shell MO 's are very nearly equal to the inner-shell atomic orbitals (AO 's) of the corresponding free atoms. This question will be discussed in more detail at the end of Sec. III.

We ask now for the best AP , that is, the AP for which the energy reaches its absolute minimum. We then have to minimize the expression (20) by varying the MO 's within the limits permitted by the requirement that they form an orthonormal set, as expressed by Eq. (18).

When each MO φ_i is varied by an infinitesimal amount $\delta\varphi_i$, the variation of the energy becomes

$$\begin{aligned} \delta E &= 2 \sum_i \delta H_i + \sum_{ij} (2\delta J_{ij} - \delta K_{ij}) \\ &= 2 \sum_i \int (\delta \bar{\varphi}_i) H \varphi_i dv + \sum_{ij} \left\{ \int (\delta \bar{\varphi}_i) (2J_j - K_j) \varphi_i dv \right. \\ &\quad \left. + \int (\delta \bar{\varphi}_j) (2J_i - K_i) \varphi_j dv \right\} + 2 \sum_i \int \bar{\varphi}_i H (\delta \varphi_i) dv \\ &\quad + \sum_{ij} \left\{ \int \bar{\varphi}_i (2J_j - K_j) (\delta \varphi_i) dv \right. \\ &\quad \left. + \int \bar{\varphi}_j (2J_i - K_i) (\delta \varphi_j) dv \right\}. \end{aligned}$$

For each of the two expressions in curly brackets, the second term gives, after complete summation over i and j , the same result as the first term. If we also make use of the hermitian property of the operators H , J_i , K_i ,

¹⁵ The treatment of Fock's equations presented in this chapter is an elaboration of the treatment given by F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chapters VI and VII, where also references to original papers can be found.

we may write

$$\begin{aligned} \delta E = 2 \sum_i \int (\delta \bar{\varphi}_i) \{H + \sum_j (2J_j - K_j)\} \varphi_i dv \\ + 2 \sum_i \int (\delta \varphi_i) \{\bar{H} + \sum_j (2\bar{J}_j - \bar{K}_j)\} \bar{\varphi}_i dv. \end{aligned} \quad (27)$$

The MO 's φ_i always have to conform to the orthonormality conditions (18); the resulting restrictions on the variations $\delta \varphi_i$, obtained by varying (18), are as follows:

$$\int (\delta \bar{\varphi}_i) \varphi_j dv + \int (\delta \varphi_j) \bar{\varphi}_i dv = 0. \quad (28)$$

In order that E may reach its absolute minimum, it is necessary, although not sufficient, that $\delta E = 0$ for any choice of the $\delta \varphi_i$'s in (27) which is compatible with the restrictions (28). The standard mathematical technique to solve this problem is the method of the lagrangian multipliers:¹⁶ multiply each Eq. (28) by a factor, to be determined later, called a lagrangian multiplier, and add them all to δE , to give, say, $\delta E'$. The problem of finding the conditions for $\delta E = 0$ for any choice of the $\delta \varphi_i$'s compatible with (28) now becomes the problem of finding the conditions for $\delta E' = 0$ for any choice of the $\delta \varphi_i$'s without restrictions, and at the same time of giving suitable values to the lagrangian multipliers. The conditions for $\delta E' = 0$ are that in the integrands the coefficient of each individual $\delta \bar{\varphi}_i$ and $\delta \varphi_i$ vanishes.

We multiply each Eq. (28) by the lagrangian multiplier $-2\epsilon_{ji}$ and add the resulting equations together; we obtain

$$-2 \sum_{ij} \epsilon_{ji} \int (\delta \bar{\varphi}_i) \varphi_j dv - 2 \sum_{ij} \epsilon_{ji} \int (\delta \varphi_j) \bar{\varphi}_i dv = 0,$$

which can be written in the form

$$-2 \sum_{ij} \epsilon_{ji} \int (\delta \bar{\varphi}_i) \varphi_j dv - 2 \sum_{ij} \epsilon_{ij} \int (\delta \varphi_i) \bar{\varphi}_j dv = 0. \quad (29)$$

This we add now to δE of Eq. (27), and obtain

$$\begin{aligned} \delta E' = 2 \sum_i \int (\delta \bar{\varphi}_i) \\ \times \left[\{H + \sum_j (2J_j - K_j)\} \varphi_i - \sum_j \varphi_j \epsilon_{ji} \right] dv \\ + 2 \sum_i \int (\delta \varphi_i) \\ \times \left[\{\bar{H} + \sum_j (2\bar{J}_j - \bar{K}_j)\} \bar{\varphi}_i - \sum_j \bar{\varphi}_j \epsilon_{ij} \right] dv. \end{aligned} \quad (30)$$

¹⁶ For the method of lagrangian multipliers in the case of real functions see reference 10, pp. 140, 190. The generalization to the case of complex functions is obtained by considering each auxiliary condition and its conjugate complex as two independent auxiliary conditions; after their elimination by means of the lagrangian multipliers, the variation of every function and its conjugate complex are independent variations.

The conditions for $\delta E' = 0$ are now given by

$$\left. \begin{aligned} \{H + \sum_j (2J_j - K_j)\} \varphi_i = \sum_j \varphi_j \epsilon_{ji}, \\ \{\bar{H} + \sum_j (2\bar{J}_j - \bar{K}_j)\} \bar{\varphi}_i = \sum_j \bar{\varphi}_j \epsilon_{ij}. \end{aligned} \right\} \quad (31)$$

We show now that the lagrangian multipliers must be the elements of an hermitian matrix. Taking the complex conjugate of the second one of Eqs. (31), and subtracting it from the first one, we obtain

$$\sum_j \varphi_j (\epsilon_{ji} - \bar{\epsilon}_{ij}) = 0;$$

since the MO 's φ_j are linearly independent, it follows that

$$\epsilon_{ji} = \bar{\epsilon}_{ij}, \quad (32)$$

that is, the matrix ϵ of which ϵ_{ij} are the elements is hermitian. A consequence of this is that the two Eqs. (31) become equivalent (each others conjugate complex).

We define now the total electron interaction operator G and the Hartree-Fock hamiltonian operator F by

$$G = \sum_i (2J_i - K_i), \quad (33)$$

$$F = H + G. \quad (34)$$

The Eqs. (31) which the best MO 's have to satisfy can now be written

$$F \varphi_i = \sum_j \varphi_j \epsilon_{ji}, \quad (35)$$

or, in matrix notation

$$F \phi = \phi \epsilon. \quad (35')$$

We now subject the set of MO 's ϕ to a transformation by means of a unitary matrix U to give the new set ϕ' :

$$\phi' = \phi U, \quad (36)$$

with

$$U^* U = E. \quad (37)$$

If we also define the transformed matrix ϵ' by

$$\epsilon' = U^* \epsilon U, \quad (38)$$

it follows from Eqs. (35'), (36), (37), and (38) that

$$F \phi' = \phi' \epsilon'. \quad (39)$$

We note that Eq. (39) does not yet have the exact same form as Eq. (35'). Namely, the operator F , which is defined in terms of the MO 's φ_i (via G), operates in Eq. (35') on these same MO 's; this is not the case in Eq. (39). However, if we construct the operator F' which is defined in terms of the MO 's φ'_i just like F

¹⁷ We write \bar{U} for the complex conjugate, U^\dagger for the transpose, and U^* for the hermitian conjugate of the matrix U . The symbol E is used for the unit matrix.

was defined in terms of φ_i , we can show that $F' = F$. We have, namely,

$$\begin{aligned} \sum_i \bar{\varphi}'_i{}^\mu \varphi'_i{}^\nu &= \sum_{jk} \bar{\varphi}_j{}^\mu \varphi_k{}^\nu \sum_i \bar{U}_{ji} U_{ki} \\ &= \sum_{jk} \bar{\varphi}_j{}^\mu \varphi_k{}^\nu \delta_{jk} = \sum_i \bar{\varphi}_j{}^\mu \varphi_j{}^\nu; \end{aligned}$$

from this equality it follows easily that

$$\sum_i J'_i = \sum_i J_i, \quad \sum_i K'_i = \sum_i K_i,$$

hence also $G' = G$ and

$$F' = F. \quad (40)$$

As a result, we may rewrite Eq. (39) as

$$F' \phi' = \phi' \epsilon'. \quad (41)$$

We see thus that if the "best" MO 's φ_i are subjected to a unitary transformation, then the set of transformed MO 's φ'_i satisfies a set of equations of exactly the same form as did the MO 's φ_i . This result was to be expected. For the two sets of MO 's both give rise to the same $2n$ -electron wave function (except for a phase factor); hence each of these two sets furnishes a set of "best" MO 's.

The explicit transformation of the AP Φ into Φ' is found as follows. From the two sets of MO 's ϕ and ϕ' we construct the two sets of M SO 's ψ and ψ' according to Eq. (16'):

$$\psi = \phi \times \mathbf{n}, \quad \psi' = \phi' \times \mathbf{n};$$

the transformation matrix for the M SO 's follows from $\psi' = (\phi \mathbf{U}) \times \mathbf{n} = (\phi \mathbf{U}) \times (\mathbf{n} \mathbf{E}) = (\phi \times \mathbf{n})(\mathbf{U} \times \mathbf{E}) = \psi(\mathbf{U} \times \mathbf{E})$.

For the AP follows then according to Eq. (11):

$$\Phi' = \Phi \text{Det}(\mathbf{U} \times \mathbf{E}) = \Phi \text{Det}^2(\mathbf{U}).^{18} \quad (42)$$

Since the matrix ϵ is hermitian, there exists a unitary matrix \mathbf{U} so that $\epsilon' = \mathbf{U}^* \epsilon \mathbf{U}$ is a diagonal matrix with real diagonal elements. It is therefore no loss of generality if we assume that our set of "best" MO 's satisfies the simpler equations

$$F \varphi_i = \epsilon_i \varphi_i. \quad (43)$$

The set of Eqs. (43) is the most commonly known form of Fock's equations; they state that the MO 's which give the best AP are all eigenfunctions of the same hermitian operator F , which in turn is defined in terms of these MO 's.

Let us assume for the moment that we know the solutions of Fock's equations; that is, that we know a set of n MO 's which are eigenfunctions of the operator F calculated with this set. F being thus known, let us consider the equation

$$F \varphi = \epsilon \varphi. \quad (44)$$

¹⁸ Note that the dimensions of \mathbf{U} and \mathbf{E} are n and 2 , respectively. If $\mathbf{A}^{(m)}$ and $\mathbf{B}^{(n)}$ are $m \times m$ and $n \times n$ matrices, then $\text{Det}(\mathbf{A}^{(m)} \times \mathbf{B}^{(n)}) = \text{Det}^n(\mathbf{A}^{(m)}) \text{Det}^m(\mathbf{B}^{(n)})$; applying this to the present case, we obtain $\text{Det}(\mathbf{U} \times \mathbf{E}) = \text{Det}^2(\mathbf{U}) \text{Det}^n(\mathbf{E}) = \text{Det}^2(\mathbf{U})$.

Equation (44) is the eigenvalue problem of the hermitian operator F .

It is well known that the following statements hold for an hermitian operator:

- (1) All the eigenvalues are real.
- (2) Eigenfunctions belonging to different eigenvalues are mutually orthogonal.
- (3) Any eigenfunction belonging to a particular eigenvalue is expressible as a linear combination of a number, say p , of linearly independent eigenfunctions; conversely, any linear combinations of these p functions is an eigenfunction. The number p is called the degree of degeneracy of the eigenvalue.
- (4) The p linearly independent eigenfunctions belonging to a particular eigenvalue can always be chosen so as to form an orthonormal set; this set is determined except for a unitary transformation of these p functions among themselves (this reduces, in the case $p=1$, to multiplication by a phase factor).
- (5) After orthonormalization has been carried out for every eigenvalue, all the eigenfunctions of the operator form together an orthonormal set.

Among the solutions ϵ , φ of Eq. (44) there will be, of course, the set ϵ_i , φ_i , $i=1, 2, \dots, n$, which satisfied Eqs. (43). The n eigenvalues ϵ_i must evidently be the n lowest eigenvalues of the operator F , for if we did not take the n lowest eigenvalues, we would actually be solving Fock's equations for an excited state. This result is not surprising, for Fock's equations were obtained as necessary, but not sufficient, conditions that the energy may reach its absolute minimum. The n functions φ_i we shall call *ground-state orbitals*. The remaining eigenfunctions of F^{19} we shall call excited orbitals; in order to avoid confusion, we shall label them with the indices a, b running up from $n+1$, $n+2, \dots$; the labels i, j, k, l will be reserved exclusively for the ground-state orbitals. If we do not want to specify whether we refer to ground-state orbitals or excited orbitals, we shall use the labels f, g . The eigenvalues ϵ_f (that is, ϵ_i and ϵ_a) we shall call *Hartree-Fock orbital energies*.

The general procedure for solving Fock's equations is one of trial and error. One assumes a set of φ_i 's, calculates the operator G (hence F), solves Eq. (44) for the n lowest eigenvalues, and compares the resulting φ_i 's with the assumed ones. Guided by this comparison, a new set of φ_i 's is chosen and the procedure is repeated. This process is then repeated until the assumed and

¹⁹ Whether F has any eigenfunctions aside from the φ_i 's, and if so, how many, is a question which is open to some doubt. Namely, if F operates on a function φ_i , it represents a $2n-1$ electron field; this is due to the fact that the operators J_i and K_i become equal when they operate on φ_i , as can be seen from Eqs. (24). However, if F operates on any function φ which is orthogonal to all the φ_i 's, then F represents approximately a $2n$ -electron field. This can be seen by observing that such a function φ cannot penetrate the closed-shell orbitals φ_i very much (φ has to be orthogonal to all the φ_i 's); hence, the exchange operators K_i become in this case small compared with the coulomb operators J_i . The operators $2\sum_i J_i$ just represent the potential energy arising from the charge distribution of the closed shell. Such a function φ therefore roughly represents an *extra* electron moving at the outside of the molecule. It is known that negative ions do not exist for every molecule, and if so, only in a limited number of states. Therefore, it will depend upon the particular molecule whether F has any eigenfunctions aside from the φ_i 's.

calculated φ_i 's agree. This method for solving Fock's equations is called the Hartree-Fock *self-consistent field* (SCF) method.

III. THE LCAO SELF-CONSISTENT FIELD METHOD FOR A CLOSED-SHELL GROUND STATE

For atoms, the problem of solving Fock's equations is greatly simplified by the central symmetry. For molecules, because of the absence of central symmetry, the situation is less fortunate; solving Fock's equations for molecules is such a difficult mathematical problem that it is at present out of the question except perhaps for the simplest cases. We therefore have to use approximations to the best *MO*'s. In most *MO* treatments, the inner-shell electrons of the molecule are represented by free-atom *atomic orbitals* (*AO*'s); for each of the valence-shell *MO*'s one takes then a *linear combination of atomic orbitals* (*LCAO*). We generalize this procedure by representing *all* the electrons of the molecule by *LCAO MO*'s, as given by

$$\varphi_i = \sum_p \chi_p C_{pi}, \quad (45)$$

where the χ_p 's are normalized *AO*'s, that is,

$$\int \bar{\chi}_p \chi_p dv = 1. \quad (46)$$

It is useful to introduce the following matrix notation:

$$\left. \begin{aligned} \boldsymbol{\chi} &= (\chi_1 \quad \chi_2 \quad \cdots \quad \chi_m), \\ \mathbf{c}_i &= \begin{bmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{mi} \end{bmatrix}, \\ \mathbf{C} &= \begin{bmatrix} C_{11} & C_{12} & \cdots & C_{1n} \\ C_{21} & C_{22} & \cdots & C_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ C_{m1} & C_{m2} & \cdots & C_{mn} \end{bmatrix} \end{aligned} \right\} \quad (47)$$

We may write then for Eq. (45)

$$\varphi_i = \boldsymbol{\chi} \mathbf{c}_i \quad (45')$$

and also

$$\boldsymbol{\phi} = \boldsymbol{\chi} \mathbf{C}. \quad (45'')$$

Equation (45') is useful if we consider a particular *MO* φ_i , and Eq. (45'') is useful if we consider the whole set of *MO*'s φ_i .

Note that the first index on C_{pi} refers to the *AO*'s and the second one to the *MO*'s. These two labelings have to be clearly distinguished. As general indices we shall use for the *MO*'s, as before, i, j, k, l ; and for the

AO's p, q, r, s . As can be seen from (47), we denote the total number of *MO*'s and *AO*'s by n and m , respectively. Since we have to construct n linearly independent *MO*'s from m *AO*'s, we must have $m \geq n$.

An *AP* built from *LCAO MO*'s is obviously a less good approximation to the exact wave function than the *AP* built from the Hartree-Fock *MO*'s, since the latter one is the best possible *AP*. In order that an *LCAO AP* be not too bad, the *LCAO MO*'s should resemble the Hartree-Fock *MO*'s rather well. Whether this can be achieved depends on the choice of the *AO*'s from which the *MO*'s are to be built. In the past, mostly Slater-type *AO*'s have been used; for the screening constants, usually those values were taken which give the best results for the isolated atoms. It has been pointed out by several investigators^{5,20} that these values might not give the best results for the *MO*'s. It is also quite possible that atomic Hartree-Fock orbitals will give considerably better results than Slater orbitals. These questions are far from settled, but will not be pursued any further here.

In the previous section we asked for the *best MO*'s for a closed-shell ground state. In this section we shall ask for the *best LCAO MO*'s for a closed-shell ground state, considering the *AO*'s as given functions. Apparently then, our problem is to find that set of coefficients C_{pi} for which the energy of the corresponding *AP* reaches its absolute minimum.

In the mathematical treatment of this problem it is useful to define for every one-electron operator M the corresponding matrix elements M_{pq} evaluated with the set of *AO*'s, and the matrix \mathbf{M} which collects all the matrix elements M_{pq} :

$$\left. \begin{aligned} M_{pq} &= \int \bar{\chi}_p M \chi_q dv, \\ \mathbf{M} &= \begin{bmatrix} M_{11} & M_{12} & \cdots & M_{1m} \\ M_{21} & M_{22} & \cdots & M_{2m} \\ \cdot & \cdot & \cdot & \cdot \\ M_{m1} & M_{m2} & \cdots & M_{mm} \end{bmatrix} \end{aligned} \right\} \quad (48)$$

If the operator M is hermitian,¹² then it is easy to show that the matrix \mathbf{M} is also hermitian, that is, $\bar{M}_{pq} = M_{qp}$ or $\mathbf{M}^* = \mathbf{M}$. Corresponding to the (hermitian) operators H, J_i, K_i, G , and F we shall make use of the (hermitian) matrices $\mathbf{H}, \mathbf{J}_i, \mathbf{K}_i, \mathbf{G}$, and \mathbf{F} . The operators J_i, K_i, G , and F were defined in terms of the *MO*'s φ_i . In the previous section we assumed implicitly that they were defined in terms of the *best MO*'s. Here we shall assume that they are defined in terms of the *best LCAO MO*'s. There is one more (hermitian) matrix which will play a role in the following discussion, namely the matrix \mathbf{S} the elements of which are the

²⁰ C. A. Coulson, Trans. Faraday Soc. 33, 1479 (1937); R. S. Mulliken, J. Chem. Phys. 8, 241 (1940).

overlap integrals

$$S_{pq} = \int \bar{\chi}_p \chi_q dv; \quad (49)$$

obviously, the matrix \mathbf{S} corresponds to the identity operator. Equation (46) states that the diagonal elements of \mathbf{S} are unity.

The usefulness of the matrix notation (48) is obvious from the following equation:

$$\int \varphi_i M \varphi_j dv = \mathbf{c}_i^* \mathbf{M} \mathbf{c}_j. \quad (50)$$

Equation (50) follows easily by substituting for $\bar{\varphi}_i$ and φ_j in the integral the expression (45).

Again we may assume without loss of generality that the *LCAO MO*'s form an orthonormal set, for if they did not, we could subject them to a linear transformation which would make them orthonormal; after this transformation, they would still be *LCAO MO*'s. We shall assume then that the *LCAO MO*'s satisfy Eq. (18); in view of Eqs. (49) and (50) this leads to

$$\int \varphi_i \varphi_j dv = \mathbf{c}_i^* \mathbf{S} \mathbf{c}_j = \delta_{ij}. \quad (51)$$

Similarly, we find from Eqs. (21), (25), and (50)

$$H_i = \mathbf{c}_i^* \mathbf{H} \mathbf{c}_i, \quad (52)$$

$$\left. \begin{aligned} J_{ij} &= \mathbf{c}_i^* \mathbf{J}_j \mathbf{c}_i = \mathbf{c}_j^* \mathbf{J}_i \mathbf{c}_j, \\ K_{ij} &= \mathbf{c}_i^* \mathbf{K}_j \mathbf{c}_i = \mathbf{c}_j^* \mathbf{K}_i \mathbf{c}_j. \end{aligned} \right\} \quad (53)$$

In order to determine the best *LCAO MO*'s we carry out a variational treatment analogous to that of the previous section. We vary the vectors \mathbf{c}_i by infinitesimal amounts $\delta \mathbf{c}_i$ (that is, the coefficients C_{pi} are varied by the amounts δC_{pi}) and find for the variation of the energy

$$\begin{aligned} \delta E &= 2 \sum_i \delta H_i + \sum_{ij} (2\delta J_{ij} - \delta K_{ij}) \\ &= 2 \sum_i (\delta \mathbf{c}_i^*) \mathbf{H} \mathbf{c}_i + \sum_{ij} \{ (\delta \mathbf{c}_i^*) (2\mathbf{J}_j - \mathbf{K}_j) \mathbf{c}_i \\ &\quad + (\delta \mathbf{c}_j^*) (2\mathbf{J}_i - \mathbf{K}_i) \mathbf{c}_j \} + 2 \sum_i \mathbf{c}_i^* \mathbf{H} (\delta \mathbf{c}_i) \\ &\quad + \sum_{ij} \{ \mathbf{c}_i^* (2\mathbf{J}_j - \mathbf{K}_j) (\delta \mathbf{c}_i) + \mathbf{c}_j^* (2\mathbf{J}_i - \mathbf{K}_i) (\delta \mathbf{c}_j) \}; \end{aligned}$$

this expression we simplify, using methods similar to those of the previous section, to

$$\begin{aligned} \delta E &= 2 \sum_i (\delta \mathbf{c}_i^*) \{ \mathbf{H} - \sum_j (2\mathbf{J}_j - \mathbf{K}_j) \} \mathbf{c}_i \\ &\quad + 2 \sum_i (\delta \mathbf{c}_i^*) \{ \bar{\mathbf{H}} - \sum_j (2\bar{\mathbf{J}}_j - \bar{\mathbf{K}}_j) \} \bar{\mathbf{c}}_i, \end{aligned}$$

²¹ Note that \mathbf{c}_i^* is the row vector $(\bar{C}_{1i} \bar{C}_{2i} \dots \bar{C}_{mi})$; see also footnote 17.

or

$$\delta E = 2 \sum_i (\delta \mathbf{c}_i^*) \mathbf{F} \mathbf{c}_i + 2 \sum_i (\delta \mathbf{c}_i^\dagger) \bar{\mathbf{F}} \bar{\mathbf{c}}_i. \quad (54)$$

The restricting conditions for the $\delta \mathbf{c}_i$'s which result from the orthonormality of the *MO*'s are obtained by varying Eq. (51):

$$(\delta \mathbf{c}_i^*) \mathbf{S} \mathbf{c}_j + \mathbf{c}_i^* \mathbf{S} (\delta \mathbf{c}_j) = 0,$$

or

$$(\delta \mathbf{c}_i^*) \mathbf{S} \mathbf{c}_j + (\delta \mathbf{c}_j^\dagger) \bar{\mathbf{S}} \bar{\mathbf{c}}_i = 0. \quad (55)$$

We multiply the restricting conditions (55) by the lagrangian multipliers $-2\epsilon_{ji}$ and add them together:

$$-2 \sum_{ij} (\delta \mathbf{c}_i^*) \mathbf{S} \mathbf{c}_j \epsilon_{ji} - 2 \sum_{ij} (\delta \mathbf{c}_j^\dagger) \bar{\mathbf{S}} \bar{\mathbf{c}}_i \epsilon_{ji} = 0,$$

or

$$-2 \sum_{ij} (\delta \mathbf{c}_i^*) \mathbf{S} \mathbf{c}_j \epsilon_{ji} - 2 \sum_{ij} (\delta \mathbf{c}_j^\dagger) \bar{\mathbf{S}} \bar{\mathbf{c}}_i \epsilon_{ij} = 0. \quad (56)$$

Adding (56) to the variation of the energy (54), we obtain

$$\begin{aligned} \delta E' &= 2 \sum_i (\delta \mathbf{c}_i^*) (\mathbf{F} \mathbf{c}_i - \sum_j \mathbf{S} \mathbf{c}_j \epsilon_{ji}) \\ &\quad + 2 \sum_i (\delta \mathbf{c}_i^\dagger) (\bar{\mathbf{F}} \bar{\mathbf{c}}_i - \sum_j \bar{\mathbf{S}} \bar{\mathbf{c}}_j \epsilon_{ij}). \end{aligned} \quad (57)$$

The condition for $\delta E' = 0$ for any choice of the vectors $\delta \mathbf{c}_i$ and $\delta \bar{\mathbf{c}}_i$, or $\delta \mathbf{c}_i^\dagger$ and $\delta \mathbf{c}_i^*$, are given by

$$\left. \begin{aligned} \mathbf{F} \mathbf{c}_i &= \sum_j \mathbf{S} \mathbf{c}_j \epsilon_{ji} \\ \bar{\mathbf{F}} \bar{\mathbf{c}}_i &= \sum_j \bar{\mathbf{S}} \bar{\mathbf{c}}_j \epsilon_{ij} \end{aligned} \right\} \quad (58)$$

In the same way as in the previous section it follows that the ϵ_{ij} 's are the elements of an hermitian matrix ϵ ; the two equations (58) then become equivalent. We may write then for Eqs. (58)

$$\mathbf{F} \mathbf{c}_i = \mathbf{S} \mathbf{c}_i \epsilon_i. \quad (58')$$

Again we may assume without loss of generality that ϵ is a diagonal matrix with real diagonal elements ϵ_i ; Eq. (58') then reduces to

$$\mathbf{F} \mathbf{c}_i = \epsilon_i \mathbf{S} \mathbf{c}_i. \quad (59)$$

Let us assume for the moment that the Eqs. (59) have been solved, that is, that we have found a set of n vectors \mathbf{c}_i satisfying Eqs. (59), where the matrix \mathbf{F} in turn is calculated from this set.

Now regarding \mathbf{F} as a given matrix, that is, assuming \mathbf{F} to be expressed explicitly in terms of the solutions of Eqs. (59), we consider the equation

$$\mathbf{F} \mathbf{c} = \epsilon \mathbf{S} \mathbf{c}, \quad \text{or} \quad (\mathbf{F} - \epsilon \mathbf{S}) \mathbf{c} = 0. \quad (60)$$

In Eq. (60), \mathbf{F} and \mathbf{S} are given matrices, and \mathbf{c} and ϵ are to be found. Equation (60) is a generalization of the eigenvalue equation for an hermitian matrix; Eq. (60) becomes identical with the latter if \mathbf{S} is replaced by the unit matrix. It is convenient to use the standard terminology of eigenvalues and eigenvectors for the solutions of Eq. (60); however, these eigenvalues and eigenvectors depend on both matrices \mathbf{F} and \mathbf{S} .

In Appendix II it is shown that all the important statements about the eigenvalues and eigenvectors of an hermitian matrix still hold with slight modifications for the eigenvalues and eigenvectors of Eq. (60), namely:

(1) The eigenvalues of Eq. (60) are the roots of the secular equation

$$\text{Det}(\mathbf{F} - \epsilon\mathbf{S}) = 0; \quad (61)$$

this equation is always of the m th degree in ϵ (\mathbf{F} and \mathbf{S} are $m \times m$ matrices), and all its m roots are real.

(2) Eigenvectors belonging to different eigenvalues are mutually orthogonal.²²

(3) Any eigenvector belonging to a p -fold root of Eq. (61) is expressible as a linear combination of p linearly independent eigenvectors; conversely, any linear combination of these p independent vectors is an eigenvector. The number p is called the degree of degeneracy of the eigenvalue.

(4) The p linearly independent eigenvectors belonging to a p -fold degenerate eigenvalue can always be chosen so as to form an orthonormal set;²² this set is determined except for a unitary transformation of these p vectors among themselves (this reduces, in the case of $p=1$, to multiplication by a phase factor).

(5) After orthonormalization has been carried out for every eigenvalue, all the m eigenvectors form together an orthonormal set.

Among the solutions ϵ , \mathbf{c} of Eq. (60) there will of course be the set ϵ_i , \mathbf{c}_i , $i=1, 2, \dots, n$, which satisfied Eqs. (59). The n eigenvectors \mathbf{c}_i must belong to the n lowest eigenvalues of Eq. (60), since otherwise we would be dealing with an excited state. The n eigenvectors \mathbf{c}_i represent the n ground-state orbitals; the remaining eigenvectors $\mathbf{c}_{n+1}, \dots, \mathbf{c}_m$ represent excited orbitals. As in the Hartree-Fock method, we label the ground-state orbitals with the indices $i, j, k, l=1, 2, \dots, n$; the excited orbitals with $a, b=n+1, n+2, \dots, m$; and either ground state or excited orbitals with $f, g=1, 2, \dots, m$. We shall call the eigenvalues of Eq. (60) *LCAO orbital energies*.

The general procedure for solving Eqs. (59) is one of trial and error. One assumes a set of vectors \mathbf{c}_i , calculates the matrix \mathbf{G} (hence \mathbf{F}), solves (60) and (61) for the n lowest eigenvalues, and compares the resulting \mathbf{c}_i 's with the assumed ones. Guided by this comparison, a new set of \mathbf{c}_i 's is chosen and the outlined procedure repeated. This process is then continued until the assumed and calculated \mathbf{c}_i 's agree. Because of the great similarity with the Hartree-Fock self-consistent field method, we shall call this procedure the *LCAO self-consistent field method*.

²² Ordinarily, orthogonality of the vectors \mathbf{c}_i and \mathbf{c}_j is expressed by $\mathbf{c}_i^* \mathbf{c}_j = 0$. However, in the present case we define \mathbf{c}_i and \mathbf{c}_j to be orthogonal if $\mathbf{c}_i^* \mathbf{S} \mathbf{c}_j = 0$. Another way of saying this is that \mathbf{S} is the metric fundamental tensor in the space subtended by the vectors \mathbf{c}_i .

The Hartree-Fock and *LCAO* self-consistent field methods have been developed above along analogous lines and yielded analogous results. The most important difference between the two methods from a practical point of view is the amount of labor required for carrying out the numerical calculations; the *LCAO* method is usually feasible and rather straightforward, whereas the Hartree-Fock method is a very complicated mathematical problem.

For the set of *AO*'s from which the *MO*'s are to be constructed, we take all the *AO*'s of the corresponding free atoms that are occupied in their ground states, and those unoccupied ones which differ little in energy from the occupied ones. This means for the elements in the first row of the periodic table the $1s$, $2s$, and $2p$ *AO*'s. The $1s$ *AO*'s are then commonly called the *inner shell AO*'s. We assume that the *AO*'s on the same atom are orthonormal; this involves no loss of generality, since they can always first be orthogonalized.

We now expect that the matrices \mathbf{S} and \mathbf{F} have approximately the following block form

$$\left[\begin{array}{cccc} \text{inner sh.} & 0 & 0 & 0 \\ \text{atom } a & & & \\ 0 & \text{inner sh.} & 0 & 0 \\ & \text{atom } b & & \\ 0 & 0 & \text{valence sh.} & \text{interaction} \\ & & \text{atom } a & \text{val. sh. } a \text{ and } b \\ 0 & 0 & \text{interaction} & \text{valence sh.} \\ & & \text{val. sh. } a \text{ and } b & \text{atom } b \end{array} \right]$$

for a diatomic molecule; the generalization to the case of a polyatomic molecule is obvious. Then the linear equation (60) and the corresponding secular equation (61) break down into inner shell equations, one for each atom, and a valence shell equation involving all the atoms of the molecule. The inner shell equations should be nearly identical with the corresponding equations for the free atoms; then the *MO*'s and orbital energies of the *molecular* inner shells are practically identical with those of the *atomic* inner shells. There is one exception to this, namely, when there is degeneracy among the inner shell *AO*'s of the different atoms, which is to be expected in case the molecule has symmetry. Then the very small interaction between degenerate *AO*'s which is always present is sufficient to make the correct *MO*'s quite different from single atom *AO*'s although the *MO* energies are still practically identical with the *AO* energies. So, for instance, in N_2 , if $1s$ and $1s'$ are the two inner shell *AO*'s of the two nitrogen atoms, the correct inner shell *MO*'s which can be built from these are $2^{-1/2}(1s+1s')$ and $2^{-1/2}(1s-1s')$; and in the more general case of a polyatomic molecule the inner shell *MO*'s are obtained by a unitary transformation of the inner shell *AO*'s. Since in the molecule *all* the inner shell *MO*'s will be occupied, we can subject these *MO*'s to a unitary transformation by which we obtain back the inner shell *AO*'s; the total *AP* wave function then

undergoes a transformation of the type (42), i.e., remains unchanged. Hence it makes no difference in the total wave function whether the inner shell electrons are assigned to the MO 's or AO 's.

Frequently, Eqs. (60) and (61) can be reduced to still smaller blocks by using the molecular symmetry if present. These matters will be discussed in detail in Sec. VI.

We finally note that in all important problems of molecule formation the number of valence AO 's always exceeds the number of $LCAO$ MO 's that is necessary for the ground state AP : $m \geq n$. This guarantees that Eqs. (60) and (61) have always more eigenvectors and eigenvalues than are required for the ground-state AP ; consequently, by solving the ground-state problem we obtain always a number of "excited orbitals."

IV. IONIZATION AND EXCITATION ENERGIES

For the calculation of molecular ionization and excitation energies, we have to set up approximate wave functions for the ionized or excited states. In the two preceding sections, we obtained a fairly simple theoretical framework for the following reasons:

(1) We restricted ourselves to a single AP of the closed-shell type.

(2) In the process of minimizing the energy, the AP was not subjected to any auxiliary condition (keeping the MO 's orthonormal was no restriction on the AP).

For ionized and excited states, however, matters are more complicated because:

(1) Most ionized and excited states in which we are interested do not have a closed-shell structure.

(2) For an excited state, the approximate wave function must be kept orthogonal to the wave functions of all the states of lower energy, which is a rather unpleasant auxiliary condition when minimizing the energy. This difficulty disappears, however, if the excited state under consideration is the lowest state of its symmetry species, since the required orthogonality is then automatically achieved by permitting only functions of the correct symmetry species in the variational process.

(3) For many excited states a single AP is inadequate, and we have to use a *linear combination of AP 's* ($LCAP$), or, in the case of a degenerate state, a set of several $LCAP$'s; this also complicates the procedure of minimizing the energy in an unpleasant way.

These mathematical complications, aside from making a treatment analogous to that of the previous sections rather cumbersome, necessitate in practically every type of case a special treatment. We shall therefore develop a less accurate but much simpler method, which can be used as an extension of both the Hartree-Fock and the $LCAO$ method.

The basic idea of this procedure is that for an ionized or excited state we do not set up and solve the appropriate variational problem by which all the MO 's have to be determined for that particular state, but we make use of the MO 's which were found from the variational problem for the ground state.

The wave function of an ionized state is now obtained

by omitting one (or several) of the MO 's from the ground-state AP .²³

The wave function for the ground state is given by

$${}^1\Phi_0 = [(2n)!]^{1/2} (\varphi_1\alpha)^{n_1} (\varphi_1\beta)^{n_2} \cdots (\varphi_n\alpha)^{2n_1-1} (\varphi_n\beta)^{2n_2}. \quad (19)$$

We shall use the shorthand notation

$${}^1\Phi_0 = (\varphi_1\alpha)(\varphi_1\beta) \cdots (\varphi_n\alpha)(\varphi_n\beta). \quad (62)$$

The left superscript on Φ refers to the multiplicity (that is, degree of spin degeneracy) of the electronic state; a closed-shell ground state is of course a singlet. The subscript 0 refers to the ground state.

The energy of the ground state is given by

$$E({}^1\Phi_0) = 2 \sum_i H_i + \sum_{ij} (2J_{ij} - K_{ij}). \quad (20)$$

Let us consider the singly ionized state obtained by removing either of the two electrons occupying the MO φ_i , and let us first assume that φ_i does not belong to a degenerate set. The wave functions for this ionized state are in our approximation

$${}^2\Phi_i = (\varphi_1\alpha)(\varphi_1\beta) \cdots (\varphi_{i-1}\alpha)(\varphi_{i-1}\beta) \times \begin{Bmatrix} (\varphi_i\alpha) \\ (\varphi_i\beta) \end{Bmatrix} (\varphi_{i+1}\alpha)(\varphi_{i+1}\beta) \cdots (\varphi_n\alpha)(\varphi_n\beta). \quad (63)$$

This state is a doublet, the two wave functions (63) having the energy²⁴

$$\begin{aligned} E({}^2\Phi_i) &= 2 \sum_{j \neq i} H_j + H_i + \sum_{j, k \neq i} (2J_{jk} - K_{jk}) \\ &+ \sum_{j \neq i} (2J_{ij} - K_{ij}) = 2 \sum_j H_j \\ &+ \sum_{jk} (2J_{jk} - K_{jk}) - H_i - \sum_j (2J_{ij} - K_{ij}) \\ &= E({}^1\Phi_0) - H_i - \sum_j (2J_{ij} - K_{ij}). \end{aligned}$$

Hence, in this approximation, the energy required for removing one of the electrons occupying φ_i is given by

$$E({}^2\Phi_i) - E({}^1\Phi_0) = -H_i - \sum_j (2J_{ij} - K_{ij}). \quad (64)$$

Equation (64) can be written in a more convenient form. Namely, in the Hartree-Fock method (see Eqs. (21), (25), (33), and (43)) we have

$$\begin{aligned} H_i + \sum_j (2J_{ji} - K_{ji}) &= \int \bar{\varphi}_i \{ H + \sum_j (2J_j - K_j) \} \varphi_i dv \\ &= \int \bar{\varphi}_i F \varphi_i dv = \epsilon_i \int \bar{\varphi}_i \varphi_i dv = \epsilon_i. \end{aligned}$$

²³ The procedure of using the ground state MO 's gives rather good approximations for singly ionized states; see reference 25. For multiple ionization the approximation is expected to become progressively worse.

²⁴ This expression can easily be found by an argument analogous to that of footnote 14.

Similarly, in the *LCAO* method (see Eqs. (52), (53), and (59)) we have

$$H_i + \sum_j (2J_{ji} - K_{ji}) = \mathbf{c}_i^* \{ \mathbf{H} + \sum_j (2\mathbf{J}_j - \mathbf{K}_j) \} \mathbf{c}_i \\ = \mathbf{c}_i^* \mathbf{F} \mathbf{c}_i = \epsilon_i \mathbf{c}_i^* \mathbf{S} \mathbf{c}_i = \epsilon_i.$$

Hence in both the Hartree-Fock and *LCAO* method Eq. (64) reduces to

$$E(^2\Phi_i) - E(^1\Phi_0) = -\epsilon_i. \quad (65)$$

In Eq. (65), if $^1\Phi_0$ and $^2\Phi_i$ are built from Hartree-Fock *MO*'s, then ϵ_i is the Hartree-Fock orbital energy of φ_i ; if $^1\Phi_0$ and $^2\Phi_i$ are built from *LCAO MO*'s, then ϵ_i is the *LCAO* orbital energy.

If $^1\Phi_0$ and $^2\Phi_i$ (Hartree-Fock or *LCAO*) are reasonable approximations to the exact wave functions of the corresponding electronic states, then the $-\epsilon_i$'s should give reasonable approximations to experimental ionization potentials; this justifies the name "orbital energy" for ϵ_i .

It is remarkable that the ionization potentials calculated by means of (65) are in closer agreement with experiment than those obtained by solving the variational problems for the energies of the ground state and the ionized state separately, and subtracting. The explanation for this was given by Mulliken.²⁵

If in the ground-state *AP* the orbitals $\varphi_i, \dots, \varphi_{i+p-1}$ form a p -fold degenerate set, then we can construct p pairs of wave functions of the type (63), corresponding to removal of an electron from any one of the *MO*'s $\varphi_i, \dots, \varphi_{i+p-1}$. These wave functions all have the same energy. The ionized state therefore has, apart from spin duplicity, the same degeneracy as the orbitals $\varphi_i, \dots, \varphi_{i+p-1}$.

Ionized states obtained by removing two or more electrons can be treated in a fashion analogous to that for singly ionized states. The treatment, however, is more complicated. Since these states are also less important from an experimental point of view, we shall not develop the theory for them.

For the lowest excited states, approximate wave functions are obtained by replacing one *MSO* of the ground-state *AP* by a new *MSO*, which has to be orthogonal to all the ground-state *MSO*'s, in particular to the one which it replaces. Let us first assume that an electron is excited from φ_i to φ_a , and that neither φ_i nor φ_a is a member of a degenerate set. Then, corresponding to the different possibilities with respect to the spin functions, we have to consider simultaneously the four wave functions

$$(\varphi_1\alpha)(\varphi_1\beta) \cdots (\varphi_{i-1}\alpha)(\varphi_{i-1}\beta) \left\{ \begin{array}{l} (\varphi_i\alpha)(\varphi_a\alpha) \\ (\varphi_i\alpha)(\varphi_a\beta) \\ (\varphi_i\beta)(\varphi_a\alpha) \\ (\varphi_i\beta)(\varphi_a\beta) \end{array} \right\} \\ \times (\varphi_{i+1}\alpha)(\varphi_{i+1}\beta) \cdots (\varphi_n\alpha)(\varphi_n\beta).$$

These four wave functions have to be considered on an equal footing; hence we should be prepared if necessary to take four new linear combinations of these four. Indeed, it is well known that they give rise to a singlet and a triplet state for which the correct linear combinations are given by

$$^1\Phi_{ia} = (\varphi_1\alpha) \cdots (\varphi_{i-1}\beta) \\ \times \frac{1}{\sqrt{2}} \{ (\varphi_i\alpha)(\varphi_a\beta) - (\varphi_i\beta)(\varphi_a\alpha) \} \\ \times (\varphi_{i+1}\alpha) \cdots (\varphi_n\beta), \\ ^3\Phi_{ia} = (\varphi_1\alpha) \cdots (\varphi_{i-1}\beta) \\ \times \left\{ \begin{array}{l} (\varphi_i\alpha)(\varphi_a\alpha) \\ \frac{1}{\sqrt{2}} \{ (\varphi_i\alpha)(\varphi_a\beta) + (\varphi_i\beta)(\varphi_a\alpha) \} \\ (\varphi_i\beta)(\varphi_a\beta) \end{array} \right\} \\ \times (\varphi_{i+1}\alpha) \cdots (\varphi_n\beta). \quad (66)$$

The three triplet wave functions have, of course, the same energy, since we neglect spin-orbit coupling throughout this paper; the triplet energy ordinarily is below the singlet energy (Hund's rule; see Eq. (67)). We note that in (66) the singlet wave function and one of the triplet wave functions are *LCAP*'s whereas the two other triplet wave functions are still *AP*'s.

In the case that either φ_i or φ_a is a member of a p -fold degenerate set, then there are p sets of wave functions of the type (66); all the singlets have the same energy, and the same holds for the triplets.

If both φ_i and φ_a belong to a degenerate set, then the wave functions of the type (66) are in general no longer good approximations to the exact wave functions. In this case wave functions of the relatively simple type (66) do not belong to particular symmetry species. We have then to form suitable linear combinations of wave functions of the type (66); there will result various *LCAP*'s of different symmetry species and different energies. An interesting example of this case is provided by the lowest excited states of benzene.⁵

This last case, where it is impossible to set up wave functions of correct symmetry of the type (66), is a special case of the frequently occurring phenomenon of *configurational mixing*. Namely, if there are two or more sets of wave functions of the type (66) which belong to the same symmetry species and whose energies lie fairly close together, then in general no such single set is acceptable; but an acceptable wave function can then be formed as a linear combination from these various sets. Such an acceptable *LCAP* consists then of a mixture of different orbital excitations, that is, a mixture of different configurations.

We now turn to the question of how an excited *MO* φ_a is to be determined. If we want to find the best wave function for the excitation from one particular *MO* φ_i to

²⁵ R. S. Mulliken, *J. chim. phys.* **46**, 497 (1949).

an excited MO φ_a , then we have to minimize the average energy of the singlet and triplet states given by (66). However, if we want to use the *same* MO φ_a to describe excitations from different MO 's φ_i , then we have to minimize the average energy of all the singlets and triplets which are under consideration. It is obvious then that we obtain different equations for determining φ_a according to what use we want to make of φ_a . In addition, such equations for φ_a are rather complicated. It therefore seems hardly worth while to develop the theory for the most general cases.

However, in the $LCAO$ treatment of molecules of considerable symmetry the excited MO 's are often uniquely determined by the symmetry and/or the required orthogonality of the excited MO to the ground-state MO 's. In these cases the excited MO 's are identical with the excited MO 's which are found from the linear equations (60); the latter satisfy the requirements just mentioned of symmetry (see Sec. VI) and orthogonality (see Sec. III). It seems likely that in those cases where the symmetry and orthogonality requirements do not uniquely determine the excited MO 's, the excited MO 's found from Eqs. (60) may still be acceptable for describing actual excitation processes.

The energies of the singlet and triplet states given by the wave functions (66) are²⁶

$$E(^{1,3}\Phi_{ia}) = 2 \sum_{j \neq i} H_j + H_i + H_a + \sum_{j,k \neq i} (2J_{jk} - K_{jk}) \\ + \sum_{j \neq i} (2J_{ij} - K_{ij}) + \sum_{j \neq i} (2J_{ja} - K_{ja}) + J_{ia} \pm K_{ia},$$

where the plus sign holds for the singlet, and the minus sign for the triplet. This expression reduces to

$$E(^{1,3}\Phi_{ia}) = \sum_j H_j + \sum_{jk} (2J_{jk} - K_{jk}) - H_i \\ - \sum_j (2J_{ij} - K_{ij}) + H_a + \sum_j (2J_{ja} - K_{ja}) \\ - (J_{ia} - K_{ia}) \pm K_{ia},$$

where the summations now are to be taken over all the ground-state MO 's. Comparing this result with Eq. (20), we find for the excitation energy

$$E(^{1,3}\Phi_{ia}) - E(^1\Phi_0) = H_a + \sum_j (2J_{ja} - K_{ja}) \\ - H_i - \sum_j (2J_{ij} - K_{ij}) - (J_{ia} - K_{ia}) \pm K_{ia}. \quad (67)$$

If we apply this result now to the $LCAO$ treatment of a case where φ_a is obtained from Eqs. (60), we obtain

$$E(^{1,3}\Phi_{ia}) - E(^1\Phi_0) = \epsilon_a - \epsilon_i - (J_{ia} - K_{ia}) \pm K_{ia}. \quad (68)$$

It is to be noted that the average excitation energy of the singlet and triplet is not what one would expect

²⁶ The case where both φ_i and φ_a are degenerate is here to be excluded.

offhand, namely, $\epsilon_a - \epsilon_i$. The reason for this is that ϵ_i and ϵ_a are both eigenvalues of the self-consistent field $LCAO$ hamiltonian of the ground state; for the excited state the quantity ϵ_a can therefore not be expected to have the same meaning as the orbital energies ϵ_i of the ground-state MO 's.²⁷

V. THE USE OF MOLECULAR SYMMETRY IN THE HARTREE-FOCK TREATMENT OF A CLOSED-SHELL GROUND STATE²⁸

When a molecule has symmetry, group theory provides a powerful means of simplifying the problem of finding the exact electronic wave functions. From the fact that the total hamiltonian operator \mathcal{H} is invariant under any operation of the symmetry group of the molecule, it follows that the exact wave function(s) of a particular electronic state belong(s) to an irreducible representation of that symmetry group (or, in the very improbable case of accidental degeneracy, that the wave functions can always be chosen in sets so that each set belongs to an irreducible representation).²⁸ The wave functions of the various states can then be classified according to the *symmetry species* (irreducible representations) to which they belong.

It would be gratifying if it could be shown that for a molecule the best Hartree-Fock AP or the best $LCAO$ AP also necessarily belongs to a particular symmetry species.

That this is by no means obvious is known from self-consistent field calculations on atoms. Namely, in the Hartree-Fock method for many non-closed-shell atoms, and also in the older Hartree method (orbital product wave function instead of AP), the field for the individual electrons is not always spherically symmetrical. As a result, the self-consistent field AO 's, and consequently also, the total wave functions, do not belong to irreducible representations of the group of rotations and reflections around the center of symmetry. Therefore, in most applications in the past the Hartree and Hartree-Fock methods have been modified so as to give the best AO 's which do belong to irreducible representations.

In this section we shall prove the following facts for the Hartree-Fock method of a *closed-shell ground state*; these are equally valid for atoms using AO 's and for molecules using MO 's:

(1) The AP built from Hartree-Fock MO 's in the manner described in Sec. II is a singlet and is totally symmetrical; that is, it belongs to the identical representation of both the spin and symmetry groups.

(2) The Hartree-Fock MO 's used may be grouped in sets such that each set belongs to an irreducible representation of the symmetry group.

(3) The Hartree-Fock MO 's can always be chosen real.

²⁷ The ϵ_a as defined here is called an "unacceptable" ϵ by Mulliken; he defines our $\epsilon_a - J_{ia} + K_{ia}$ as the orbital energy—see reference 25.

²⁸ The methods used in this chapter follow closely those of E. Wigner, reference 13, especially Chapters XI and XII.

In Sec. I we have made implicit use of some of these facts; namely, in the definition of electron shells and of a closed-shell ground state, we assumed that degeneracy can occur for the MO 's, usually as a result of molecular symmetry. We therefore have to give a new definition of a closed-shell ground state which does not involve molecular symmetry.

We now define a molecule with a closed-shell ground state as a molecule for which there exists, aside from an arbitrary phase factor, only one AP which makes the energy reach its absolute minimum.

The first conclusion which can be drawn from this definition is that each MO in the closed-shell AP occurs twice, once with either spin function. For if this were not the case, then we could obtain by changing spin functions one or several other AP 's for which the energy would also reach its absolute minimum. An AP representing a closed-shell ground state therefore has the form (19).

Next we show that the AP belongs to a one-dimensional representation of the symmetry group. Let $f(\mathbf{r})$ be any function of \mathbf{r} , the radius vector of the point (x, y, z) . We subject \mathbf{r} to the transformation

$$\mathbf{r} \rightarrow \mathbf{r}' \equiv \mathcal{R}\mathbf{r}, \quad (69)$$

where \mathcal{R} is the operator symbolizing the transformation. The transformed function $f'(\mathbf{r})$, or $\mathcal{R}f(\mathbf{r})$,²⁹ we define by means of

$$f'(\mathbf{r}') = f(\mathbf{r}), \quad (70)$$

which expresses that the function $f'(\mathbf{r})$, evaluated at the transformed point \mathbf{r}' , has the same numerical value as the function $f(\mathbf{r})$ at the untransformed point \mathbf{r} . Using the operator notation, we can write for Eq. (70)

$$\mathcal{R}f(\mathcal{R}\mathbf{r}) = f(\mathbf{r}),$$

or, if the operator \mathcal{R} has an inverse,

$$\mathcal{R}f(\mathbf{r}) = f(\mathcal{R}^{-1}\mathbf{r}). \quad (71)$$

Equation (71) defines the function $\mathcal{R}f$ in terms of the function f .

It is easily established that the operator \mathcal{R} is linear, that is

$$\mathcal{R}(af + bg) = a(\mathcal{R}f) + b(\mathcal{R}g), \quad (72)$$

and that

$$\mathcal{R}(fg) = (\mathcal{R}f)(\mathcal{R}g), \quad (73)$$

where f and g are any functions, and a and b any constants. The correctness of Eqs. (72) and (73) is easily seen by applying the definition (70) to both sides of the equations.

Let $\Phi(\mathbf{r})$ be the normalized AP representing the closed-shell ground state, where \mathbf{r} now stands as an abbreviation for all the space coordinates of the $2n$

electrons; then

$$\int \bar{\Phi}(\mathbf{r})\Phi(\mathbf{r})d\tau = 1, \quad (74)$$

$$\int \bar{\Phi}(\mathbf{r})\mathcal{H}\Phi(\mathbf{r})d\tau = E_{\min}. \quad (75)$$

Now let \mathcal{R} be any operation of the symmetry group of the molecule; this is expressed by²⁸

$$\mathcal{H}\mathcal{R} = \mathcal{R}\mathcal{H}. \quad (76)$$

Performing in Eqs. (74) and (75) the operation \mathcal{R}^{-1} under the integral signs on the *integration variables* obviously does not change the values of these integrals. Since \mathcal{R}^{-1} effects an orthogonal transformation on the coordinates of the electrons, the volume element $d\tau$ remains unchanged. Hence we find

$$1 = \int \bar{\Phi}(\mathcal{R}^{-1}\mathbf{r})\Phi(\mathcal{R}^{-1}\mathbf{r})d\tau = \int \overline{\mathcal{R}\Phi}(\mathbf{r})\mathcal{R}\Phi(\mathbf{r})d\tau,$$

$$\begin{aligned} E_{\min} &= \int \bar{\Phi}(\mathcal{R}^{-1}\mathbf{r})\mathcal{H}\Phi(\mathcal{R}^{-1}\mathbf{r})d\tau \\ &= \int \overline{\mathcal{R}\Phi}(\mathbf{r})\mathcal{H}\mathcal{R}\Phi(\mathbf{r})d\tau = \int \overline{\mathcal{R}\Phi}(\mathbf{r})\mathcal{H}\mathcal{R}\Phi(\mathbf{r})d\tau. \end{aligned} \quad (77)$$

We see thus that the transformed wave function $\mathcal{R}\Phi$ is also normalized and minimizes the energy. *Since it was assumed that there is only one AP which minimizes the energy*, $\mathcal{R}\Phi$ can differ from Φ only by a phase factor:

$$\mathcal{R}\Phi = c_{\mathcal{R}}\Phi, \quad c_{\mathcal{R}}c_{\mathcal{R}} = 1. \quad (77)$$

For any two successive operations of the group we have

$$c_{\mathcal{S}\mathcal{R}}\Phi = \mathcal{S}\mathcal{R}\Phi = \mathcal{S}c_{\mathcal{R}}\Phi = c_{\mathcal{R}}\mathcal{S}\Phi = c_{\mathcal{R}}c_{\mathcal{S}}\Phi = c_{\mathcal{S}\mathcal{C}\mathcal{R}}\Phi,$$

where the third equality sign holds because of (72). we now have the result

$$c_{\mathcal{S}\mathcal{R}} = c_{\mathcal{S}}c_{\mathcal{R}}; \quad (78)$$

so that the numbers $c_{\mathcal{R}}$ furnish a one-dimensional representation of the symmetry group. We shall see presently that this representation has to be the identical representation, that is, $c_{\mathcal{R}} = 1$ for every \mathcal{R} .

We show now that the Hartree-Fock MO 's furnish a representation of the symmetry group. Writing out Eq. (77) in terms of MO 's, and using Eqs. (72) and (73), we obtain

$$\begin{aligned} &(\mathcal{R}\varphi_1\alpha)^{l_1} \cdots (\mathcal{R}\varphi_n\alpha)^{n} (\mathcal{R}\varphi_1\beta)^{n+1} \cdots (\mathcal{R}\varphi_n\beta)^{2n_l} \\ &= c_{\mathcal{R}}(\varphi_1\alpha)^{l_1} \cdots (\varphi_n\alpha)^{n} (\varphi_1\beta)^{n+1} \cdots (\varphi_n\beta)^{2n_l}. \end{aligned} \quad (79)$$

Now the orthonormal set of functions φ_i , $i=1, 2, \dots, n$ can always be supplemented by additional func-

²⁹ Note that $\mathcal{R}f$ is used as the symbol for a function of \mathbf{r} just as f is used.

³⁰ Note that $\mathcal{H}\mathcal{R}\Phi$ is treated as *one* function symbol like $\mathcal{R}\Phi$. Then from (71) and (76) follows $\mathcal{H}\mathcal{R}\Phi(\mathcal{R}^{-1}\mathbf{r}) = \mathcal{R}\mathcal{H}\Phi(\mathbf{r}) = \mathcal{H}\mathcal{R}\Phi(\mathbf{r})$.

tions φ_a , $a=n+1, n+2, \dots$ in such a way that the set φ_f , $f=1, 2, \dots, n, n+1, n+2, \dots$ is a complete orthonormal set. Then any one-electron function can be developed in terms of this set. We develop the function $\mathfrak{R}\varphi_i$:

$$\mathfrak{R}\varphi_i = \sum_{f=1}^{\infty} \varphi_f U_{fi}, \quad i=1, 2, \dots, n, \quad (80)$$

where the coefficients U_{fi} are to be determined. Inserting (80) into the left side of Eq. (79), we obtain

$$\begin{aligned} & \sum_{f_1 \dots f_{2n}} U_{f_1 1} \dots U_{f_n n} U_{f_{n+1} 1} \dots U_{f_{2n} n} (\varphi_{f_1} \alpha)^{l_1} \\ & \dots (\varphi_{f_n} \alpha)^{n} (\varphi_{f_{n+1}} \beta)^{n+1} \dots (\varphi_{f_{2n}} \beta)^{2n l_2} \\ & = c_{\mathfrak{R}} (\varphi_1 \alpha)^{l_1} \dots (\varphi_n \alpha)^n (\varphi_1 \beta)^{n+1} \dots (\varphi_n \beta)^{2n l_2}. \end{aligned} \quad (81)$$

Equation (81) must be an identity. The left side is seen to be a sum over AP 's, while the right side is a single AP . The AP 's which represent different spin-orbital configurations are all linearly independent. Hence, upon expansion of the summation in the left side of Eq. (81), we can put the coefficient of the ground-state AP equal to $c_{\mathfrak{R}}$, whereas the coefficients of all the other configurations have to vanish. The ground-state AP occurs whenever f_1, \dots, f_n , and f_{n+1}, \dots, f_{2n} are permutations of $1, \dots, n$. It is easily seen that the coefficients of all these terms add up to

$$\begin{vmatrix} U_{11} & \dots & U_{1n} \\ \dots & \dots & \dots \\ U_{n1} & \dots & U_{nn} \end{vmatrix}^2$$

Similarly, for the configuration

$$\begin{aligned} & (\varphi_1 \alpha)^{l_1} \dots (\varphi_{i-1} \alpha)^{i-1} (\varphi_a \alpha)^i (\varphi_{i+1} \alpha)^{i+1} \\ & \dots (\varphi_n \alpha)^n (\varphi_1 \beta)^{n+1} \dots (\varphi_n \beta)^{2n l_2}, \end{aligned}$$

where $a > n$, the coefficient is found to be

$$\begin{vmatrix} U_{11} & \dots & U_{1n} \\ \dots & \dots & \dots \\ U_{i-1,1} & \dots & U_{i-1,n} \\ U_{a1} & \dots & U_{an} \\ U_{i+1,1} & \dots & U_{i+1,n} \\ \dots & \dots & \dots \\ U_{n1} & \dots & U_{nn} \end{vmatrix} \times \begin{vmatrix} U_{11} & \dots & U_{1n} \\ \dots & \dots & \dots \\ U_{n1} & \dots & U_{nn} \end{vmatrix}.$$

Hence, we find

$$\text{Det}^2(\mathbf{U}) = c_{\mathfrak{R}}, \quad (82)$$

$$\text{Det}(\mathbf{U}) \sum_{j=1}^n U_{aj} \text{cofactor}(U_{ij}) = 0, \quad (83)$$

where \mathbf{U} is an abbreviation for the matrix

$$\begin{pmatrix} U_{11} & \dots & U_{1n} \\ \dots & \dots & \dots \\ U_{n1} & \dots & U_{nn} \end{pmatrix}.$$

We multiply Eq. (83) by U_{ik} , and sum over i ; the result is

$$\begin{aligned} 0 &= \text{Det}(\mathbf{U}) \sum_{i,j=1}^n U_{ik} U_{aj} \text{cofactor}(U_{ij}) \\ &= \text{Det}(\mathbf{U}) \sum_{j=1}^n U_{aj} \sum_{i=1}^n U_{ik} \text{cofactor}(U_{ij}) \\ &= \text{Det}^2(\mathbf{U}) \sum_{j=1}^n U_{aj} \delta_{kj} = \text{Det}^2(\mathbf{U}) U_{ak} = c_{\mathfrak{R}} U_{ak}; \end{aligned}$$

and since $c_{\mathfrak{R}} \neq 0$,

$$U_{ai} = 0 \quad \text{for } i=1, \dots, n, \quad a=n+1, \dots \quad (84)$$

Inserting Eq. (84) into Eq. (80), we see that under the operation \mathfrak{R} the MO 's transform among themselves:

$$\mathfrak{R}\varphi_i = \sum_{j=1}^n \varphi_j U_{ji}, \quad (85)$$

or, in matrix notation

$$\mathfrak{R}\phi = \phi \mathbf{U}. \quad (85')$$

We show now that the matrix \mathbf{U} is unitary. The MO 's φ_i are normalized:

$$\int \bar{\varphi}_i \varphi_j d\nu = \delta_{ij}.$$

The same holds for the transformed MO 's $\mathfrak{R}\varphi_i$. Transforming the integration variables $\mathbf{r} \rightarrow \mathfrak{R}^{-1}\mathbf{r}$ we find that the MO 's $\mathfrak{R}\varphi_i$ are also orthonormal:

$$\int \overline{\mathfrak{R}\varphi_i} \mathfrak{R}\varphi_j d\nu = \delta_{ij}. \quad (86)$$

Inserting (85) into (86), we obtain

$$\sum_{kl} \bar{U}_{ki} U_{lj} \int \bar{\varphi}_k \varphi_l d\nu = \sum_{kl} \bar{U}_{ki} U_{lj} \delta_{kl} = \sum_k \bar{U}_{ki} U_{kj} = \delta_{ij},$$

or

$$\mathbf{U}^* \mathbf{U} = \mathbf{E}; \quad (87)$$

that is, the matrix \mathbf{U} is unitary.

The matrices \mathbf{U} furnish a representation of the symmetry group. Namely,

$$\phi \mathbf{U}_{\mathfrak{S}\mathfrak{R}} = \mathfrak{S}\mathfrak{R}\phi = \mathfrak{S}(\phi \mathbf{U}_{\mathfrak{R}}) = (\mathfrak{S}\phi) \mathbf{U}_{\mathfrak{R}} = \phi \mathbf{U}_{\mathfrak{S}\mathfrak{R}},$$

or

$$U_{\beta\alpha} = U_{\alpha\beta}^* \quad (88)$$

In Sec. II it was shown that the Hartree-Fock operator F is invariant if the MO 's are subjected to a unitary transformation. The Hartree-Fock MO 's then have to be eigenfunctions of a totally symmetrical operator; therefore, we can apply what was said about exact wave functions in the first paragraph of this section, namely, that they can always be grouped in sets, each set belonging to an irreducible representation.

We show now that the MO 's can always be chosen real. This follows from the fact that \mathcal{H} is a real operator. Namely, if Φ is the closed-shell AP which minimizes the energy, then the same is true for $\bar{\Phi}$; and since it was assumed that there is only one such AP aside from an arbitrary phase factor, $\bar{\Phi} = c\Phi$. The operation of taking the complex conjugate can therefore be considered as another symmetry operation; it is easily seen that this operation satisfies Eqs. (72) and (73). Using the same type of argument as before for the transformed MO 's, we find

$$\bar{\phi} = \phi U, \quad (89)$$

where the matrix U is unitary. Taking the complex conjugate and the inverse of Eq. (89), we obtain

$$\phi = \bar{\phi} \bar{U}, \quad \phi = \bar{\phi} U^*,$$

hence, $\bar{U} = U^*$, or

$$U = U^\dagger, \quad (90)$$

that is, the matrix U is, aside from being unitary, also symmetrical.

In Appendix III it is shown that if a unitary matrix is also symmetrical, then it can always be written as the square of another symmetrical unitary matrix. Hence there exists a matrix V so that

$$U = V^2, \quad V^*V = E, \quad V = V^\dagger. \quad (91)$$

Using this result in Eq. (89), we get

$$\bar{\phi} = \phi V^2,$$

and

$$\phi V = \bar{\phi} V^* = \overline{(\phi V^\dagger)} = \overline{(\phi V)};$$

so that the new set of MO 's defined by

$$\phi' = \phi V \quad (92)$$

is real:

$$\bar{\phi}' = \phi'. \quad (93)$$

Finally, we show that Φ is totally symmetrical. We can choose the MO 's all real. Subjecting them to a molecular symmetry operation, there result again real orbitals, since the arguments of the MO 's have been subjected to a real orthogonal transformation. Therefore, the transformation matrices U_{α} are all real orthogonal matrices, hence

$$\text{Det}(U_{\alpha}) = \pm 1. \quad (94)$$

From Eq. (82) it follows then that

$$c_{\alpha} = \text{Det}^2(U_{\alpha}) = 1. \quad (95)$$

It is to be noted that it is not always possible to choose the MO 's so that they belong to irreducible representations and are at the same time real. This is the case if the symmetry group of the molecule is C_n , S_n , C_{nh} , $n > 2$, or T , T_h . These groups have some irreducible representations which are necessarily complex. In that case we can obtain MO 's which are all real and occur in sets, each set belonging either to a real irreducible representation or to a reducible representation which consists of two irreducible conjugate complex representations.

VI. THE USE OF MOLECULAR SYMMETRY IN THE LCAO PROCEDURE

In the previous section we defined a molecule with a closed-shell ground state as a molecule for which there exists, aside from a phase factor, only one AP built from Hartree-Fock MO 's which minimizes the energy.

The *LCAO* procedure, developed in Sec. III, was founded on the expectation that it is possible to approximate the best MO 's reasonably well by *LCAO* MO 's; whether this can be achieved or not depends to a considerable extent upon the choice of the AO 's from which the *LCAO* MO 's are to be built. If the *LCAO* method works at all, we expect it to give the same qualitative features as the Hartree-Fock method. In particular, if for a particular molecule there is only one Hartree-Fock AP which minimizes the energy, we also expect there to be only one *LCAO* AP which minimizes the energy. Starting from this assumption, we can derive for a molecule with a *closed-shell ground state* the following statements:

(1) The *LCAO* AP which minimizes the energy is necessarily a singlet and is totally symmetrical with respect to the symmetry group of the molecule.

(2) The best *LCAO* MO 's can be chosen so that they belong in sets to irreducible representations of the symmetry group of the molecule.

(3) The best *LCAO* MO 's can all be chosen real.

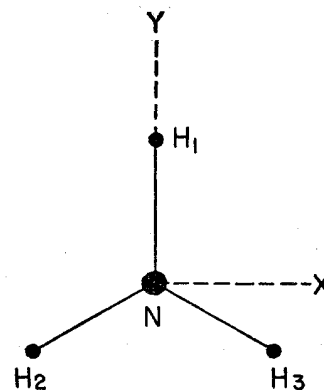
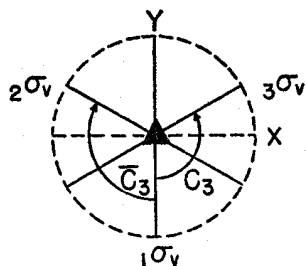


FIG. 1. The NH_3 molecule. The origin is taken at the N nucleus. The three H atoms are located in a plane below and parallel to the XY -plane.

FIG. 2. The symmetry elements of C_{3v} .

The proof is analogous to that for the Hartree-Fock case discussed in the preceding section.

In a symmetrical molecule, there are in general sets of equivalent atoms, that is, of atoms which can be transformed into each other by applying a symmetry operation. So, for instance, in benzene the six carbon atoms form a set of equivalent atoms, and so do the six hydrogen atoms. The set of AO 's from which the $LCAO MO$'s are to be built must contain like AO 's on equivalent atoms. Thus in the NH_3 molecule (see Fig. 1) we use for the three hydrogen atoms three $1s$ AO 's which are identical analytical functions in the local coordinate systems centered in the respective hydrogen atoms. For the nitrogen atom, we use the $1s$, $2s$, $2p_z$, $2p_x$, and $2p_y$ AO 's.

If we perform a group operation \mathcal{R} on the set of AO 's χ_p , then the set of transformed AO 's $\mathcal{R}\chi_p$ is a permutation of the original set χ_p , followed in general by a spatial orthogonal transformation on some subsets. In our example of NH_3 , for a rotation by 120° , the three hydrogen $1s$ AO 's undergo a cyclic permutation; the nitrogen $1s$, $2s$, and $2p_z$ AO 's remain unchanged; and the pair $2p_x$, $2p_y$ undergoes a rotation by 120° . In general, it is clear that the set $\mathcal{R}\chi$ is a unitary transformation of the set χ :

$$\mathcal{R}\chi = \chi A_{\mathcal{R}} \quad (96)$$

where $A_{\mathcal{R}}$ is a unitary matrix. Using the same method which established Eq. (88), we find that the matrices $A_{\mathcal{R}}$ furnish a representation of the symmetry group, namely,

$$A_{S\mathcal{R}} = A_S A_{\mathcal{R}}. \quad (97)$$

The representation $A_{\mathcal{R}}$ will in general be reducible. Since it is a unitary representation, it can be reduced by means of a suitable unitary matrix U . Then in the

equivalent representation $B_{\mathcal{R}}$ given by

$$B_{\mathcal{R}} = U^* A_{\mathcal{R}} U \quad (98)$$

every matrix $B_{\mathcal{R}}$ appears as a step matrix:

$$B_{\mathcal{R}} = \begin{bmatrix} B_{\mathcal{R}}^{(1)} & 0 & \dots & 0 \\ 0 & B_{\mathcal{R}}^{(2)} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & B_{\mathcal{R}}^{(s)} \end{bmatrix}, \quad (99)$$

where the steps $B_{\mathcal{R}}^{(1)}$, $B_{\mathcal{R}}^{(2)}$, \dots , $B_{\mathcal{R}}^{(s)}$ are square matrices, and furnish irreducible representations. In general, among these irreducible representations there will occur equivalent ones; if that is the case, then we can always choose the matrix U so that the equivalent ones are identical and appear adjacently; we shall hereafter assume this to be done.

To illustrate the representations $A_{\mathcal{R}}$ and $B_{\mathcal{R}}$, let us again consider NH_3 . The symmetry group is C_{3v} ; the symmetry elements and their notation are shown in Fig. 2. The irreducible representations are listed in Table I. The generating elements of the group C_{3v} are C_3 and $1\sigma_v$; hence it is sufficient to consider the matrices $A_{\mathcal{R}}$ and $B_{\mathcal{R}}$ for $\mathcal{R} = C_3$ and $\mathcal{R} = 1\sigma_v$.

We number the AO 's as follows: $1sN = \chi_1$, $1sH_1 = \chi_2$, $1sH_2 = \chi_3$, $1sH_3 = \chi_4$, $2sN = \chi_5$, $2p_zN = \chi_6$, $2p_xN = \chi_7$, $2p_yN = \chi_8$. The transformation matrices $A_{\mathcal{R}}$ for $\mathcal{R} = C_3$ and $\mathcal{R} = 1\sigma_v$ are found as follows:

$$\begin{aligned} C_3(\chi_1 \chi_2 \chi_3 \chi_4 \chi_5 \chi_6 \chi_7 \chi_8) \\ &= (\chi_1 \chi_3 \chi_4 \chi_2 \chi_5 \chi_6 -\frac{1}{2}\chi_7 + \frac{1}{2}\sqrt{3}\chi_8 -\frac{1}{2}\sqrt{3}\chi_7 -\frac{1}{2}\chi_8) \\ &= (\chi_1 \chi_2 \chi_3 \chi_4 \chi_5 \chi_6 \chi_7 \chi_8) \\ &\times \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{1}{2}\sqrt{3} \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{bmatrix}; \end{aligned}$$

TABLE I. The irreducible representations of C_{3v} .

C_{3v}	E	C_3	\bar{C}_3	$1\sigma_v$	$2\sigma_v$	$3\sigma_v$
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	-1
E	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{1}{2}\sqrt{3} \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{1}{2}\sqrt{3} \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{pmatrix}$

$$1\sigma_g(\chi_1 \chi_2 \chi_3 \chi_4 \chi_5 \chi_6 \chi_7 \chi_8) = (\chi_1 \chi_2 \chi_4 \chi_3 \chi_5 \chi_6 - \chi_7 \chi_8)$$

$$= (\chi_1 \chi_2 \chi_3 \chi_4 \chi_5 \chi_6 \chi_7 \chi_8) \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

The two matrices are A_{C_3} and $A_{1\sigma_g}$, respectively.

We now wish to completely reduce the representation $A_{\mathcal{R}}$. This reduction is achieved by means of the following transformation matrix:

$$U = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3^{-\frac{1}{2}} & 0 & 0 & 0 & -2 \cdot 3^{-\frac{1}{2}} & 0 & 0 \\ 0 & 3^{-\frac{1}{2}} & 0 & 0 & -2^{-\frac{1}{2}} & -6^{-\frac{1}{2}} & 0 & 0 \\ 0 & 3^{-\frac{1}{2}} & 0 & 0 & 2^{-\frac{1}{2}} & -6^{-\frac{1}{2}} & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

for if we use this U in Eqs. (98), we find

$$B_{C_3} = U \cdot A_{C_3} \cdot U$$

$$= \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{1}{2}\sqrt{3} \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{pmatrix};$$

$$B_{1\sigma_g} = U \cdot A_{1\sigma_g} \cdot U = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

Referring to Table I, it is seen that the representation $B_{\mathcal{R}}$ consists of four times A_1 and twice E .

We return now to the general theory. From Eqs. (96) and (97) it is easily established that the symmetry orbitals σ_p defined by

$$\sigma_p = \sum_q \chi_q U_{qp}, \quad (100)$$

or

$$\sigma = \chi U \quad (100')$$

transform under the operations \mathcal{R} according to the representation $B_{\mathcal{R}}$:

$$\mathcal{R}\sigma = \sigma B_{\mathcal{R}}. \quad (101)$$

Since $B_{\mathcal{R}}$ is in completely reduced form, the symmetry orbitals appear in sets such that each set belongs to an irreducible representation or symmetry species.

In our example the symmetry orbitals are

$$\begin{aligned} (\sigma_1 \sigma_2 \sigma_3 \sigma_4 \sigma_5 \sigma_6 \sigma_7 \sigma_8) &= (\chi_1 \chi_2 \chi_3 \chi_4 \chi_5 \chi_6 \chi_7 \chi_8) U \\ &= (\chi_1 3^{-\frac{1}{2}}(\chi_2 + \chi_3 + \chi_4) \chi_5 \chi_6 \\ &\quad \times 2^{-\frac{1}{2}}(-\chi_3 + \chi_4) 6^{-\frac{1}{2}}(2\chi_2 - \chi_3 - \chi_4) \chi_7 \chi_8), \end{aligned}$$

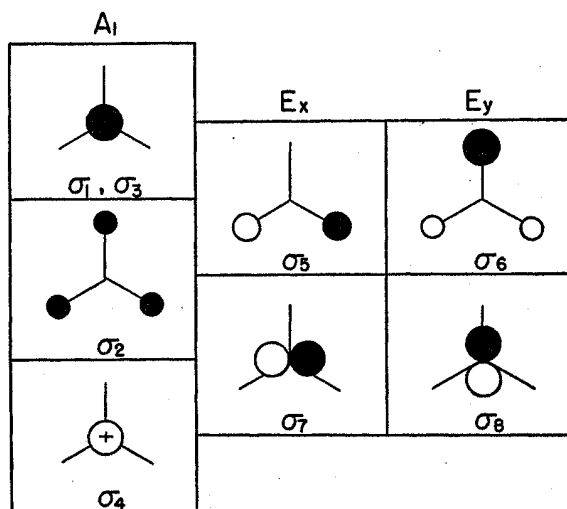


FIG. 3. A set of symmetry orbitals of NH_3 . The full and open circles represent s AO's with positive and negative signs, respectively. The dumbbells represent p AO's with axes in the plane of the paper. The open circle with + sign represents a p AO pointing upward. The magnitude of the coefficients of the AO's in the symmetry orbitals are indicated by the sizes of the circles and dumbbells.

where U is as given above. These symmetry orbitals are drawn schematically in Fig. 3. In such drawings, we shall use the following symbols:

- s AO, positive;
- s AO, negative;
- ⊙ p AO, with axis in the plane of the paper, positive part at the right;
- ⊕ p AO, with axis perpendicular to the plane of the paper, positive above this plane;
- ⊖ p AO, with axis perpendicular to the plane of the paper, negative above this plane.

The magnitude of the coefficient with which an AO enters a symmetry orbital will be indicated by the size of the symbol.

The choice of the symmetry orbitals is in general not unique. First, there is freedom in choosing the explicit forms of the degenerate representations. In C_{3v} we chose the doubly degenerate representation so as to be the explicit transformation of the base vectors (\mathbf{i}, \mathbf{j}) along the X and Y axes. Secondly, if the same irreducible representation occurs more than once in \mathbf{B}_R , then any linear combination of the symmetry orbitals of that species is still a symmetry orbital of that species. Hence, we can replace the set belonging to a particular species by any linear transformation of that set. In NH_3 we can thus replace the set $\sigma_1, \sigma_2, \sigma_3, \sigma_4$ by any linear transformation of this set, and similarly the set σ_5, σ_7 , provided we subject σ_6, σ_8 to the same transformation.

In order to obtain the symmetry orbitals in a nearly unique manner, we shall use the following procedure. First, we pick the degenerate representations in a convenient manner, preferably in real form. Then we arrange the natural AO 's (no hybrids) in sets of equivalent AO 's; these are the smallest possible sets which transform within themselves under the symmetry operations. Finally, we construct then from each set of equivalent AO 's a set of symmetry orbitals. This procedure is unique, except for the choice of the explicit forms of the degenerate representations, and except for an arbitrary phase factor for each symmetry orbital (or, in the case of degeneracy, a common phase factor for all the members of the degenerate set). This method has been followed in our construction of the symmetry orbitals of NH_3 .

Just as we defined the matrix elements

$$M_{pq} = \int \bar{\chi}_p M \chi_q dv$$

corresponding to the operator M , we can now define the corresponding matrix elements M_{pq}^σ evaluated with the symmetry orbitals:

$$M_{pq}^\sigma = \int \bar{\sigma}_p M \sigma_q dv; \quad (102)$$

we shall use the symbol \mathbf{M}^σ for the matrix the elements of which are M_{pq}^σ . It is easily seen that the matrices \mathbf{M} and \mathbf{M}^σ are connected by

$$\mathbf{M}^\sigma = \mathbf{U}^* \mathbf{M} \mathbf{U}, \quad (103)$$

where \mathbf{U} is the matrix which forms the symmetry orbitals from the AO 's (see Eq. (100')). Similarly, we define the vectors \mathbf{c}_f^σ by means of

$$\mathbf{c}_f^\sigma = \mathbf{U}^* \mathbf{c}_f, \quad (104)$$

so that the MO 's φ_f can be expressed either in the

AO 's χ or the symmetry orbitals σ :

$$\varphi_f = \chi \mathbf{c}_f = \sigma \mathbf{c}_f^\sigma. \quad (105)$$

The linear equations (60) and the secular equation (61) can now be transformed into

$$\mathbf{F}^\sigma \mathbf{c}^\sigma = \epsilon \mathbf{S}^\sigma \mathbf{c}^\sigma, \quad (106)$$

$$\text{Det}(\mathbf{F}^\sigma - \epsilon \mathbf{S}^\sigma) = 0, \quad (107)$$

where \mathbf{F}^σ and \mathbf{S}^σ are defined by means of (102) or (103).

Now let the irreducible representations or symmetry species of the symmetry group of the molecule be $\Gamma^{(1)}, \Gamma^{(2)}, \dots, \Gamma^{(\pi)}, \dots$. The symmetry orbitals belong in sets to these representations. We relabel the symmetry orbitals accordingly with triple indices: $\sigma_{\alpha\pi\kappa}$. The index π indicates that $\sigma_{\alpha\pi\kappa}$ belongs to $\Gamma^{(\pi)}$. If there are several sets of symmetry orbitals belonging to $\Gamma^{(\pi)}$, then we number these sets: 1, 2, \dots , α , \dots ; $\sigma_{\alpha\pi\kappa}$ is a member of the α th set of species $\Gamma^{(\pi)}$. Finally, if $\Gamma^{(\pi)}$ is a p -fold degenerate representation, then a set of symmetry orbitals of this species transforms under group operations like the base vectors of a p -dimensional vector space: $\mathbf{e}^{(1)}, \mathbf{e}^{(2)}, \dots, \mathbf{e}^{(p)}$; the index κ indicates that $\sigma_{\alpha\pi\kappa}$ behaves like $\mathbf{e}^{(\kappa)}$.³¹

The following statement is a well-known result from group theory.³² If M is a totally symmetrical operator, then

$$\left. \begin{aligned} \int \bar{\sigma}_{\alpha\pi\kappa} M \sigma_{\beta\rho\lambda} dv &= 0, \quad \text{unless } \pi = \rho \text{ and } \kappa = \lambda; \\ \text{if this is the case, then} \\ \int \bar{\sigma}_{\alpha\pi\kappa} M \sigma_{\beta\pi\kappa} dv &= \int \bar{\sigma}_{\alpha\pi\mu} M \sigma_{\beta\pi\mu} dv \\ &\text{for any } \kappa \text{ and } \mu. \end{aligned} \right\} \quad (108)$$

If we take for M the identity operator or the operator F , then theorem (108) is seen to apply to the elements of \mathbf{S}^σ and \mathbf{F}^σ . Writing out Eqs. (106) and (107) according to the triple indices, we have

$$\sum_{\beta\rho\lambda} (F_{\alpha\pi\kappa, \beta\rho\lambda}^\sigma - \epsilon S_{\alpha\pi\kappa, \beta\rho\lambda}^\sigma) c_{\beta\rho\lambda} = 0, \quad (106')$$

$$\text{Det}(F_{\alpha\pi\kappa, \beta\rho\lambda}^\sigma - \epsilon S_{\alpha\pi\kappa, \beta\rho\lambda}^\sigma) = 0; \quad (107')$$

these equations reduce, because of (108), to

$$\sum_{\beta} (F_{\alpha\pi, \beta\pi}^\sigma - \epsilon S_{\alpha\pi, \beta\pi}^\sigma) c_{\beta\pi\kappa} = 0 \quad (106'')$$

$$\text{Det}(F_{\alpha\pi, \beta\pi}^\sigma - \epsilon S_{\alpha\pi, \beta\pi}^\sigma) = 0. \quad (107'')$$

³¹ A special case of these triple indices is encountered in the customary notation for AO 's: (n, l, m) . Here the quantum number l indicates the irreducible representation; the quantum number m labels the different members in the same irreducible representation; and the quantum number n is an index to distinguish between AO 's which cannot be distinguished any more by symmetry characteristics.

³² See reference 13, p. 124.

There is a set of this type for each symmetry species $\Gamma^{(\pi)}$; if $\Gamma^{(\pi)}$ is p -fold degenerate, then we get the same set p times, once for each value of the index κ , which we omitted accordingly.

The multiple indices which we used to formulate these general results are somewhat cumbersome in practical cases. In explicit calculations it is usually simpler to use the simple numbering of the symmetry orbitals.

In our example of NH_3 the equations (107) and (108) are a set of 4×4 for the A_1 orbitals, and two identical sets of 2×2 for the E orbitals.

APPENDIX I†

If $\rho(x, y, z)$ is any continuous electrostatic charge distribution, which may be positive, negative, or partially positive and partially negative, and which vanishes sufficiently strongly at infinity, then the total

$$\begin{aligned} K_{ij} &= e^2 \int \frac{(\xi_i - i\eta_i)^\mu (\xi_j - i\eta_j)^\nu (\xi_j + i\eta_j)^\mu (\xi_i + i\eta_i)^\nu}{r^{\mu\nu}} d\tilde{v}^{\mu\nu} \\ &= e^2 \int \frac{\{\xi_i \xi_j + \eta_i \eta_j + i(\xi_i \eta_j - \eta_i \xi_j)\}^\mu \{\xi_i \xi_j + \eta_i \eta_j - i(\xi_i \eta_j - \eta_i \xi_j)\}^\nu}{r^{\mu\nu}} d\tilde{v}^{\mu\nu} = \int \frac{(\rho_1 + i\rho_2)^\mu (\rho_1 - i\rho_2)^\nu}{r^{\mu\nu}} d\tilde{v}^{\mu\nu}, \end{aligned}$$

where $\rho_1 = e^2(\xi_i \xi_j + \eta_i \eta_j)$, $\rho_2 = e^2(\xi_i \eta_j - \eta_i \xi_j)$. Hence

$$K_{ij} = \int \frac{\rho_1^\mu \rho_1^\nu}{r^{\mu\nu}} d\tilde{v}^{\mu\nu} + \int \frac{\rho_2^\mu \rho_2^\nu}{r^{\mu\nu}} d\tilde{v}^{\mu\nu} \geq 0,$$

the equal sign holding if and only if

$$\rho_1 = 0, \quad \rho_2 = 0,$$

or

$$\xi_i \xi_j + \eta_i \eta_j = 0, \quad \xi_i \eta_j - \eta_i \xi_j = 0.$$

Multiplying the second one of these equations by i , and adding the results to the first one, we obtain

$$\bar{\varphi}_i \varphi_j = 0;$$

hence for any point in space either $\varphi_i = 0$ or $\varphi_j = 0$, that is, φ_i and φ_j do not penetrate each other. This establishes the first relation expressed in (26).

Finally,

$$\begin{aligned} 0 &\leq \frac{e^2}{2} \int \frac{|\varphi_i^\mu \varphi_j^\nu - \varphi_i^\nu \varphi_j^\mu|^2}{r^{\mu\nu}} d\tilde{v}^{\mu\nu} \\ &= \frac{e^2}{2} \int \frac{(\bar{\varphi}_i^\mu \bar{\varphi}_j^\nu - \bar{\varphi}_j^\mu \bar{\varphi}_i^\nu)(\varphi_i^\mu \varphi_j^\nu - \varphi_j^\mu \varphi_i^\nu)}{r^{\mu\nu}} d\tilde{v}^{\mu\nu} \\ &= J_{ij} - K_{ij}, \end{aligned}$$

the equal sign holding if and only if

$$\varphi_i^\mu \varphi_j^\nu = \varphi_j^\mu \varphi_i^\nu, \quad \text{or} \quad \varphi_i^\mu / \varphi_j^\mu = \varphi_i^\nu / \varphi_j^\nu;$$

† The author is indebted to Professor K. F. Herzfeld for valuable advice on the proofs in this appendix.

energy of this charge distribution is given by

$$\int \frac{\rho^\mu \rho^\nu}{r^{\mu\nu}} d\tilde{v}^{\mu\nu} = \frac{1}{8\pi} \int E^2 d\tilde{v} \geq 0,$$

where $\rho^\mu = \rho(x^\mu, y^\mu, z^\mu)$, $\text{div} \mathbf{E} = 4\pi\rho$; the equal sign holding if and only if $\rho = 0$ for all values of x, y, z .

Now let $\rho = e^2(\bar{\varphi}_i \varphi_i - \bar{\varphi}_j \varphi_j)$; then

$$0 \leq e^2 \int \frac{(\bar{\varphi}_i \varphi_i - \bar{\varphi}_j \varphi_j)^\mu (\bar{\varphi}_i \varphi_i - \bar{\varphi}_j \varphi_j)^\nu}{r^{\mu\nu}} d\tilde{v}^{\mu\nu} = J_{ii} + J_{jj} - 2J_{ij},$$

or

$$J_{ij} \leq \frac{1}{2}(J_{ii} + J_{jj}),$$

the equal sign holding if and only if $\bar{\varphi}_i \varphi_i = \bar{\varphi}_j \varphi_j$, or $|\varphi_i| = |\varphi_j|$. This establishes the third relation expressed in (26).

Next let $\varphi_i = \xi_i + i\eta_i$, $\varphi_j = \xi_j + i\eta_j$, where ξ and η are real. Then

the left- and right-hand side of this equation are functions of different arguments, hence equal to a constant, or $\varphi_i = c\varphi_j$. Since the MO 's φ_i and φ_j occur in the same AP , this linear dependence implies identity, $\varphi_i = \varphi_j$. This establishes the second relation expressed in (26).

APPENDIX II

The necessary and sufficient condition that there is a nonvanishing vector \mathbf{c} satisfying

$$(\mathbf{F} - \epsilon \mathbf{S})\mathbf{c} = 0$$

is given by the secular equation

$$\text{Det}(\mathbf{F} - \epsilon \mathbf{S}) = 0.$$

This equation is of the m th degree in ϵ , where m is the dimension of the matrices \mathbf{F} and \mathbf{S} ; the coefficient of ϵ^m is $(-1)^m \text{Det}(\mathbf{S})$. We show first that this coefficient cannot vanish. The necessary and sufficient condition for $\text{Det}(\mathbf{S}) = 0$ is a linear dependence of the columns (or rows) of \mathbf{S} :

$$\sum_q S_{pq} c_q = 0,$$

the trivial case $c_1 = c_2 = \dots = c_m = 0$ being excluded. Such a linear dependence, however, leads to a contradiction; namely, multiply the last equation by \bar{c}_p and sum over p :

$$\sum_{pq} \bar{c}_p S_{pq} c_q = 0, \quad \text{or} \quad \int \left(\sum_p \bar{c}_p \chi_p \right) \left(\sum_q c_q \chi_q \right) d\tilde{v} = 0$$

from which we conclude

$$\sum_p c_p \chi_p = 0,$$

which is clearly an impossibility, since the AO 's are linearly independent. Therefore, $\text{Det}(\mathbf{S}) \neq 0$, and the secular equation is always of the m th degree in ϵ . As a consequence, the secular equation has always m roots ϵ_f , $f=1, 2, \dots, m$, provided we count multiple roots as often as their multiplicity.

We show now that all the roots ϵ_f are real. For a root ϵ_f there exists at least one nonvanishing vector \mathbf{c}_f so that

$$\mathbf{F}\mathbf{c}_f = \epsilon_f \mathbf{S}\mathbf{c}_f, \quad \mathbf{c}_f^* \mathbf{F} = \bar{\epsilon}_f \mathbf{c}_f^* \mathbf{S},$$

the second equation being the hermitian conjugate of the first one. Multiplying the first equation from the left by \mathbf{c}_f^* and the second one from the right by \mathbf{c}_f , there results

$$\mathbf{c}_f^* \mathbf{F}\mathbf{c}_f = \epsilon_f \mathbf{c}_f^* \mathbf{S}\mathbf{c}_f = \bar{\epsilon}_f \mathbf{c}_f^* \mathbf{S}\mathbf{c}_f.$$

Now $\mathbf{c}_f^* \mathbf{S}\mathbf{c}_f \neq 0$, since otherwise the AO 's χ_p would be linearly dependent. Hence

$$\bar{\epsilon}_f = \epsilon_f.$$

Next we show that if $\epsilon_f \neq \epsilon_g$, eigenvectors corresponding to ϵ_f and ϵ_g are mutually orthogonal in the sense that \mathbf{S} is the metric fundamental tensor: $\mathbf{c}_g^* \mathbf{S}\mathbf{c}_f = 0$. Namely,

$$\mathbf{F}\mathbf{c}_f = \epsilon_f \mathbf{S}\mathbf{c}_f, \quad \mathbf{F}\mathbf{c}_g = \epsilon_g \mathbf{S}\mathbf{c}_g.$$

Taking the hermitian conjugate of the second one of these equations, and observing that ϵ_g is real, we obtain

$$\mathbf{c}_g^* \mathbf{F} = \epsilon_g \mathbf{c}_g^* \mathbf{S}.$$

Multiplying the first equation from the left by \mathbf{c}_g^* and the second one from the right by \mathbf{c}_f , there results

$$\mathbf{c}_g^* \mathbf{F}\mathbf{c}_f = \epsilon_f \mathbf{c}_g^* \mathbf{S}\mathbf{c}_f = \epsilon_g \mathbf{c}_g^* \mathbf{S}\mathbf{c}_f;$$

and since $\epsilon_f \neq \epsilon_g$, we conclude that

$$\mathbf{c}_g^* \mathbf{S}\mathbf{c}_f = 0.$$

Assuming now that the eigenvalues ϵ_f are all distinct, it follows that there are at least m eigenvectors \mathbf{c}_f which are mutually orthogonal. It is no loss of generality if we assume the vectors \mathbf{c}_f to be also normalized; they form then an orthonormal set, that is,

$$\mathbf{c}_g^* \mathbf{S}\mathbf{c}_f = \delta_{gf}.$$

This relation implies that the vectors \mathbf{c}_f are linearly independent, for a relation

$$\sum_f \alpha_f \mathbf{c}_f = 0$$

gives upon multiplication by $\mathbf{c}_g^* \mathbf{S}$ from the left

$$\sum_f \alpha_f \mathbf{c}_g^* \mathbf{S}\mathbf{c}_f = \sum_f \alpha_f \delta_{gf} = \alpha_g = 0.$$

Since there can be at most m m -dimensional vectors in an orthonormal set, there are exactly m vectors \mathbf{c}_f , one for each eigenvalue ϵ_f , which are determined except for an arbitrary phase factor.

Finally, we have to show that if the secular equation has one or several multiple roots, then for each root there can be found as many linearly independent eigenvectors as the multiplicity of the root, which can be chosen so as to form an orthonormal set. The validity of these statements is easily established in the following way. If the matrices \mathbf{F} and \mathbf{S} are such that their eigenvalue problem furnishes multiple eigenvalues, then \mathbf{F} and \mathbf{S} can be obtained from matrices \mathbf{F}' and \mathbf{S}' for which this is not the case by changing \mathbf{F}' and \mathbf{S}' continuously. In this continuous process, eigenvalues and eigenvectors also change continuously (except for the phase factors of the latter), and the set of eigenvectors remains orthonormal throughout this process. In this way the existence of an orthonormal set of m eigenvectors has been established for the degenerate case. This set is not unique, however; namely, if there are p linearly independent eigenvectors belonging to a p -fold eigenvalue, then any linear combination of these vectors is also an eigenvector belonging to that eigenvalue. Restricting these p eigenvectors to be orthonormal, they are therefore determined except for a unitary transformation among themselves.

APPENDIX III

A unitary matrix \mathbf{U} can be transformed into a diagonal matrix \mathbf{D} by means of another unitary matrix \mathbf{W}

$$\mathbf{W}^* \mathbf{U} \mathbf{W} = \mathbf{D}.$$

If the diagonal elements of \mathbf{D} are not all distinct, then we can always choose the matrix \mathbf{W} such that equal diagonal elements appear adjacently; we assume this to be the case. Then \mathbf{D} has the form

$$\begin{pmatrix} d_1 \mathbf{E}_1 & \mathbf{0} & \cdots & \mathbf{0} \\ \mathbf{0} & d_2 \mathbf{E}_2 & \cdots & \mathbf{0} \\ \cdot & \cdot & \cdot & \cdot \\ \mathbf{0} & \mathbf{0} & \cdots & d_p \mathbf{E}_p \end{pmatrix},$$

where d_1, d_2, \dots, d_p are all distinct, and $\mathbf{E}_1, \mathbf{E}_2, \dots, \mathbf{E}_p$ are unit matrices of the appropriate dimensions. The numbers d_1, d_2, \dots, d_p are all of modulus unity, since they are the eigenvalues of the unitary matrix \mathbf{U} .

Now let the unitary matrix U be also symmetrical: $U^\dagger = U$. Then

$$(WDW^*)^\dagger = WDW^*,$$

or

$$\bar{W}DW^\dagger = WDW^*.$$

Multiplying this equation from the left by W^\dagger and from the right by W , there results

$$DS = SD, \quad \text{where } S = W^\dagger W.$$

We write the matrix S in block form according to the structure of D :

$$\begin{pmatrix} S_1 & S_{12} & \cdots & S_{1p} \\ S_{21} & S_2 & \cdots & S_{2p} \\ \cdot & \cdot & \cdot & \cdot \\ S_{p1} & S_{p2} & \cdots & S_p \end{pmatrix}.$$

We have then from $DS = SD$:

$$\begin{pmatrix} d_1 S_1 & d_1 S_{12} & \cdots & d_1 S_{1p} \\ d_2 S_{21} & d_2 S_2 & \cdots & d_2 S_{2p} \\ \cdot & \cdot & \cdot & \cdot \\ d_p S_{p1} & d_p S_{p2} & \cdots & d_p S_p \end{pmatrix} = \begin{pmatrix} d_1 S_1 & d_2 S_{12} & \cdots & d_p S_{1p} \\ d_1 S_{21} & d_2 S_2 & \cdots & d_p S_{2p} \\ \cdot & \cdot & \cdot & \cdot \\ d_1 S_{p1} & d_2 S_{p2} & \cdots & d_p S_p \end{pmatrix};$$

hence for $\alpha \neq \beta$: $(d_\alpha - d_\beta)S_{\alpha\beta} = 0$, and since $d_\alpha \neq d_\beta$, $S_{\alpha\beta} = 0$. It follows that S is a step matrix:

$$\begin{pmatrix} S_1 & 0 & \cdots & 0 \\ 0 & S_2 & \cdots & 0 \\ \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \cdots & S_p \end{pmatrix},$$

where S_1, S_2, \dots, S_p are square matrices which have the same dimensions as E_1, E_2, \dots, E_p . With the matrix S

$$\begin{pmatrix} c_1 E_1 & 0 & \cdots & 0 \\ 0 & c_2 E_2 & \cdots & 0 \\ \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \cdots & c_p E_p \end{pmatrix},$$

where c_1, c_2, \dots, c_p are arbitrary numbers; in particular, S commutes with the matrix D^\dagger , defined by

$$D^\dagger = \begin{pmatrix} (d_1)^\dagger E_1 & 0 & \cdots & 0 \\ 0 & (d_2)^\dagger E_2 & \cdots & 0 \\ \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \cdots & (d_p)^\dagger E_p \end{pmatrix}.$$

This matrix is unitary, since $(d_1)^\dagger, (d_2)^\dagger, \dots, (d_p)^\dagger$ are numbers of modulus unity. From $D^\dagger S = S D^\dagger$ follows

$$D^\dagger W^\dagger W = W^\dagger W D^\dagger.$$

Multiplication from the left by \bar{W} and from the right by W^* gives

$$\bar{W} D^\dagger W^\dagger = W D^\dagger W^*,$$

or

$$(W D^\dagger W^*)^\dagger = W D^\dagger W^*.$$

Hence the unitary matrix V defined by

$$V = W D^\dagger W^*$$

is symmetric:

$$V^\dagger = V,$$

and

$$U = WDW^* = W D^\dagger D^\dagger W^* = W D^\dagger W^* W D^\dagger W^* = V^2.$$

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