

Single Determinant Wave Functions

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Proc. R. Soc. Lond. A 1961 **263**, 483-493

doi: 10.1098/rspa.1961.0175

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Single determinant wave functions

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(Communicated by H. Jones, F.R.S.—Received 14 March 1961—

Revised 31 May 1961)

The theory of wave functions which have the form of a single determinant, but without the restriction to doubly occupied orbitals, is developed in general terms. The unrestricted molecular orbitals, the natural spin orbitals, the natural orbitals and the corresponding orbitals are defined and some of their properties deduced. The use of annihilators and projection operators to produce eigenfunctions of spin is investigated. The role of molecular symmetry and of a truncated set of basic functions in forcing a single determinant to be an eigenfunction of spin is discussed. A theorem on the diagonalization of a rectangular matrix by two unitary matrices is proved and applied to density matrices.

I. INTRODUCTION

The method of different orbitals for different spins is an attempt to find a more accurate treatment of electronic structure than the Hartree–Fock method without losing the physical advantages of an interpretation which assigns electrons to orbitals. The first such calculations were those of Hylleraas (1929) and Eckart (1930) on the He atom and the idea has been revived more recently by Slater (1953), Pople & Nesbet (1954), Löwdin (1954, 1955), Pratt (1956) and Hurst, Gray, Brigman & Matsen (1958). In this theory, although the electrons are still assigned to orbitals, the spatial orbitals associated with α -spin are different from those with β -spin and this additional freedom enables the electron correlation to be treated more accurately. A determinant of these orbitals is no longer an eigenfunction of S^2 and the theory has a number of different modifications depending on whether one or more determinants are used as the wave functions.

The purpose of this paper is to develop further the theory of the method; we use the single determinant as far as possible but investigate the elaborations needed to produce a spin eigenfunction. There are many different ways of choosing the orbitals without changing this determinant and some of these are defined and interrelated. In particular, the use of matrices formally similar to charge and bond order matrices is found to be convenient mathematically although their physical interpretation is not so direct.

2. UNRESTRICTED MOLECULAR ORBITALS

A wave function in the form of a single determinant

$$\Psi = (n!)^{-\frac{1}{2}} \det \{ \psi_1(1) \alpha(1), \dots, \psi_p(p) \alpha(p) \phi_1(p+1) \beta(p+1), \dots, \phi_q(n) \beta(n) \} \quad (2.01)$$

gives the simplest form of the different orbital theory and the one with the most transformation properties. Without loss of generality, the functions ψ_r can be taken as orthonormal and also the functions ϕ_r and $p \geq q$. These functions can also be transformed among themselves with unitary transformations

$$\chi_r = \sum_s^p \psi_s U_{sr}, \quad \eta_r = \sum_s^q \phi_s V_{sr} \quad (2.02)$$

and still leave the determinant Ψ unaltered.

The first order density matrix is written as

$$\gamma(1|2) = \rho_\alpha(1|2) \alpha^*(1) \alpha(2) + \rho_\beta(1|2) \beta^*(1) \beta(2), \quad (2.03)$$

where the functions

$$\rho_\alpha(1|2) = \sum_r^p \psi_r^*(1) \psi_r(2) = \sum_s^p \chi_s^*(1) \chi_s(2), \quad (2.04)$$

$$\rho_\beta(1|2) = \sum_s^q \phi_s^*(1) \phi_s(2) = \sum_s^q \eta_s^*(1) \eta_s(2) \quad (2.05)$$

are invariant with respect to the unitary transformations (2.02). Since Ψ has the single determinant form all the higher-order density matrices, and, hence, all the expectation values, can be written in terms of this first-order matrix.

A practical method of finding the best orbitals is to expand them in terms of some set of $m(\geq n)$ suitable orthonormal functions ω_r ,

$$\psi_r = \sum_s^m \omega_s a_{sr}, \quad \phi_r = \sum_s^m \omega_s b_{sr}. \quad (2.06)$$

The unknown coefficients a_{sr} and b_{sr} can then be found by minimizing the total energy subject to the orthonormality conditions. This leads (cf. Pople & Nesbet 1954) to the equations

$$\sum_u^m \left[H_{su} + \sum_j^p \sum_{tv}^m a_{tj}^* \{ (st|uv) - (st|vu) \} a_{vj} + \sum_j^q \sum_{tv}^m b_{tj}^* (st|uv) b_{vj} \right] a_{ui} = \sum_u^p a_{su} E_{ui}, \quad (2.07)$$

$$\sum_u^m \left[H_{su} + \sum_j^p \sum_{tv}^m a_{tj}^* (st|uv) a_{vj} + \sum_j^q \sum_{tv}^m b_{tj}^* \{ (st|uv) - (st|vu) \} b_{vj} \right] b_{ui} = \sum_u^q b_{su} E'_{ui}, \quad (2.08)$$

where

$$H_{ts} = \int \omega_t^* \left(-\frac{1}{2} \nabla^2 - \sum_\alpha z_\alpha / r_\alpha \right) \omega_s d\tau, \quad (2.09)$$

$$(st|uv) = \int \omega_s^*(1) \omega_t^*(2) 1/r_{12} \omega_u(1) \omega_v(2) d\tau_{12}. \quad (2.10)$$

The degrees of freedom in (2.02) can be used to diagonalize E_{ui} and E'_{ui} so that

$$E_{ui} = E_i \delta_{ui}, \quad E'_{ui} = E'_i \delta_{ui}. \quad (2.11)$$

Since there are no constraints between the functions ψ_s and the functions ϕ_s these are known as the unrestricted molecular orbitals and for them the equations (2.07) and (2.08) reduce to eigenvalue form.

Koopman's theorem (1933) that the molecular orbitals are the orbitals best suited to describing ionization applies equally well to the unrestricted molecular orbitals and gives them their physical significance. On ionization an electron is to be regarded as removed from one of the unrestricted molecular orbitals and the ionization potential is $-E_r$ if its spin is α and $-E'_r$ for β -spin.

In terms of the functions ω_r the first-order density matrices become

$$\rho_\alpha(1|2) = \sum_{uv}^m P_{uv} \omega_v^*(1) \omega_u(2), \quad (2.12)$$

$$\rho_\beta(1|2) = \sum_{uv}^m Q_{uv} \omega_v^*(1) \omega_u(2), \quad (2.13)$$

with the charge- and bond-order matrices

$$P_{uv} = \sum_r^p a_{ur} a_{vr}^*, \quad (2.14)$$

$$Q_{uv} = \sum_r^q b_{ur} b_{vr}^*. \quad (2.15)$$

If the coefficients a_{rs} are symbolized by a matrix **A** of order $p \times m$ and b_{rs} by **B** of order $q \times m$ then the bond-order matrices are

$$\mathbf{P} = \mathbf{A}\mathbf{A}^\dagger, \quad \mathbf{Q} = \mathbf{B}\mathbf{B}^\dagger. \quad (2.16)$$

The transformation (2.02) turns **A** into **AU** and **B** into **BV** but **P** and **Q** remain unchanged. On the other hand, a transformation of the ω_r to new orthonormal functions ν_r with

$$\omega_s = \sum_r^m \nu_r T_{rs} \quad (2.17)$$

turns **A** into **TA** and **B** into **TB** while **P** becomes **TPT**[†] and **Q** becomes **TQT**[†].

The energy can be expressed, using the matrices **P** and **Q**, as

$$W = \sum_{st}^m (P_{ts} + Q_{ts}) H_{st} + \frac{1}{2} \sum_{stuv}^m \{P_{us} P_{vt} + Q_{us} Q_{vt}\} \{(st|uv) - (st|vu)\} + \sum_{stuv}^m P_{us} Q_{vt} (st|uv). \quad (2.18)$$

From this the bond-order matrices can be found directly by minimizing W subject to the conditions

$$\mathbf{P}^2 = \mathbf{P}, \quad \mathbf{Q}^2 = \mathbf{Q}, \quad (2.19)$$

$$\text{tr} \mathbf{P} = p, \quad \text{tr} \mathbf{Q} = q, \quad (2.20)$$

which follow from the orthonormality of the orbitals. A practical mathematical method of doing this will be discussed in detail elsewhere. Thus the bond orders can be calculated without first finding the orbitals, although, because of the transformations (2.02), the bond orders do not determine the orbitals uniquely.

3. SYMMETRY

The symmetry of a molecule has various consequences for its orbitals. The electron density will be taken to have the full symmetry of the group, and, since the spin functions are eigenfunctions of the spin-free Hamiltonian, the density associated with α -spin alone, $\rho_\alpha(1|1)$, and with β -spin alone, $\rho_\beta(1|1)$, must also be fully symmetrical. This makes the operators on the left-hand sides of (2.07) and (2.08) fully symmetrical. Thus the unrestricted molecular orbitals are determined by eigenvalue equations with symmetrical operators and so must be symmetry orbitals transforming according to the various irreducible representations of the group.

It follows from group theory that, if ρ_α and ρ_β are to be fully symmetrical, the orbitals with α -spin and those with β -spin must each span an integral number of representations completely. If the representations are not completely spanned there will be spatial degeneracy among the wave-functions and the Jahn–Teller theorem will imply the instability of the nuclear configuration.

Just as the single determinant used in this theory need not be an eigenfunction of S^2 so the theory can be extended to include determinants which do not, by themselves, satisfy the symmetry requirements. One such determinant gives an electron density which does not have the full symmetry of the molecular group though it may of a subgroup. The unrestricted molecular orbitals are symmetry orbitals, then, but only of this subgroup. The full wave function is a linear combination of several determinants (see Nesbet 1961).

4. MOLECULAR GROUND STATES

Almost all molecules have an even number of electrons which are coupled together to give a fully symmetric singlet wave function for the ground state. This singlet character forces the number of α orbitals to equal the number of β orbitals so that

$$p = q. \quad (4.01)$$

Under these conditions the solution of equations (2.06) and (2.08) has

$$\psi_r = \phi_r, \quad (4.02)$$

unless, as for some excited states, the ψ_r span irreducible representations not all identical with those of the ϕ_r . Thus the more general form of the wave function leads to the same result as if the orbitals had been originally assumed to be doubly occupied.

On the other hand, molecules, ions or radicals, which have an odd number of electrons, will have $p \neq q$ and the orbitals, in general, will be different. Furthermore, the first excited state of most molecules is the lowest triplet state and the $S_z = 1$ component of this has $p = q + 2$ so that the degeneracy is again prevented.

These results explain why a number of general theorems which are valid for molecular ground states in the Hartree-Fock theory are valid for ions, radicals, etc., only in the unrestricted molecular orbital theory. These theorems include Koopman's theorem already mentioned, Brillouin's theorem (Nesbet 1961) and the stability theorem (Hall 1961).

5. NATURAL ORBITALS

The unrestricted molecular orbitals are not the only interesting type of orbital. The natural spin orbitals, which diagonalize the first-order density matrix, and the natural orbitals, which enable the reduced first-order density matrix to be diagonal, are also of importance.

For the wave function (2.01) the first-order density matrix is

$$\gamma(1|2) = \sum_r^p \psi_r^*(1) \psi_r(2) \alpha^*(1) \alpha(2) + \sum_r^q \phi_r^*(1) \phi_r(2) \beta^*(1) \beta(2). \quad (5.01)$$

This is already in diagonal form and, since the spin orbitals are orthonormal, they are natural spin orbitals. The natural spin orbitals are not unique, however, since the unitary transformations (2.02) leave the form of (5.01) invariant.

The reduced density matrix is derived from (5.01) by identifying the spin variables and integrating over spin. This gives

$$\rho(1|2) = \sum_r^p \psi_r^*(1) \psi_r(2) + \sum_s^q \phi_s^*(1) \phi_s(2) \quad (5.02)$$

and would be in diagonal form except that the ψ_r and ϕ_s are not spatially orthogonal. The unitary transformations (2.02) also leave the form of (5.02) invariant and can be used to define orbitals that are more nearly orthogonal. When \mathbf{U} and \mathbf{V} are determined as in the appendix then the new orbitals have the property that their spatial overlap integral

$$T_{rs} = \int \chi_r^* \eta_s \, d\tau \quad (5.03)$$

is diagonal

$$T_{rs} = T_r \delta_{rs}. \quad (5.04)$$

These orbitals will be called corresponding orbitals because of this property. The existence of such orbitals has been suggested, without proof, by Löwdin (1958, private communication). In terms of the basic functions ω_r the corresponding orbitals χ_r and η_r are readily shown to be the eigenvectors of the matrices \mathbf{PQP} and \mathbf{QPQ} , respectively. The non-zero eigenvalues of these matrices are equal and give the values of T_r^2 .

In terms of these corresponding orbitals the reduced density matrix is

$$\rho(1|2) = \sum_r^p \chi_r^*(1) \chi_r(2) + \sum_s^q \eta_s^*(1) \eta_s(2), \quad (5.05)$$

where the χ_r are spatially orthogonal to each other and to the η_s except when $r = s$. If these functions are replaced by the orthonormal combinations

$$\lambda_r = (\chi_r + \eta_r) (2 + 2T_r)^{-\frac{1}{2}}, \quad (5.06)$$

$$\mu_r = (\chi_r - \eta_r) (2 - 2T_r)^{-\frac{1}{2}}, \quad (5.07)$$

then all the functions are orthonormal and (5.05) becomes

$$\rho(1|2) = \sum_r^q (1 + T_r) \lambda_r^*(1) \lambda_r(2) + \sum_s^q (1 - T_s) \mu_s^*(1) \mu_s(2) + \sum_{t=q+1}^p \chi_t^*(1) \chi_t(2). \quad (5.08)$$

These functions λ_r, μ_s, χ_t are therefore the natural orbitals. The corresponding orbitals are thus the natural spin orbitals which are most easily related to the natural orbitals and their overlap integrals determine the occupation numbers of the natural orbitals.

The reduced density matrix can be written directly in terms of the ω_r as

$$\rho(1|2) = \sum_{rs}^m \omega_r(2) (P_{rs} + Q_{rs}) \omega_s^*(1). \quad (5.09)$$

Since both P_{rs} and Q_{rs} are symmetrical this quadratic form can be diagonalized by a unitary change of variables and the new orbitals will be the natural orbitals. To relate this definition to the previous one, the partitioned matrix \mathbf{C} , of order $m \times n$, is considered

$$\mathbf{C} = (\mathbf{AB}). \quad (5.10)$$

From the equations (2.25) and (2.26) it follows that

$$\mathbf{CC}^\dagger = \mathbf{P} + \mathbf{Q} \quad (5.11)$$

and, from the appendix, this has the same non-zero eigenvalues as $\mathbf{C}^\dagger \mathbf{C}$. Now $\mathbf{C}^\dagger \mathbf{C}$ has the partitioned form

$$\mathbf{C}^\dagger \mathbf{C} = \begin{pmatrix} \mathbf{I}_p & \mathbf{S} \\ \mathbf{S}^\dagger & \mathbf{I}_q \end{pmatrix} \quad (5.12)$$

where \mathbf{I}_p is the unit matrix of order p , and the unitary matrices \mathbf{U} and \mathbf{V} enable it to be brought to the form

$$\begin{pmatrix} \mathbf{U}^\dagger & 0 \\ 0 & \mathbf{V}^\dagger \end{pmatrix} \begin{pmatrix} \mathbf{I} & \mathbf{S} \\ \mathbf{S}^\dagger & \mathbf{I} \end{pmatrix} \begin{pmatrix} \mathbf{U} & 0 \\ 0 & \mathbf{V} \end{pmatrix} = \begin{pmatrix} \mathbf{I} & \mathbf{T} \\ \mathbf{T}^\dagger & \mathbf{I} \end{pmatrix}. \quad (5.13)$$

There are, then, $2q$ eigenvalues of the form

$$1 \pm T_r \quad (5.14)$$

and $(p-q)$ eigenvalues are unity exactly as in (5.08).

6. REFINEMENTS OF SINGLE DETERMINANT WAVE FUNCTIONS

The single determinant wave function of the unrestricted molecular orbital method is not, in general, an eigenfunction of S^2 . The mean value of S^2 is given by

$$\langle S^2 \rangle = \frac{1}{4}(p-q)^2 + \frac{1}{2}(p+q) - L, \quad (6.01)$$

where

$$L = \text{tr } \mathbf{PQ} = \sum_{rs} P_{rs} Q_{sr} \quad (6.02)$$

may be interpreted as the number of doubly occupied orbitals. The wave function is a mixture of components of various multiplicities but the values of $(p-q)$ puts a lower limit to the spin quantum number so that

$$\frac{1}{2}(p+q) \geq S \geq S_z = \frac{1}{2}(p-q). \quad (6.03)$$

To remove these unwanted components and improve the wavefunction the use of a projection operator has been suggested by Löwdin (1955). The operator

$$A_s = S^2 - s(s+1) \quad (6.04)$$

acting on a mixture of components will annihilate the component of multiplicity $(2s+1)$. This can be repeated for all the unwanted components and, since these components have higher energies, their removal will improve the energy as well as the spin properties. On the other hand, the high multiplicities have energies so high that they can contribute little to the wave function. The annihilation of the lower multiplicities is therefore the more important.

The projection operator O_m which selects out the spin eigenfunction of multiplicity $(2m+1)$ is a product of these A_s , namely

$$O_m = \prod_{l \neq m} \frac{S^2 - l(l+1)}{m(m+1) - l(l+1)} \quad (6.05)$$

where S^2 can be taken as

$$S^2 = \frac{1}{4}(p+q)(4-p-q) + \sum'_{ij} P_{ij}^\sigma \quad (6.06)$$

and P_{ij}^σ interchanges the spin functions of electrons i and j . The energy of the spin eigenfunction projected from the single determinant Ψ is

$$W = \int \Psi^* H O_m \Psi \, d\tau / \int \Psi^* O_m \Psi \, d\tau. \quad (6.07)$$

The operators O_m and HO_m are, therefore, of the many electron type and their integrals involve high-order density matrices. For the single determinant these can all be expressed in terms of \mathbf{P} and \mathbf{Q} so that \mathbf{P} and \mathbf{Q} remain fundamental quantities in the more general theory although they no longer have the same connexion with the first order density matrix. The order of density matrix required in the energy formula depends on the number of annihilators used in O_m and this in turn depends on the number of electrons in the molecule and its symmetry (see §8). If k is the number of annihilators used the highest order required will be $2k + 2$. Nevertheless, the complicated form of O_m makes it difficult to evaluate (6.07) and so find the best possible \mathbf{P} and \mathbf{Q} by minimization.

TABLE 1. CLASSIFICATION OF REFINEMENTS OF MOLECULAR ORBITAL THEORY

method	wave functions used to find		eigen-function of S^2	energy
	$\mathbf{P}, \mathbf{Q},$	W		
m.o.	det	det	yes	W_1
unrestricted m.o.	det	det	no	$W_2 < W_1$
unrestricted m.o. with A_s	det	$A_s \det$	no	$W_3 < W_2$
unrestricted m.o. with O_m	det	$O_m \det$	yes	$W_4 < W_3$
extended m.o. with A_s	$A_s \det$	$A_s \det$	no	$W_5 < W_3$
extended m.o. with O_m	$O_m \det$	$O_m \det$	yes	$W_6 < W_5$

There are two possible ways of applying these refinements to obtain better energies. In the first, which is less accurate but easier, the \mathbf{P} and \mathbf{Q} of the unrestricted molecular orbital method are kept fixed but the wave function and the energy are improved by using A_s or O_m . Because of the results in §4 this method is not generally useful for molecular ground states. In the second method the energy is corrected using A_s or O_m before the best \mathbf{P} and \mathbf{Q} are found by minimization. This may be called the extended molecular orbital method. These various possibilities are shown in table 1. Examples of the unrestricted methods will be given in §7. The Hylleraas-Eckart wave functions and the alternant molecular orbitals (Löwdin 1955) are examples of extended molecular orbitals with O_m .

7. WAVE FUNCTIONS WITH A SINGLE ANNIHILATOR

A determinantal wave function whose major component has a spin quantum number s can be refined by using A_{s+1} to annihilate the next component. Higher components, with spin $S + 2$, etc., are often negligible because of their much higher energy. When this is so, A_{s+1} can be treated as idempotent and the energy is then

$$W = \frac{\int \Psi^* H [S^2 - (s+1)(s+2)] \Psi d\tau}{\int \Psi^* [S^2 - (s+1)(s+2)] \Psi d\tau}, \quad (7.01)$$

and will involve density matrices of up to the fourth order. In terms of \mathbf{P} and \mathbf{Q} its value is

$$W = W_0 - \frac{1}{2x} \left[2 \operatorname{tr}(\mathbf{PQP} + \mathbf{QPQ} - 2\mathbf{PQ}) \mathbf{H} + \sum_{stuv} \{ [\mathbf{PQP} + \mathbf{QPQ} - 2\mathbf{PQ}]_{st} [\mathbf{P} + \mathbf{Q}]_{uv} + [\mathbf{P}(\mathbf{P} - \mathbf{Q})]_{st} [(\mathbf{P} - \mathbf{Q})\mathbf{Q}]_{uv} \} (tv|us) - \sum_{stuv} \{ [\mathbf{PQP}]_{st} P_{uv} + [\mathbf{QPQ}]_{st} Q_{uv} - [\mathbf{PQ}]_{st} [\mathbf{P} + \mathbf{Q}]_{uv} \} (tv|su) \right], \quad (7.02)$$

where W_0 is the energy for a single determinant and

$$x = (s+1)(s+2) - \frac{1}{4}(p-q)^2 - \frac{1}{2}(p+q) + L.$$

The mean value of S^2 now improves to

$$\langle S^2 \rangle = \frac{1}{4}(p-q)^2 + \frac{1}{2}(p+q) - L - (1/x) \{ (q-L)(p-L) + 2L - 2 \operatorname{tr}(\mathbf{PQPQ}) \}$$

and the first-order density matrix is

$$\gamma(1|2) = \sum_{rs} J_{rs} \omega_s^*(1) \omega_r(2) \alpha^*(1) \alpha(2) + \sum_{rs} K_{rs} \omega_s^*(1) \omega_r(2) \beta^*(1) \beta(2),$$

where

$$\mathbf{J} = \mathbf{P} - (\mathbf{PQP} - \frac{1}{2}\mathbf{PQ} - \frac{1}{2}\mathbf{QP})/x$$

$$\mathbf{K} = \mathbf{Q} - (\mathbf{QPQ} - \frac{1}{2}\mathbf{PQ} - \frac{1}{2}\mathbf{QP})/x.$$

The new natural spin orbitals can be found by diagonalizing \mathbf{J} and \mathbf{K} while the new natural orbitals diagonalize $(\mathbf{J} + \mathbf{K})$. The energy cannot be expressed in terms of \mathbf{J} and \mathbf{K} alone but their introduction enables it to be put into the simpler form

$$W = \operatorname{tr}(\mathbf{J} + \mathbf{K}) \mathbf{H} + \frac{1}{2} \operatorname{tr} \mathbf{JF} + \frac{1}{2} \operatorname{tr} \mathbf{KG} - C,$$

where

$$F_{st} = \sum_{uv} P_{uv} [(sv|tu) - (sv|ut)] + \sum_{uv} Q_{uv} (sv|tu),$$

$$G_{st} = \sum_{uv} Q_{uv} [(sv|tu)] - (sv|ut) + \sum_{uv} P_{uv} (sv|tu),$$

$$C = -(1/2x) \sum_{stuv} [\mathbf{P}(\mathbf{P} - \mathbf{Q})]_{st} [(\mathbf{P} - \mathbf{Q})\mathbf{Q}]_{uv} (tv|us)$$

and tr denotes the trace of the matrix. The final correction term C is generally small.

The single determinant wave function Ψ is a mixture of pure spin states Ψ_s , Ψ_{s+1} , ..., and can be written as

$$\Psi = \lambda \Psi_s + \mu \Psi_{s+1} + \nu \Psi_{s+2} + \dots$$

For the examples considered here, components higher than Ψ_{s+2} cannot occur and λ^2 , μ^2 , ν^2 can be calculated from $\langle S^2 \rangle$ and $\langle S^4 \rangle$. The results are shown in table 2 and illustrate the rapid decrease in the coefficients. For details of the method of calculation and further applications see Amos (1962). Table 3 shows the effect on the energy W and on $\langle S^2 \rangle$ of one annihilator A_{s+1} and of O_s . The energies given are relative to the energies of the localized orbitals and are multiples of β which has the numerical value -4.79 eV. The use of A_{s+1} is seen to produce appreciable improvements in both W and $\langle S^2 \rangle$ but the remaining annihilators in O_s have little effect on W despite the improvement in $\langle S^2 \rangle$.

TABLE 2. RELATIVE WEIGHTS OF HIGHER SPIN STATES IN SINGLE DETERMINANT WAVE FUNCTIONS

molecular state	S	λ^2	μ^2	ν^2
allyl radical	$\frac{1}{2}$	0.9628	0.0372	0
butadiene lowest triplet	1	1	0	0
pyridine lowest π triplet	1	0.9568	0.0427	0.0005
pyrazine lowest π triplet	1	0.9556	0.0439	0.0005

TABLE 3. ENERGIES AND $\langle S^2 \rangle$ FOR UNRESTRICTED M.O. WAVE FUNCTIONS

molecular state	Ψ		$A_{s+1}\Psi$		$O_s\Psi$	
	W_2	$\langle S^2 \rangle$	W_3	$\langle S^2 \rangle$	W_4	$\langle S^2 \rangle$
allyl radical	8.58	0.8612	8.61	0.75	unchanged	
butadiene lowest triplet	13.83	2	unchanged		unchanged	
pyridine lowest π triplet	35.58	2.1708	35.62	2.0022	35.62	2
pyrazine lowest π triplet	35.97	2.1755	36.02	2.0026	36.02	2

8. FORCED EIGENFUNCTIONS

Although these more general determinantal wave functions are not generally eigenfunctions of S^2 there are several ways in which they can be forced to be. These derive from the fact that the orbitals are expressed as linear combinations of a limited number of basis functions. The symmetry of the molecule also introduces considerable restrictions.

The simplest example of a forced eigenfunction occurs when the unrestricted molecular orbitals are uniquely determined by symmetry alone. In this event the ψ_r are either identical with some of the ϕ_r or are spatially orthogonal to them. Thus the orbitals are either doubly occupied or singly occupied. If the singly occupied orbitals all have the same spin the single determinant is an eigenfunction of spin. This type of forcing occurs frequently among the states of benzene although for some excited states the spatial symmetry requires wave functions with several determinants so that the argument is made more complicated.

Forcing can still occur, however, when the molecular orbitals are not fully determined by symmetry. If there are sufficient molecular orbitals of one spin and one irreducible representation to span completely the space of all functions of that symmetry then, in particular, the molecular orbitals of the opposite spin and the same symmetry can be expressed in terms of them. Thus, although the unrestricted molecular orbitals themselves may be different, it is possible to transform them into orbitals some doubly occupied and some singly occupied. If all the molecular orbitals satisfy this condition or are uniquely determined by symmetry the determinant will be forced to be an eigenfunction of S^2 . The lowest triplet state of butadiene, for example, has two electrons of α spin in two symmetrical orbitals and one in an antisymmetrical orbital. The single β electron is in a symmetrical orbital but since the α orbitals span the two-dimensional space of symmetrical orbitals they

can be transformed to give a doubly occupied and a singly occupied symmetrical orbital and, consequently, the determinant is an eigenfunction of S^2 (see tables 2 and 3).

Even when the symmetry and the truncation are not sufficient to force the determinant to be an eigenfunction they may restrict it considerably. Thus, instead of being resolvable into a mixture of components with a wide range of multiplicities, the determinant may be restricted to a few components of the lower multiplicities. A few annihilators will then suffice to produce a spin eigenfunction.

The authors wish to thank the Department of Scientific and Industrial Research for the award of a Research Grant to one of us (A. T. A.).

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APPENDIX

Let \mathbf{S} be a rectangular matrix of order $a \times b$ and of rank a , where $a < b$. The product $\mathbf{S}^+\mathbf{S}$ has order $b \times b$ and is Hermitian and positive definite. It can be diagonalized, therefore, by a unitary matrix whose columns are eigencolumns and these columns can be so ordered that the eigenvalues are in decreasing order. If \mathbf{V} is this matrix then

$$(\mathbf{S}^+\mathbf{S})\mathbf{V} = \mathbf{V}\mathbf{D} \quad (\text{A } 1)$$

where \mathbf{D} is the diagonal matrix of eigenvalues.

From this equation, by multiplication with \mathbf{S} , it follows that

$$(\mathbf{S}\mathbf{S}^+)(\mathbf{S}\mathbf{V}) = (\mathbf{S}\mathbf{V})\mathbf{D}. \quad (\text{A } 2)$$

This is also an eigenvalue equation with the same eigenvalues and with the columns of $(\mathbf{S}\mathbf{V})$ as eigencolumns of $(\mathbf{S}\mathbf{S}^+)$. Since \mathbf{S} has rank a , $(\mathbf{S}\mathbf{V})$ has also rank a and, therefore a independent columns. Its remaining $(b-a)$ columns could repeat eigencolumns or could be zeros. But

$$(\mathbf{S}\mathbf{V})^+(\mathbf{S}\mathbf{V}) = \mathbf{D} \quad (\text{A } 3)$$

so that all the b columns are orthogonal and repetitions are excluded. The extra $(b-a)$ columns are then zeros and so have zero length. Thus from (A 3) they correspond to zero eigenvalues in \mathbf{D} and therefore to the last $(b-a)$ columns.

The first a eigencolumns may not be normalized but, when they are made normal, they will form a unitary matrix since $\mathbf{S}\mathbf{S}^+$ also is Hermitian. The matrix $\mathbf{S}\mathbf{V}$, therefore, must have the form

$$\mathbf{S}\mathbf{V} = \mathbf{U}\mathbf{T}. \quad (\text{A } 4)$$

where \mathbf{U} is unitary and \mathbf{T} has non-zero elements only on the diagonal. Thus the rectangular matrix \mathbf{S} is brought into diagonal form \mathbf{T} by the pair of unitary matrices \mathbf{U} and \mathbf{V} so that

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{V} = \mathbf{T}. \quad (\text{A } 5)$$

This theorem can also be applied to an antisymmetric wave function of arbitrary form. The wave function can be expanded into the form

$$\Psi = \sum_{rs} S_{rs} \phi_r(1) \Phi_s(2, \dots, n) \quad (\text{A } 6)$$

where the functions $\phi_r(1)$ are orthonormal and also the functions $\Phi_s(2, \dots, n)$. The first-order density matrix is then

$$\gamma(1'|1) = n \sum_{urs} S_{rs} S_{us}^* \phi_u^*(1') \phi_r(1) \quad (\text{A } 7)$$

while the $(n-1)$ st order density matrix is

$$\Gamma(2', \dots, n'|2, \dots, n) = n \sum_{vrs} S_{rv}^* S_{rs} \Phi_v^*(2', \dots, n') \Phi_s(2, \dots, n). \quad (\text{A } 8)$$

According to the theorem the matrix \mathbf{U} defines the natural spin orbitals n_r by diagonalizing $\mathbf{S} \mathbf{S}^\dagger$ and giving

$$\gamma(1'|1) = \sum_r d_r n_r^*(1') n_r(1), \quad (\text{A } 9)$$

where the occupation numbers d_r are the diagonal elements of \mathbf{D} . Similarly \mathbf{V} defines the natural spin functions F_r for which

$$\Gamma(2', \dots, n'|2, \dots, n) = \sum_r d_r F_r^*(2', \dots, n') F_r(2, \dots, n). \quad (\text{A } 10)$$

The well-known equality of the occupation numbers d_r follows from the theorem. The theorem also shows that the wave function itself reduces to the form

$$\Psi = \sum_r t_r n_r(1) F_r(2, \dots, n), \quad (\text{A } 11)$$

where t_r are the diagonal elements of \mathbf{T} and $t_r^2 = d_r$. These results are readily extended to a factorization into natural spin functions of order s and ones of order $(n-s)$.