Quantum-Mechanical Calculation of One-Electron Properties. I. General Formulation*

MARTIN KARPLUS, ARON KUPPERMANN, AND LEONARD M. ISAACSON†

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

(Received April 15, 1958)

For a one-electron operator, general formulas for weighted transition functions, weighted density functions, and their integrals are introduced. A detailed treatment is given of the expressions that are obtained from these formulas when they are applied to a system whose wave functions are expanded in a series of determinants of one-electron spin orbitals. Explicit consideration is given to the nonorthogonality problem and a method for the exact inclusion of overlap terms is formulated. The simplifications resulting from the use of the single determinant approximation and orthonormal functions are discussed. A brief evaluation of the suitability of the formulation for digital computer calculation is given.

1. INTRODUCTION

MANY important properties of atoms and molecules are one-electron properties in the sense that the associated quantum-mechanical operator $\mathfrak{A}$ has the form

$$\mathfrak{A}(\mathbf{q}) = \mathfrak{A}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N) = \sum_{i=1}^N \alpha(\mathbf{q}_i) \quad (1)$$

for an N -electron system. Here $\mathbf{q}_i$ represents the space coordinate $\mathbf{R}_i$ and the spin coordinate $\mathbf{s}_i$ of electron i , $\mathbf{q}$ corresponds to the set of coordinates $(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)$, and $\alpha(\mathbf{q}_i)$ is an operator which is the same for all electrons except for the index identifying the particular electron under consideration. Typical of the one-electron operators are the moment operators for which $\alpha(\mathbf{q}_i)$ has the form

$$\alpha(\mathbf{q}_i) = X_i^\alpha Y_i^\beta Z_i^\gamma \quad \alpha + \beta + \gamma = m, \quad (2)$$

where α , β , γ , and m are non-negative integers and X_i , Y_i , and Z_i are the Cartesian coordinates of electron i defined in terms of a coordinate system fixed with respect to a charge distribution. Quantities such as the quadrupole coupling constant,¹ the electric and magnetic susceptibility,² and the transition probability can be calculated or approximated by expressions involving only one-electron operators.

Since most computations of expectation values or transition probabilities are carried out with the use of approximate wave functions, the error of the result is an important consideration. In general, two one-electron properties weigh differently the contribution of a given point in space. Consequently, a study of the errors requires consideration not of the approximate wave

function itself but rather of a function weighted in a manner appropriate to the particular operator.

In Sec. 2 of this paper general expressions for weighted one-electron transition functions and weighted one-electron density functions are given. Transition probabilities and expectation values of one-electron operators can be obtained by integrating these functions. To display explicitly the simplifications introduced by the form of $\mathfrak{A}$, the N -electron wave functions for the system under consideration are expanded in terms of sums of products of one-electron spin orbitals (see Sec. 3). Explicit consideration is given to the non-orthogonality problem and the exact calculation of the overlap contributions to the one-electron properties is discussed. Section 4 presents a brief evaluation of the suitability of the formulation for calculations by means of electronic digital computers.

Other papers in this series are concerned specifically with the moment integrals resulting from the use of linear combinations of Slater-type orbitals as the one-electron functions. Attempts are made to determine molecular charge densities from experimental data as well as to examine the results calculated with wave functions obtained by means of variational computations.

2. DEFINITIONS AND GENERAL FORMULAS

Let $\Psi_s(\mathbf{q})$, $s=1, 2, \dots$, be the time-independent state functions³ of an N -electron system. If $\mathfrak{A}(\mathbf{q})$ is the quantum-mechanical operator associated with a dynamical variable of this system, it is useful to define the weighted transition integral $\langle \mathfrak{A} \rangle_{s,t}$,

$$\langle \mathfrak{A} \rangle_{s,t} = \frac{\int \Psi_s^*(\mathbf{q}) \mathfrak{A}(\mathbf{q}) \Psi_t(\mathbf{q}) d\mathbf{q}}{\left(\int |\Psi_s(\mathbf{q})|^2 d\mathbf{q} \int |\Psi_t(\mathbf{q})|^2 d\mathbf{q} \right)^{1/2}}, \quad (3)$$

* Work supported in part by grants from the University of Illinois Graduate Research Board and the National Science Foundation.

† Present address: Electronic Computer Center, Standard Oil Company of California, San Francisco, California.

¹ C. H. Townes and A. L. Schalow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955), Chap. 6 and 8.

² J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), Chap. X; J. Guy and J. Tillien, *J. Chem. Phys.* **24**, 1117 (1956).

³ A straightforward generalization of the arguments developed in this paper would make them applicable to the time-dependent wave functions $\Psi_s(\mathbf{q}, t)$. Since inclusion of the time would serve only to further complicate the notation, we have chosen to restrict our equations to time-independent functions.

where $d\mathbf{q}$ is the volume element in the space defined by the spin-orbit coordinates of the N electrons.

If $s=t$ this expression defines the expectation value $\langle \mathfrak{A} \rangle_{s,s}$ (or simply $\langle \mathfrak{A} \rangle_s$) of the dynamical variable $\mathfrak{A}$ for the system in the state s . Although for normalized wave functions the integrals in the denominator of Eq. (3) are unity, they are here included to permit explicit consideration of the complications introduced by the use of non-normalized wave functions.

If $\mathfrak{A}$ is a one-electron operator [Eq. (1)], we define the weighted transition function $A_{s,t}(\mathbf{q}_i)$ associated with it by the equation

$$A_{s,t}(\mathbf{q}_i) = \frac{\int \Psi_s^*(\mathbf{q}) \mathfrak{A}(\mathbf{q}_i) \Psi_t(\mathbf{q}) d\mathbf{q}^i}{\left(\int |\Psi_s(\mathbf{q})|^2 d\mathbf{q} \cdot \int |\Psi_t(\mathbf{q})|^2 d\mathbf{q} \right)^{\frac{1}{2}}}, \quad (4)$$

where $d\mathbf{q}^i$ is the volume element in the subspace formed by the spin-orbit coordinates of all electrons except electron i .

From Eqs. (1), (3), and (4) it follows that

$$\langle \mathfrak{A} \rangle_{s,t} = \sum_{i=1}^N \int A_{s,t}(\mathbf{q}_i) d\mathbf{q}_i, \quad (5)$$

where $d\mathbf{q}_i$ is the volume element in the subspace defined by the spin-orbit coordinate of electron i . Because of the permutation antisymmetry of the wave functions $\Psi_s(\mathbf{q})$, $A_{s,t}(\mathbf{q}_i)$ is, like $\mathfrak{A}(\mathbf{q}_i)$, the same for all electrons except for the identifying subscript. Consequently,

$$\langle \mathfrak{A} \rangle_{s,t} = N \int A_{s,t}(\mathbf{q}_i) d\mathbf{q}_i. \quad (6)$$

It is often advantageous, especially for operators that are functions of only the configuration space coordinates $\mathbf{R}_i$, i.e.,

$$\mathfrak{A}(\mathbf{q}_i) = \mathfrak{A}(\mathbf{R}_i) \quad (7)$$

to define the spinless weighted transition function $A_{s,t}(\mathbf{R}_i)$

$$A_{s,t}(\mathbf{R}_i) = \int A_{s,t}(\mathbf{q}_i) d\mathbf{s}_i, \quad (8)$$

where $d\mathbf{s}_i$ is the volume element for the spin coordinate $\mathbf{s}_i$.

Similarly, the weighted spin transition function $A_{s,t}(\mathbf{s}_i)$ can be defined as

$$A_{s,t}(\mathbf{s}_i) = \int A_{s,t}(\mathbf{q}_i) d\mathbf{R}_i, \quad (9)$$

where $d\mathbf{R}_i$ is the volume element for the configuration space coordinate of electron i . For $s=t$, Eqs. (4), (8), and (9) define the weighted one-electron density functions $A_{s,s}(\mathbf{q}_i)$, $A_{s,s}(\mathbf{R}_i)$ and $A_{s,s}(\mathbf{s}_i)$ [or simply $A_s(\mathbf{q}_i)$, $A_s(\mathbf{R}_i)$ and $A_s(\mathbf{s}_i)$].

If, in particular,

$$\mathfrak{A}(\mathbf{q}_i) = 1, \quad i=1, 2, \dots, N \quad (10)$$

$A_{s,t}(\mathbf{q}_i)$ becomes (in the system of Hartree atomic units⁴ used throughout this paper) the spin-orbital transition charge density function $\rho_{s,t}(\mathbf{q}_i)$. From Eqs. (4) and (8) it follows that

$$\begin{aligned} \rho_{s,t}(\mathbf{R}_i) &= \int \rho_{s,t}(\mathbf{q}_i) d\mathbf{s}_i \\ &= \frac{\int \Psi_s^*(\mathbf{q}) \Psi_t(\mathbf{q}) d\mathbf{q}^i d\mathbf{s}_i}{\left(\int |\Psi_s(\mathbf{q})|^2 d\mathbf{q} \cdot \int |\Psi_t(\mathbf{q})|^2 d\mathbf{q} \right)^{\frac{1}{2}}} \end{aligned} \quad (11)$$

and for $s=t$ this expression furnishes the usual one-electron charge density function $\rho_{s,s}(\mathbf{R}_i)$ [or simply $\rho_s(\mathbf{R}_i)$] for the system in state $\Psi_s(\mathbf{q})$. For multiplicative operators, $\mathfrak{A}'(\mathbf{R}_i)$, such as the moment operators defined by Eq. (2), which obey the relationship

$$\Psi_s^*(\mathbf{q}) \mathfrak{A}'(\mathbf{R}_i) \Psi_t(\mathbf{q}) = \mathfrak{A}'(\mathbf{R}_i) \Psi_s^*(\mathbf{q}) \Psi_t(\mathbf{q}) \quad (12)$$

it can be seen that

$$\langle \mathfrak{A}' \rangle_{s,t} = N \int \mathfrak{A}'(\mathbf{R}_i) \rho_{s,t}(\mathbf{R}_i) d\mathbf{R}_i, \quad (13)$$

which expresses $\langle \mathfrak{A}' \rangle_{s,t}$ in terms of the transition charge density function, or for the case $s=t$, the expectation value of $\mathfrak{A}'$ in terms of the charge density function, $\rho_s(\mathbf{R}_i)$.

3. ONE-ELECTRON FUNCTION EXPANSION

The wave function $\Psi_s(\mathbf{q})$ can be expressed as a series of products of one-electron spin-orbital functions in the form

$$\begin{aligned} \Psi_s(\mathbf{q}) &= \sum_{l_1, l_2, \dots, l_N} d_{l_1, l_2, \dots, l_N}^s \psi_{l_1}(\mathbf{q}_1) \psi_{l_2}(\mathbf{q}_2) \cdots \psi_{l_N}(\mathbf{q}_N) \\ &= \sum_L d_L^s \prod_{i=1}^N \psi_{l_i}(\mathbf{q}_i), \end{aligned} \quad (14)$$

where the $d_{l_1, l_2, \dots, l_N}^s$ are constants, the $l_1, l_2, \dots, l_N$ are positive integers, L is a shorthand notation for the $l_1, l_2, \dots, l_N$, and $\psi_1(\mathbf{q}_1), \psi_2(\mathbf{q}_2), \dots (i=1, 2, \dots, N)$ form a discrete infinite set of spin-orbital functions complete in the N -electron spin-orbit coordinate space. The summation extends over all possible values of $l_1, l_2, \dots, l_N$. The functions $\psi_i(\mathbf{q}_i)$ are not necessarily orthogonal or normalized. Because of the antisymmetry of the $\Psi_s(\mathbf{q})$ required by the Pauli principle, there are certain relations^{5,6} among the d_L^s and Eq. (14) can be rewritten as

$$\Psi_s(\mathbf{q}) = \sum_L \sigma_L \det[\psi_{l_\nu}(\mathbf{q}_\mu)], \quad (15)$$

where the σ_L are appropriate constants, μ and ν , respectively, label the rows and columns of the N th

⁴ D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1928).

⁵ S. F. Boys, Proc. Roy. Soc. (London) **A200**, 542 (1950).

⁶ P. O. Löwdin, Phys. Rev. **97**, 1474 (1955). In his elegant treatment of N -electron operators, Löwdin obtains many of the results developed here for one-electron operators in the special case $s=t$. He does not consider the transition functions arising when $s \neq t$.

column. Introduction of $[\mathbf{S}^{L',L}]^{\mu j}$, the cofactor of $[\mathbf{S}^{L',L}]_{\mu j}$, and, therefore, of $[\mathbf{S}^{L',L}(j, \mathbf{q}_i)]_{\mu j}$, yields the expression

$$\rho_{s,t}(\mathbf{q}_i) = \frac{(1/N) \sum_{L',L} \sigma_{L'}^* \tau_L \sum_{j=1}^N \sum_{\mu=1}^N [\mathbf{S}^{L',L}]^{\mu j} \psi_{L'\mu}^*(\mathbf{q}_i) \psi_{Lj}(\mathbf{q}_i)}{[(\sum_{L',L} \sigma_{L'}^* \sigma_L \det \mathbf{S}^{L',L}) (\sum_{L',L} \tau_{L'}^* \tau_L \det \mathbf{S}^{L',L})]^{\frac{1}{2}}}, \quad (26)$$

or

$$\rho_{s,t}(\mathbf{q}_i) = \frac{1}{N} \sum_{k',k=1}^{\infty} c_{k'k} \psi_{k'}^*(\mathbf{q}_i) \psi_k(\mathbf{q}_i), \quad (27)$$

where the coefficient $c_{k'k}$ has the form

$$c_{k'k} = \frac{\sum_{L',L} \sum_{\mu,j=1}^N \sigma_{L'}^* \tau_L \delta_{k',L'\mu} \delta_{k,Lj} [\mathbf{S}^{L',L}]^{\mu j}}{[(\sum_{L',L} \sigma_{L'}^* \sigma_L \det \mathbf{S}^{L',L}) (\sum_{L',L} \tau_{L'}^* \tau_L \det \mathbf{S}^{L',L})]^{\frac{1}{2}}}, \quad (28)$$

where now the indices k' and k range over all the spin orbitals in the infinite set used to expand $\Psi_s(\mathbf{q})$ and $\Psi_t(\mathbf{q})$. The coefficients $c_{k'k}$ can be used in a generalized population analysis, related to that developed by Mulliken for the single determinant LCAO-MO approximation.⁷ In particular, the diagonal coefficients c_{kk} can be regarded as occupation numbers⁸ in the spin-orbital transition charge density. If the $\psi_k(\mathbf{q}_i)$ are expressed as linear combinations of atomic spin orbitals $\phi_\lambda(\mathbf{q}_i)$ with

$$\psi_k(\mathbf{q}_i) = \sum_{\lambda=1}^{\infty} b_{k\lambda} \phi_\lambda(\mathbf{q}_i), \quad (29)$$

where the $b_{k\lambda}$ are coefficients, $\rho_{s,t}(\mathbf{q}_i)$ becomes

$$\begin{aligned} \rho_{s,t}(\mathbf{q}_i) &= \sum_{k',k=1}^{\infty} c_{k'k} \sum_{\lambda',\lambda=1}^{\infty} b_{k'\lambda'}^* b_{k\lambda} \phi_{\lambda'}^*(\mathbf{q}_i) \phi_\lambda(\mathbf{q}_i) \\ &= \sum_{\lambda',\lambda=1}^{\infty} d_{\lambda'\lambda} \phi_{\lambda'}^*(\mathbf{q}_i) \phi_\lambda(\mathbf{q}_i), \end{aligned} \quad (30)$$

with

$$d_{\lambda'\lambda} = \sum_{k',k=1}^{\infty} b_{k'\lambda'}^* c_{k'k} b_{k\lambda}. \quad (31)$$

The occupation coefficient $d_{\lambda\lambda}$ is a direct extension of Mulliken's⁷ $N(r_k)$ to atomic spin orbitals in a many determinant wave function. Because of the general form of Eqs. (27) and (30), they could be applied in a

corresponding manner to the analysis of valence-bond functions.

3.1 Trace Expression

It is sometimes convenient to have $A_{s,t}(\mathbf{q}_i)$ expressed in a form involving the traces of matrices. To do this, we expand the determinant of the matrix ${}_s\mathbf{S}^{L',L}(j, \mathbf{q}_i)$ appearing in the numerator of Eq. (19) in terms of the elements of the j th column and their cofactors,

$$[{}_s\mathbf{S}^{L',L}(j, \mathbf{q}_i)]^{\mu j},$$

so that

$$\begin{aligned} \det {}_s\mathbf{S}^{L',L}(j, \mathbf{q}_i) &= \sum_{\mu=1}^N [{}_s\mathbf{S}^{L',L}(j, \mathbf{q}_i)]_{\mu j} [{}_s\mathbf{S}^{L',L}(j, \mathbf{q}_i)]^{\mu j} \\ &= \sum_{\mu=1}^N [{}_s\mathbf{S}^{L',L}(j, \mathbf{q}_i)]_{\mu j} [\mathbf{S}^{L',L}]^{\mu j} \end{aligned} \quad (32)$$

since, except for the j th column, the matrices $\mathbf{S}^{L',L}$ and ${}_s\mathbf{S}^{L',L}(j, \mathbf{q}_i)$ are identical. Introducing the matrix $\mathbf{A}^{L',L}(\mathbf{q}_i)$ [Eq. (21)] and making use of the fact that $\mathbf{S}^{L',L}$ is in general a nonsingular matrix, one can rewrite Eq. (32) in the form

$$\begin{aligned} \det {}_s\mathbf{S}^{L',L}(j, \mathbf{q}_i) &= \sum_{\mu=1}^N [\mathbf{A}^{L',L}(\mathbf{q}_i)]_{\mu j} [\mathbf{S}^{L',L}]^{\mu j} \\ &= [(\mathbf{S}^{L',L})^{-1} \mathbf{A}^{L',L}(\mathbf{q}_i)]_{jj} \det \mathbf{S}^{L',L}. \end{aligned} \quad (33)$$

Substitution of Eq. (33) into Eq. (19) yields

$$A_{s,t}(\mathbf{q}_i) = \frac{(1/N) \sum_{L',L} \sigma_{L'}^* \tau_L \det \mathbf{S}^{L',L} \text{Trace}[(\mathbf{S}^{L',L})^{-1} \mathbf{A}^{L',L}(\mathbf{q}_i)]}{[(\sum_{L',L} \sigma_{L'}^* \sigma_L \det \mathbf{S}^{L',L}) (\sum_{L',L} \tau_{L'}^* \tau_L \det \mathbf{S}^{L',L})]^{\frac{1}{2}}}. \quad (34)$$

Similarly, $A_s(\mathbf{q}_i)$ [Eq. (23)] becomes

$$A_s(\mathbf{q}_i) = \frac{(1/N) \sum_{L',L} \sigma_{L'}^* \sigma_L \det \mathbf{S}^{L',L} \text{Trace}[(\mathbf{S}^{L',L})^{-1} \mathbf{A}^{L',L}(\mathbf{q}_i)]}{\sum_{L',L} \sigma_{L'}^* \sigma_L \det \mathbf{S}^{L',L}} \quad (35)$$

and $\langle \mathfrak{A} \rangle_s$,

$$\langle \mathfrak{A} \rangle_s = \frac{\sum_{L',L} \sigma_{L'}^* \sigma_L \det \mathbf{S}^{L',L} \text{Trace}[(\mathbf{S}^{L',L})^{-1} \mathbf{A}^{L',L}]}{\sum_{L',L} \sigma_{L'}^* \sigma_L \det \mathbf{S}^{L',L}}, \quad (36)$$

⁷ R. S. Mulliken, Phys. Rev. **41**, 66 (1932); J. Chem. Phys. **23**, 1833, 1841 (1955).

where $\mathbf{A}^{L',L}$ is the matrix obtained from $\mathbf{A}^{L',L}(\mathbf{q}_i)$ by integrating each matrix element over the coordinate of electron i .

3.2 Single-Determinant Expressions

Since the computational difficulty involved in the evaluation of the general coefficient σ_L in Eq. (15) is insurmountable at present for most atomic and molecular systems, calculations have usually been restricted to a single determinant or a sequence of a small number of determinants.⁸ In the SCF (self-consistent field) one-electron orbital method,⁹ especially, a single determinant has been employed. For such approximate wave functions, a discussion of errors in terms of the functions defined in Sec. 2 is of the utmost importance. In the case of transition probabilities, for example, the use of the dipole length and dipole velocity methods¹⁰ often results in very different numerical values, as a consequence of the difference in the errors of the corresponding weighted transition functions. Belford, Calvin, and Belford¹¹ have recently used certain approximate $A_s(\mathbf{R}_i)$ for a study of the error in crystal field calculations of the spectra of copper chelates.

If it is assumed that the wave functions of the system are each approximated by a single determinant, Eqs. (19) and (34) reduce to

$$A_{s,t}(\mathbf{q}_i) = \frac{(1/N) \sum_{j=1}^N \det_s \mathbf{S}^{s,t}(j, \mathbf{q}_i)}{(\det \mathbf{S}^{s,s} \det \mathbf{S}^{t,t})^{\frac{1}{2}}} \quad (37)$$

and

$$A_{s,t}(\mathbf{q}_i) = \frac{\det \mathbf{S}^{s,t} \text{Trace}[(\mathbf{S}^{s,t})^{-1} \mathbf{A}^{s,t}(\mathbf{q}_i)]}{N(\det \mathbf{S}^{s,s} \det \mathbf{S}^{t,t})^{\frac{1}{2}}}, \quad (38)$$

where the superscripts on the matrices now refer to the state functions s and t , respectively. For the case $s=t$, the trace expressions are particularly convenient. Thus,

$$A_s(\mathbf{q}_i) = (1/N) \text{Trace}[(\mathbf{S}^{s,s})^{-1} \mathbf{A}^{s,s}(\mathbf{q}_i)] \quad (39)$$

and for the expectation value of $\mathfrak{A}$

$$\langle \mathfrak{A} \rangle_s = \text{Trace}[(\mathbf{S}^{s,s})^{-1} \mathbf{A}^{s,s}]. \quad (40)$$

The trace expression given in Eq. (40) is very useful in the computation of the expectation values of one-electron properties of a system whose wave function is

⁸ S. F. Boys, *Nature* **178**, 1207 (1956).

⁹ D. R. Hartree, *Repts. Progr. in Phys.* **11**, 113 (1946-1947); C. C. J. Roothaan, *Revs. Mod. Phys.* **23**, 69 (1951).

¹⁰ H. Shull in *Conference on Quantum-Mechanical Methods in Valence Theory* (Office of Naval Research, Washington, D. C., 1951), p. 21.

¹¹ Belford, Calvin, and Belford, *J. Chem. Phys.* **26**, 1165 (1957).

approximated by a single determinant of nonorthogonal one-electron wave functions. By direct use of the trace of the matrix product $(\mathbf{S}^{s,s})^{-1} \mathbf{A}^{s,s}$ the overlap terms are calculated exactly, and the approximation¹² involved in the expansion of the overlap matrix with neglect of second and higher order terms is avoided.

If the single determinant approximation corresponds to a structure with all orbitals doubly occupied and the operator under consideration is of the form $\alpha(\mathbf{R}_i)$, the matrices $\mathbf{S}^{s,s}$ and $\mathbf{A}^{s,s}$ can be expressed in the block form

$$\mathbf{S}^{s,s} = \begin{bmatrix} \mathbf{S}_{1/2}^{s,s} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}_{1/2}^{s,s} \end{bmatrix}, \quad \mathbf{A}^{s,s} = \begin{bmatrix} \mathbf{A}_{1/2}^{s,s} & \mathbf{0} \\ \mathbf{0} & \mathbf{A}_{1/2}^{s,s} \end{bmatrix}, \quad (41)$$

where the spin orbitals with one spin give rise to the first block and those with opposite spin to the second identical block. By means of Eq. (41), $\langle \mathfrak{A} \rangle_s$ reduces to

$$\langle \mathfrak{A} \rangle_s = 2 \text{trace}[(\mathbf{S}_{1/2}^{s,s})^{-1} \mathbf{A}_{1/2}^{s,s}]. \quad (42)$$

Under the same conditions, $A_s(\mathbf{R}_i)$ also takes the simpler form

$$A_s(\mathbf{R}_i) = 2 \text{trace}[(\mathbf{S}_{1/2}^{s,s})^{-1} \mathbf{A}_{1/2}^{s,s}(\mathbf{R}_i)]. \quad (43)$$

This expression is useful in the computation of the weighted charge density in a molecule whose wave function is approximated by a single determinant of doubly occupied nonorthogonal one-electron spin orbitals.¹³

3.3 Orthonormalization

If the expansion functions $\psi_\mu(\mathbf{q}_i)$ introduced in Eq. (14) are members of an orthonormal set,

$$\int \psi_\mu^*(\mathbf{q}_i) \psi_\nu(\mathbf{q}_i) d\mathbf{q}_i = \delta_{\mu\nu} \quad (44)$$

a considerable simplification results in the formulas that have been derived. From Eq. (44) and the definition of $\mathbf{S}^{L',L}$, it is evident that

$$\det \mathbf{S}^{L',L} = \delta_{L',L}. \quad (45)$$

It is assumed in Eq. (45) and in the rest of this section that the rows and columns of $\mathbf{S}^{L',L}$, $\mathbf{A}^{L',L}(j, \mathbf{q}_i)$, etc. have been ordered so that if $l'_\mu = l_\nu$ for any element, it appears along the diagonal. Similarly, it can be seen that

$$\det_s \mathbf{S}^{L',L}(j, \mathbf{q}_i) = [\mathbf{A}^{L',L}(\mathbf{q}_i)]_{jj} \prod_{r \neq j}^N \delta_{l'_r, l_r}. \quad (46)$$

¹² P. O. Löwdin, *J. Chem. Phys.* **18**, 365 (1950).

¹³ Karplus, Kuppermann, and Isaacson (to be published).

Substitution of the results of Eqs. (45) and (46) into Eq. (19) yields

$$A_{s,t}(\mathbf{q}_i) = \frac{(1/N) \sum_{L',L} \sigma_{L'}^* \tau_L \sum_{j=1}^N [A^{L',L}(\mathbf{q}_i)]_{jj} \prod_{r \neq j}^N \delta_{l'r, l_r}}{(\sum_{L',L} |\sigma_{L'}|^2 |\tau_L|^2)^{\frac{1}{2}}}. \quad (47)$$

Similarly,

$$\langle \mathcal{H} \rangle_{s,t} = \frac{\sum_{L',L} \sigma_{L'}^* \tau_L \sum_{j=1}^N [A^{L',L}]_{jj} \prod_{r \neq j}^N \delta_{l'r, l_r}}{(\sum_{L',L} |\sigma_{L'}|^2 |\tau_L|^2)^{\frac{1}{2}}}, \quad (48)$$

$$A_s(\mathbf{q}_i) = \frac{(1/N) \sum_{L',L} \sigma_{L'}^* \sigma_L \sum_{j=1}^N [A^{L',L}(\mathbf{q}_i)]_{jj} \prod_{r \neq j}^N \delta_{l'r, l_r}}{\sum_L |\sigma_L|^2}, \quad (49)$$

$$\langle \mathcal{H} \rangle_s = \frac{\sum_{L',L} \sigma_{L'}^* \sigma_L \sum_{j=1}^N [A^{L',L}]_{jj} \prod_{r \neq j}^N \delta_{l'r, l_r}}{\sum_L |\sigma_L|^2}, \quad (50)$$

and the coefficient $c_{k'k}$ in $\rho_{s,t}(\mathbf{q}_i)$ becomes

$$c_{k'k} = \frac{\sum_{L',L} \sum_{\mu} \sigma_{L'}^* \tau_L \delta_{k', l'_\mu} \delta_{k, l_\mu} \prod_{r \neq j}^N \delta_{l'r, l_r}}{(\sum_{L',L} |\sigma_{L'}|^2 |\tau_L|^2)^{\frac{1}{2}}}. \quad (51)$$

For the spin-orbital charge density function, $\rho_s(\mathbf{q}_i)$

$$c_{k'k} = \frac{\sum_{L',L} \sum_{\mu} \sigma_{L'}^* \tau_L \delta_{k', l'_\mu} \delta_{k, l_\mu} \prod_{r \neq j}^N \delta_{l'r, l_r}}{\sum_L |\sigma_L|^2} \quad (52)$$

and the occupation number reduces to

$$c_{kk} = \frac{\sum_L \sum_{\mu=1}^N |\sigma_L|^2 \delta_{k, l_\mu}}{\sum_L |\sigma_L|^2} \quad (53)$$

in agreement with the result obtained by Löwdin.⁶

In many approximate wave functions, the limited set of expansion functions used does not satisfy Eq. (44). This has been true for most valence-bond calculations, as well as for semi-empirical molecular orbital treatments based on localized bond orbitals. In such cases it is often possible to systematize the computational work by transforming to an orthonormal set of functions.¹⁴

A convenient set of orthonormal functions, $\psi'_\mu(\mathbf{q}_i)$ ($\mu=1, 2, \dots$) is obtained from the functions $\psi_\mu(\mathbf{q}_i)$ ($\mu=1, 2, \dots$) by the transformation¹²

$$\psi'_\mu(\mathbf{q}_i) = \sum_{j=1}^{\infty} [\mathbf{S}^{-1}]_{j\mu} \psi_j(\mathbf{q}_i) \quad \mu=1, 2, \dots, \quad (54)$$

where $\mathbf{S}$ is the overlap matrix for the entire set of functions. For a finite set of functions $\psi_j(\mathbf{q}_i)$ ($j=1, 2, \dots, \rho$) it is possible to find $\mathbf{S}^{-1}$ by a simple procedure. Since $\mathbf{S}$ and $\mathbf{S}^{-1}$ are Hermitian, there exists a matrix $\mathbf{Q}$, whose columns are the eigenvectors of $\mathbf{S}^{-1}$, such that

$$\mathbf{Q}^{-1} \mathbf{S}^{-1} \mathbf{Q} = \mathbf{D}, \quad (55)$$

where $\mathbf{D}$ is a diagonal matrix,

$$[\mathbf{D}]_{\mu\nu} = d_\mu \delta_{\mu\nu}. \quad (56)$$

Since

$$[\mathbf{D}^{\frac{1}{2}}]_{\mu\nu} = d_\mu^{\frac{1}{2}} \delta_{\mu\nu}, \quad (57)$$

$\mathbf{S}^{-1}$ can be easily obtained from the equation

$$\mathbf{S}^{-1} = \mathbf{Q} \mathbf{D}^{\frac{1}{2}} \mathbf{Q}^{-1}. \quad (58)$$

Finally, substitution of Eq. (58) into Eq. (54) yields

$$\psi'_\mu(\mathbf{q}_i) = \sum_{j=1}^p [\mathbf{Q} \mathbf{D}^{\frac{1}{2}} \mathbf{Q}^{-1}]_{j\mu} \psi_j(\mathbf{q}_i) \quad (59)$$

which expresses the transformation of $\psi_j(\mathbf{q}_i)$ to $\psi'_\mu(\mathbf{q}_i)$ in terms of the eigenvectors and square roots of the eigenvalues of $\mathbf{S}^{-1}$.

An application of Eq. (59) arises in the use of localized bond orbitals in molecular orbital theory. The requirement of orthogonality of the bond orbitals introduces a certain amount of delocalization which might be called "forced delocalization" in analogy to Mulliken's¹⁶ use of the term "forced hybridization." For acetylene, a comparison of the forced delocalization obtained in a semiempirical study of localized bond orbitals with the results of Maeda's¹⁶ nonlocalized SCF LCAO-MO calculation expressed in equivalent orbital form is carried out in a later paper¹³ of this series.

4. DIGITAL COMPUTER CALCULATION

For the general expansion of the wave function for N -electron systems in a series of determinants of one-electron functions, the problem of determining weighted

¹⁴ R. McWeeney, Proc. Roy. Soc. (London) **A223**, 63, 306 (1954).

¹⁵ R. S. Mulliken, J. Chem. Phys. **19**, 912 (1951).

¹⁶ S. Maeda, J. Chem. Soc. (Japan) **75**, 36 (1954).

transition functions, weighted density functions, and their integrals has been reduced to evaluating sums of determinants of matrices [e.g., Eq. (19)] or of the traces of matrix products [e.g., Eq. (34)]. Once the required elements, which are integrals of the form

$$\int \psi_{\mu}^*(\mathbf{q}_i) a(\mathbf{q}_i) \psi_{\nu}(\mathbf{q}_i) d\mathbf{q}_i$$

or products of the form $\psi_{\mu}^*(\mathbf{q}_i) a(\mathbf{q}_i) \psi_{\nu}(\mathbf{q}_i)$, have been evaluated, the remainder of the calculation can be performed with the help of codes which are a standard

part of digital computer program libraries. The necessary programs for most of the functions discussed in this paper have been tested on ILLIAC, the electronic digital computer of the University of Illinois, which has a speed comparable to many of the other high-speed computers in operation today. It was found that none of the calculations took more than ten minutes for a fourteen electron problem treated by the single determinant approximation. This indicates that the formulation developed in this paper should be generally useful in the evaluation of one-electron properties.

On the Approximate Calculation of Eigenfunctions*

B. F. GRAY

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

(Received July 23, 1958)

A method is given for determining the variable parameters in a trial wave function which is independent of the minimum energy criterion. The energy is given as the root of a secular equation, but the value obtained may be above or below the true value. It is shown that the results of the method approach those of the standard one as the trial function becomes a better approximation to the true one, by applying it to the series of two-electron ions.

INTRODUCTION

IT is well known that wave functions constructed by use of the variation theorem are by no means as accurate as the change in the calculated energy which the number of parameters might indicate. This is particularly true in the regions of the singularities, e.g., near the nucleus and at small interelectronic separations. Since a knowledge of the wave function in these regions is necessary for the interpretation of recently developed experimental methods and for the calculation of relativistic and other corrections, methods independent of the energy criterion would seem to be of interest at the moment.

Methods already used usually do not give an analytical wave function, e.g., Bartlett¹ used the fact that the ratio $\mathcal{H}\psi/\psi$ should be constant and equal to the energy over the whole of configuration space for the helium atom to obtain an approximate wave function in numerical form. The quantum-mechanical virial theorem restricts a trial function to some extent, but it does not appear possible to put it in a form convenient for fixing a number of variable parameters. Here a method is developed which is capable of determining any number of parameters, and in principle the correct wave function, when it becomes identical with the variation method.

THE METHOD OF UNIQUE COEFFICIENTS

Let the system under consideration be represented by the wave equation

$$(\mathcal{H}^0 + v)\psi = E\psi, \quad (1)$$

where

$$\mathcal{H}^0\phi_i = E_i^0\phi_i, \quad (2)$$

both equations being subjected to the same boundary conditions. We can then write

$$\psi = [\phi_0 + \Sigma' a_i \phi_i] / a_0, \quad (3)$$

where ψ is normalized such that $\int \psi \phi_0 d\tau = 1$ [we are focusing our attention on the state which passes over into ϕ_0 as $v \rightarrow 0$, ϕ_0 not necessarily being the state of lowest energy of (2), although for clarity we will assume it to be nondegenerate]. If $\mathcal{H}^0$ is Hermitian, then the $\{\phi_i\}$ will form a complete orthonormal set, so that we can write

$$\psi = \left[\phi_0 + \Sigma' \int \phi_i \psi d\tau \phi_i \right] / \int \phi_0 \psi d\tau, \quad (4)$$

and we can substitute for ψ on the right-hand side of (4) in various ways as shown in an earlier paper,² each of which we will denote by $X_k\psi$. Hence,

$$\psi = \left[\phi_0 + \Sigma' \int \phi_i X_k \psi d\tau \phi_i \right] / \int \phi_0 X_k \psi d\tau, \quad (5)$$

* Contribution No. 2377.

¹ J. H. Bartlett, Phys. Rev. **51**, 655 (1937).

² B. F. Gray and H. O. Pritchard, J. Chem. Phys. **28**, 519 (1958).