Electronic wave functions

I. A general method of calculation for the stationary states of any molecular system

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This communication deals with the general theory of obtaining numerical electronic wave functions for the stationary states of atoms and molecules. It is shown that by taking Gaussian functions, and functions derived from these by differentiation with respect to the parameters, complete systems of functions can be constructed appropriate to any molecular problem, and that all the necessary integrals can be explicitly evaluated. These can be used in connexion with the molecular orbital method, or localized bond method, or the general method of treating linear combinations of many Slater determinants by the variational procedure. This general method of obtaining a sequence of solutions converging to the accurate solution is examined. It is shown that the only obstacle to the evaluation of wave functions of any required degree of accuracy is the labour of computation. A modification of the general method applicable to atoms is discussed and considered to be extremely practicable.

1. INTRODUCTION

In this communication is described the first of a series of investigations undertaken with the general aim of developing better methods of evaluating electronic wave functions and of using these to obtain new and more accurate data on atomic and molecular structure. It is well known that if the electronic stationary state wave functions can be evaluated for the various configurations of a system of atomic nuclei, then most of the spectral, chemical and physical properties of the corresponding system of atoms can be calculated. This is true when the atoms form a stable molecule, or when the system consists of a single atom, or when the system corresponds to an unstable configuration of atoms such as occur in the intermediate stages of a chemical reaction. Hence this general problem includes in principle a large number of the problems of theoretical chemistry, and a converging method of solution would effectively solve these problems.

The first purpose of this communication is to describe such a method of successive approximation by which this stationary state electronic wave function for any configuration of atoms can be calculated to any desired degree of accuracy by inclusion of sufficient terms. This method does not depend on any numerical integration processes. Such a method has not been previously reported. The new mathematical analysis which has been carried out to make this possible consists essentially of the evaluation of the Schrödinger integrals between Gaussian probability functions. The most complicated integral which is required is that of the electronic interaction between one product of two Gaussians on different centres with another product of two other Gaussians. These integrals and the simpler ones required are all evaluated explicitly. These integrals also provide the bases for the

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evaluation of all integrals derived from these by first multiplying the Gaussians by any polynomials.

The actual procedure in which it is proposed that the Gaussian functions should be used consists of the construction of many Slater determinants from these and the use of these determinants in the Ritz variational method. The type of procedure considered most promising has been called the variational selection procedure. It corresponds in some degree to previous calculations, but it has not been formulated or discussed previously. Since this method is applicable to other sets of functions if the integrals for these can be evaluated, the general discussion of this may be regarded as a second purpose of this communication.

A third topic which it is convenient to discuss here is the fact that it is possible to use the variational selection method applied to Slater determinants constructed from simple exponential functions for atoms, and that this appears the most promising method for calculating the wave functions of complex atoms with converging accuracy. Several applications of this will be reported in subsequent papers.

Finally, the mathematical analysis on Gaussian functions may be regarded as fulfilling another purpose. Several approximate and non-converging methods of evaluating wave functions of molecules have been widely used for making deductions on the general nature of molecules. The best known of these are the molecular orbital and the localized bond methods. It has, however, never been possible to make *a priori* predictions by such procedures in cases other than the very simplest, since the requisite integrals could not be evaluated and had to be estimated empirically. However, if the orbitals used in any of these cases were taken to be linear combinations of functions derived from Gaussian functions all the required integrals could be evaluated explicitly. The analysis derived here does, therefore, provide for the first time a method of applying quantitatively, and in a fundamental way, the approximate methods of the molecular orbital and localized bond types.

The previous state of affairs in the calculation of atomic and molecular energies and wave functions is that converging methods without numerical integrations have been developed for two-electron problems such as He (Hylleraas 1929) and H_2 (James & Coolidge 1933), but no converging methods are available for more general molecules. The only method which is converging in principle for general atoms is the 'superposition of configurations' method (Hartree, Hartree & Swirles 1939), but this does not appear practicable for use with more than two or three terms, and depends on laborious numerical integrations.

With regard to the practical application of the methods described here it is not intended to apply the most general procedure immediately. It is intended first to gain experience in the variational selection procedure with Slater determinants using exponentials for atoms instead of Gaussian functions for molecules. This will provide useful data for atoms, and it will also provide an opportunity to find simplifications of the numerical techniques. The direct computation for molecules of interest would be very laborious, and it is hoped that either the numerical techniques can be considerably shortened or that the present scheme might lead to a more powerful method.

In work of this kind Slater determinants built up from orthogonal normalized single-particle functions occur so frequently that it appears worth while to suggest a short synthetic name for these. It is proposed that the word 'detor' be used to describe the Slater determinant of the general type

$$(1/n!) \sum_u \sigma_u P_u f_1(\mathbf{r}_1)\,\mu_1(v_1) f_2(\mathbf{r}_2)\,\mu_2(v_2) \ldots f_n(\mathbf{r}_n)\,\mu_n(v_n), \tag{1}$$

where
$$\int f_i^*(\mathbf{r}) f_j(\mathbf{r})\,d\mathbf{r} = \delta_{ij},$$

where v_i represent the spin variables which can only take the values $\frac{1}{2}$ and $-\frac{1}{2}$, where the μ_i can each be either the α or β function defined by

$$\begin{aligned}\alpha(\tfrac{1}{2}) &= 1, & \alpha(-\tfrac{1}{2}) &= 0, \\ \beta(\tfrac{1}{2}) &= 0, & \beta(-\tfrac{1}{2}) &= 1,\end{aligned} \tag{2}$$

where the operators P_u represent all the possible permutations of the different sets of four variables $\mathbf{r}_i$, v_i, and where σ_u is $+1$ or -1 according as the permutation is even or odd. The author proposes using such extensions as poly-detor to denote linear combinations of detors where all the original functions are orthonormal. The convenience of these definitions is that these are just the types of function for which the integrals required in the variational problem can be reduced to a very simple form. Also, as is well known and simple to prove, the detors made from an orthonormal set are themselves orthonormal.

The term 'a complete system of functions' will be used in its usual sense to mean an ordered system $\{f_r\}$ for which m and the coefficients X_r can always be chosen for any given function F of the domain under consideration, so that

$$S\left(F - \sum_r^m X_r f_r\right)^*\left(F - \sum_r^m X_r f_r\right) d\tau < \epsilon, \tag{3}$$

where ϵ is any small positive number. The term 'a complete class of functions' will be used to mean a class of functions out of which it is possible to choose at least one complete system.

We shall be concerned with the many-electron Schrödinger equation for stationary states. We shall express it in atomic units and denote it as

$$H\psi \equiv \left\{\sum_i K_i - \sum_{I,i} Z_I V_{Ii} + \tfrac{1}{2}\sum_{i,j} M_{ij}\right\}\psi = E\psi, \tag{4}$$

where
$$\begin{aligned}K_i &\equiv -\frac{1}{2}\left\{\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right\}, \\ V_{Ii} &\equiv 1/\sqrt{[(x_i - P_{Ix})^2 + (y_i - P_{Iy})^2 + (z_i - P_{Iz})^2]}, \\ M_{ij} &\equiv 1/\sqrt{[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]}\end{aligned} \tag{5}$$

where x_i, y_i, z_i, v_i are the space and spin variables corresponding to the total number of electrons, where P_{Ix}, P_{Iy}, P_{Iz} are the positions of the nuclei, which are to be regarded as fixed and with integral charges Z_I. ψ is a function anti-symmetric with respect to the different sets of variables (x_i, y_i, z_i, v_i).

The notation (| |) will be used to denote integration over all the space co-ordinates and summation over all the spin variables of the contained functions, the complex conjugate of the first function being taken. The same notation will be used for many- and single-electron functions, and for functions dependent on space and spin variables or only on either space or spin variables. The integrals are independent of the variables of integration and these will generally be omitted, thus

$$(f_r | V_I | f_s) \equiv \int d\mathbf{r} \{ f_r^*(\mathbf{r}) \, (1/r_I) f_s(\mathbf{r}) \}. \tag{6}$$

It is also convenient to define

$$[f_r f_s | \, M \, | f_t f_u] \equiv \int\int d\mathbf{r}_1 d\mathbf{r}_2 \{ f_r^*(\mathbf{r}_1) f_s(\mathbf{r}_1) \, (1/r_{12}) f_t^*(\mathbf{r}_2) f_u(\mathbf{r}_2) \}. \tag{7}$$

In § 2 we evaluate all the Schrödinger integrals between Gaussian functions which are required to establish the general scheme. § 3 deals with the convergent method of calculating energies and wave functions in terms of linear combinations of increasing numbers of detors. In § 4 are discussed other modifications of the general method and particularly the calculations for atoms, and in § 5 the general aspects of the methods are reviewed.

2. The evaluation of all the Schrödinger integrals for detors constructed from the complete class of Gaussian functions

We define the complete class of Gaussian functions to consist of all functions, and of all linear combinations of functions, of the type $x^l \, y^m \, z^n \exp(-a r_A^2)$, where l, m, n, have any integral values, where a has any positive value, where we have used the general notation

$$x_A = x - A_x, \text{ etc.,} \quad r_A^2 = x_A^2 + y_A^2 + z_A^2, \tag{8}$$

and where A_x, A_y, A_z have any real values. The fact that this class is complete in the sense defined above follows immediately, since it contains the well-known complete system of Hermitian functions around any point. It actually contains an infinite number of complete systems. If any orthonormal set of these are taken and detors constructed from them after multiplication by the α and β spin functions, we wish to show that all Schrödinger integrals among these can be evaluated by quite simple formulae. The only step of any difficulty is that of evaluating integrals of the types

$$(g_r | g_s), \quad (g_r | K | g_s), \quad (g_r | V_I | g_s), \quad [g_r g_s | M | g_t g_u], \tag{9}$$

when g_r, g_s, g_t, g_u are members of the complete class. If, however, we evaluate these integrals when g_r, g_s, g_t, g_u are restricted to belong to the subclass of functions of the type $\exp(-a r_A^2)$ we can easily derive the formulae for the general class by differentiation with respect to the parameters in the integral formulae, followed by taking the appropriate linear combinations; since we can obtain any function of the whole class from the functions of the subclass by this procedure. We shall, therefore, limit our examination to deriving all the integrals for the subclass.

The values of the first of these integrals are obtained by simple direct integration; we get

$$(aA \mid bB) = \left(\frac{\pi}{a+b}\right)^{\frac{3}{2}} \exp\left(-\frac{AB^2 ab}{a+b}\right), \tag{10}$$

$$(aA \mid K \mid bB) = \left(\frac{3ab}{a+b} - \frac{2AB^2 a^2 b^2}{(a+b)^2}\right)\left(\frac{\pi}{a+b}\right)^{\frac{3}{2}} \exp\left(-\frac{AB^2 ab}{a+b}\right), \tag{11}$$

where $\qquad aA \equiv \exp(-ar_A^2) \quad$ and $\quad AB^2 = \sum\limits_{x,y,z} (A_x - B_x)^2. \tag{12}$

To evaluate the remaining integrals we have

$$\int (1/r_{12}) \exp(-ar_{2A}^2)\, d\mathbf{r}_2$$

$$= (4\pi/r_{1A})\int_0^{r_{1A}} r_{2A}^2 \exp(-ar_{2A}^2)\, dr_2 + 4\pi \int_{r_{1A}}^{\infty} r_{2A} \exp(-ar_{2A}^2)\, dr_2$$

$$= (2\pi/ar_{1A})\int_0^{r_{1A}} \exp(-ar_{2A}^2)\, dr_2, \tag{13}$$

by the well-known transformation of the Coulomb potential of a spherical charge distribution. The integrals $(aA \mid V_c \mid bB)$, corresponding to a nucleus at C, can be reduced to an integral of the above type, since putting

$$P_x = \frac{aA_x + bB_x}{a+b}, \text{ etc.,} \tag{14}$$

we have

$$(aA \mid V_c \mid bB) = \int (1/r_c) \exp\left[-\sum\limits_{x,y,z} \{a(x-A_x)^2 + b(x-B_x)^2\}\right] d\mathbf{r}$$

$$= \exp\left(-\frac{AB^2 ab}{a+b}\right) \int (1/r_c) \exp\left[-\sum\limits_{x,y,z} (a+b)(x-P_x)^2\right] d\mathbf{r}. \tag{15}$$

If we define $\qquad\qquad F(z) = z^{-\frac{1}{2}} \int_0^{\sqrt{z}} e^{-u^2}\, du \tag{16}$

and $\qquad\qquad\qquad CP^2 = \sum\limits_{x,y,z} (C_x - P_x)^2,$

we have $\qquad (aA \mid V_c \mid bB) = \frac{2\pi}{(a+b)} \exp\left(-\frac{AB^2 ab}{a+b}\right) F\{CP^2(a+b)\}. \tag{17}$

To evaluate the remaining type of integral it is convenient first to evaluate

$$I \equiv \int\!\!\int (1/r_{12}) \exp\left\{-u \sum\limits_{x,y,z} (x_1 - P_x)^2\right\} - v \sum\limits_{x,y,z} (x_2 - Q_x)^2\, d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \frac{2\pi}{v} \int d\mathbf{r}_1 \exp\left\{-u \sum\limits_{x,y,z} (x_1 - P_x)^2\right\} (1/r_{1Q}) \int_0^{r_{1Q}} \exp(-va^2)\, da. \tag{18}$$

This transformation is obtained by integrating with respect to $d\mathbf{r}_2$ using relation (13). Now if we use the two centre variables r_P, r_Q, ϕ in place of x_1, y_1, z_1 with

$$d\mathbf{r}_1 = (r_P r_Q / PQ)\, dr_P\, dr_Q\, d\phi,$$

we obtain
$$I = \frac{2\pi}{vPQ} \left(\int_0^{PQ} dr_Q \int_{PQ-r_Q}^{PQ+r_Q} dr_P + \int_{PQ}^{\infty} dr_Q \int_{r_Q-PQ}^{r_Q+PQ} dr_P \right) \int_0^{2\pi} d\phi$$

$$\times r_P \exp(-ur_P^2) \int_0^{r_Q} \exp(-va^2)\, da$$

$$= \frac{2\pi^2}{uvPQ} \int_{-\infty}^{\infty} dr_Q \exp\{-u(PQ-r_Q)^2\} \int_0^{r_Q} \exp(-va^2)\, da. \tag{19}$$

Hence we require to evaluate an integral of the type

$$J \equiv \int_{-\infty}^{\infty} dx \exp\{-\alpha(x-R)^2\} \int_0^x \exp\{-\beta y^2\}\, dy \tag{20}$$

when $\alpha > 0$ and $\beta > 0$. We have

$$\frac{dJ}{dR} = -2\alpha \int_{-\infty}^{\infty} dx (R-x) \exp\{-\alpha(x-R)^2\} \int_0^x \exp\{-\beta y^2\}\, dy$$

$$= \sqrt{\left(\frac{\pi}{\alpha+\beta} \right)} \exp\left(-\frac{\alpha\beta R^2}{\alpha+\beta} \right), \tag{21}$$

and since $J = 0$ when $R = 0$ we obtain

$$J = \sqrt{\left(\frac{\pi}{\alpha+\beta} \right)} \int_0^R \exp\left(-\frac{\alpha\beta R^2}{\alpha+\beta} \right) dR. \tag{22}$$

Substituting this back in (19) we get

$$I = \frac{2\pi^{\frac{5}{2}}}{uv\sqrt{(u+v)}} F\left(\frac{PQ^2 uv}{u+v} \right). \tag{23}$$

The actual integral which we require to evaluate is

$$[aAbB \mid M \mid cCdD] = \iint (1/r_{12}) \exp\{-(ar_{1A}^2 + br_{1B}^2 + cr_{2C}^2 + dr_{2D}^2)\}\, d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \exp\left\{ -\frac{AB^2 ab}{a+b} - \frac{CD^2 cd}{c+d} \right\} \iint (1/r_{12}) \exp\{-(a+b) r_{1P}^2 - (c+d) r_{2Q}^2\}\, d\mathbf{r}_1 d\mathbf{r}_2, \tag{24}$$

where
$$P_x = (aA_x + bB_x)/(a+b) \quad \text{and} \quad Q_x = (cC_x + dD_x)/(c+d), \text{ etc.} \tag{25}$$

The integral is just of the form of I so that

$$[aAbB \mid M \mid cCdD]$$
$$= \frac{2\pi^{\frac{5}{2}}}{(a+b)(c+d)\sqrt{(a+b+c+d)}} \exp\left\{ -\frac{AB^2 ab}{a+b} - \frac{CD^2 cd}{c+d} \right\} F\left(\frac{PQ^2(a+b)(c+d)}{a+b+c+d} \right). \tag{26}$$

In view of the fact that the formulae for all functions of the complete Gaussian class can be derived from the above formulae by differentiation we have shown that all Schrödinger integrals can be evaluated for this class, and it only remains to show that the integrals between the derived detors reduce to these integrals. This is apparent by simple examination. The detors are merely finite linear combinations of the form
$$g_1(\mathbf{r}_1)\, \mu_1(v_1)\, g_2(\mathbf{r}_2)\, \mu_2(v_2) \cdots g_n(\mathbf{r}_n)\, \mu_n(v_n), \tag{27}$$

where g_i are members of the complete Gaussian class and each μ_i represents either α or β. Hence if we expand $(S_g \,|\, H \,|\, S'_g)$, where S_g and S'_g are detors of this type, we obtain only a finite number of terms of the types

$$\left.\begin{aligned}
(g_1 \,|\, g'_1)\,(\mu_1 \,|\, \mu'_1)\,(g_2 \,|\, g'_2) \dots (g_i \,|\, V_{iI} \,|\, g'_i) \dots (g_n \,|\, g'_n)\,(\mu_n \,|\, \mu'_n),\\
(g_1 \,|\, g'_1)\,(\mu_1 \,|\, \mu'_1) \dots (g_i \,|\, K_i \,|\, g'_1) \dots (g_n \,|\, g'_n)\,(\mu_n \,|\, \mu'_n),\\
(g_1 \,|\, g'_1)\,(\mu_1 \,|\, \mu'_1) \dots [g_i g'_i \,|\, M_{ij} \,|\, g_j g_j] \dots (g_n \,|\, g'_n)\,(\mu_n \,|\, \mu'_n).
\end{aligned}\right\} \tag{28}$$

The factors $(\mu_i \,|\, \mu'_i)$ are all 0 or 1 by the definition of the μ_i, and the other factors are all integrals of the general types which we have shown can be evaluated. In actual practice powerful techniques are available to obtain the integrals between detors without explicit expansion, but these do not affect the final form of the answer. Hence we see that all matrix elements of the form $(S_g \,|\, H \,|\, S'_g)$, where H is the Schrödinger-Hamiltonian and S_g and S'_g are detors formed from functions of the complete Gaussian class can be expressed in terms of tabulated functions.

3. THE VARIATIONAL SELECTION METHOD USING DETORS FROM A COMPLETE CLASS OF FUNCTIONS

In this section what is regarded as the most promising converging method of obtaining electronic wave functions for atoms and molecules will be explained and justified. It will not be possible to prove rigorously the theorems which are required, but we shall give what justification we can. Difficulties of rigorous justification are well known in this field, in which theorems are required, appropriate to many dimensions, concerning the solutions of equations with singularities in spaces which are not bounded. The requisite theorems may not be true for any mathematical function but are very probably true for the functions permissible for wave functions. It is probably the difficulties of knowing and introducing such conditions for permissible functions which have prevented rigorous proofs of various desirable theorems up to the present.

We shall first assume the convergence of the Ritz variational procedure for eigenvalues and eigenfunctions. It is convenient to summarize as a theorem all the assumptions that are made in applying this procedure. This theorem has not been proved rigorously, but if various plausible assumptions (such as the convergence of $\sum_s (\phi_r \,|\, H \,|\, \phi_s)\phi_s$ when the ϕ_r form a complete system of functions) are made, it can be proved except for the convergence of the higher eigenfunctions $\psi_2, \psi_3 \dots$ (see Kemble 1937). The assumption of the convergence of these is, however, generally made in practical numerical calculations.

THEOREM 1. If ψ_k and E_k are the (k)th eigenfunction and eigenvalue of

$$(H - E_k)\,\psi_k = 0, \tag{29}$$

these being labelled in order of ascending E_k, if Φ_r represents a normalized orthogonal system of functions, if $\psi_k^p = \sum_r^p X_r^{kp}\Phi_r$ and E_k^p satisfy

$$\sum_s^p (\Phi_r \,|\, H \,|\, \Phi_s)\,X_s^{kp} - E_k^p X_r^{kp} = 0, \tag{30}$$

the E_k^p being labelled in ascending order, then we have

$$E_k^p > E_k^{p+1} > E_k.$$

If Φ_r is a complete system of functions then E_k^p converge monotonically downwards to E_k, and ψ_k^p converge in the mean square sense to ψ_k.

It has been considered simplest to ignore the possibility of degenerate eigenvalues in this formulation. A considerably longer statement would be necessary to include this possibility, but this could be done without any essential difference of content.

A variational method will now be considered which is not the final method the author will advocate, but which forms an introduction and a justification of the final method. This method will be referred to as the single-system detor method, and the final method as the variational selection method. In the single-system method we commence with $\{\phi_r\}$, a single complete system of orthonormal functions of the variables x, y, z. If we are solving an n electron problem we form an ordered system of (n)th order detors constructed from the $\{\phi_r\}$ in accordance with the general procedure of placing all possible detors which contain ϕ_m but not ϕ_p for $p > m$ before all detors which contain any of ϕ_p. This system is then to be used as a complete system of functions for the variational procedure as stated in theorem 1. The E_k^M and $\psi_k^M = \sum_r^M X_r^{kM} \Phi_r$ will converge according to the theorem if $\{\Phi_r\}$ is a complete orthonormal system of functions. The orthonormality follows from the definition of the detors as mentioned above, but to show the completeness of the system a theorem is required which has not been established for general functions for the infinite ranges of integration for which it is required, although it can be proved for finite ranges of integration. The proof for finite ranges is given by Courant & Hilbert (1931, p. 47), but its general validity will be assumed for infinite ranges for the types of functions which will be used in these calculations.

THEOREM 2. If $\{\phi_r\}$ denotes a complete system of functions for the space x, y, z, then the system

$$\phi_{s1}(\mathbf{r}_1) \phi_{s2}(\mathbf{r}_2) \phi_{s3}(\mathbf{r}_3) \ldots \phi_{sn}(\mathbf{r}_n), \tag{31}$$

where each pair $s1, s2$, etc., denotes a single suffix of the r type, and where the products are ordered so that all products containing ϕ_m but no ϕ_p $(p > m)$ are placed before all products containing any of the ϕ_p, is a complete system for the space $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$.

It follows from this theorem that the products

$$\phi_{s1}(\mathbf{r}_1) \mu_{k1}(v_1) \phi_{s2}(\mathbf{r}_2) \mu_{k2}(v_2) \ldots \phi_{sn}(\mathbf{r}_n) \mu_{kn}, \tag{32}$$

where μ_{ki} have the possible values $\mu_{\frac{1}{2}} = \alpha$ and $\mu_{-\frac{1}{2}} = \beta$, is a complete system of functions for the space $(\mathbf{r}_1, v_1, \mathbf{r}_2, v_2, \ldots, \mathbf{r}_n, v_n)$, since the system would be complete for each of the combinations of the μ_{ki} functions.

If we consider an anti-symmetric function F, then by definition

$$\sigma_u P_u F = F, \tag{33}$$

and if F is expanded in terms of the complete system of products with coefficients $A(si, ki)$ we can operate on both sides of the equation and obtain

$$(1/n!) \sum_u \sigma_u P_u F = F = (1/n!) \sum_u \sigma_u P_u \sum_{si, ki} A(si, ki) \phi_{s1} \mu_{k1} \phi_{s2} \mu_{k2} \ldots \phi_{sn} \mu_{kn}, \tag{34}$$

thus expressing F as a sum of detors.

Hence for anti-symmetric functions the detor system is a complete system, and the use of the single-system detor method for obtaining converging anti-symmetric solutions of Schrödinger's equation is in accordance with theorem 1.

The variational selection method can now be stated. This is a general procedure with considerable liberty of choice, which can be applied to a complete class of functions. When approximating to a particular E_k and ψ_k we take the M(th) approximation to be given by the use in the variational method of M detors formed from any m orthonormal ϕ_r^M out of the complete class. We do not specify the choice of the ϕ_r^M or of Φ_r^M the M detors, which need not be all the detors that can be formed from the ϕ_r^M, beyond one condition. We specify that the E_k^M obtained from this choice must be less than $E_k'^M$ where this is the value given by the (M)th approximation in the single-system detor method when using some complete system of $\{\phi_r'\}$ chosen out of the complete class. This definition of the variational selection method makes it include a large variety of particular processes. For a given value of M we could take considerable pains to minimize E_k^M with respect to the various parameters which designate the members of the complete class, or we could perform many schemes of less exhaustive tests. In actual fact the postulated comparison with some single-system method will be only nominal, because in minimizing at all we shall generally have implicitly compared with the use of a single complete system of the functions. Single complete systems, such as those based on

$$\exp(-\alpha r^2),\ \exp(-2\alpha r^2),\ \text{etc.,}$$

and the spherical harmonics, would be so simple to work with that no other choice would be made, unless the energy could be considerably lowered by doing so.

The significance of the procedure is probably shown most clearly by summarizing the basic assumptions as a conjectured theorem.

THEOREM 3. If ψ_k and E_k are the (k)th eigenfunction and eigenvalue of

$$(H - E_k)\psi_k = 0,$$

these being labelled in order of ascending E_k, if $\{\phi_r\}$ denotes a complete class of functions x, y, z, if (ϕ_r') denotes a complete system of functions occurring in $\{\phi_r\}$ and $\{\Phi_r'\}$ the complete system of detors formed from these, if $E_k'^M$ denotes the (k)th eigenvalue in the variational approximation using the first M of these detors, if Φ_r^M denotes a set of M detors made from any set of orthogonal functions out of $\{\phi_r\}$ such that these give a value $E_k^M < E_k'^M$ for the (k)th eigenvalue when used in the variational procedure, then E_k^M converge monotically to E_k and ψ_k^M, the corresponding eigenfunction, converges in the mean square sense to ψ_k.

This theorem cannot be proved rigorously, but it is justified to a degree corresponding to assumptions of the ordinary variational method. The convergence of E_k^M follows from the variational theory when we assume the completeness of the detors formed from a complete system. The convergence of ψ_1^M follows from the convergence of E_1^M just as given by Kemble (1937) for the ordinary variational procedure. The convergence of $E_k^M (k > 1)$ has not been proved. However, all practical experience has justified the assumption of the variational theorem (1), and it appears practically certain that theorem (3) will be similarly justified.

The only quantities which we require to carry out the process numerically for particular molecules are the values of the Schrödinger integrals between the detors used to approximate to the wave function. But it has been shown that, if we work with the complete class of Gaussian functions, all these can be expressed very simply in terms of tabulated functions. Since this complete class contains all Gaussian and Hermitian functions situated at all points of space, it is particularly appropriate for molecules and systems of atoms where the nuclei and concentrations of electrons occur at large distances. We can facilitate the rate of convergence by using linear combinations of functions centred round the different centres of electronic concentration. The early terms can correspond to complete systems of functions on the several centres concerned. The essential virtue of the complete Gaussian class is that it is the only complete class in which there occur complete systems of functions situated round all points and for which all the integrals involved in the variational selection method of detors can be evaluated.

It has thus been established that the only difficulty which exists in the evaluation of the energy and wave function of any molecule, or other system of atomic nuclei and electrons, when the complete Gaussian class is used with the variational selection method, is the amount of computing necessary. This computing consists only of ordinary arithmetical processes and of reading from existing function tables and does not involve any numerical integrations. Whether this method will be finally used or whether a modification or a separate method may be developed, cannot at present be foreseen, but this represents a definite step forward, since it is the first time it has been possible to state such a scheme.

4. The application of the variational selection method for non-Gaussian functions, and the application to atoms

It will have been noted that the practical application of the variational selection method to detors constructed from complete classes of functions $\{f_r\}$ other than the Gaussian class would be quite possible if the integrals

$$(f_r|f_s), \quad (f_r|V_I|f_s), \quad (f_r|K|f_s), \quad [f_rf_s|M|f_tf_u] \tag{35}$$

could be evaluated. It is, however, very desirable that the complete class of functions used contains complete systems of functions which can be placed round all the different atomic nuclei in the system. No other class satisfying these requirements is known, unless we are prepared to consider the possibility of straightforward numerical integration of the necessary integrals. This is not feasible because, even allowing for considerable simplification, a numerical integration over six dimensions with infinite ranges is completely prohibitive. Hence, unless new methods of the requisite integral evaluation are developed, the use of the Gaussian class constitutes the only method for general molecules.

If the necessary integrals could be evaluated the functions which would be generally considered to be most useful and rapidly convergent would be the class composed of the functions $x^l y^m z^n \exp(-\alpha r_A)$, together with all linear combinations of these. Reasonable accuracy would be expected with small numbers of terms in this case. This follows since, if the electrons did not interact and were only subject

to the field of one nucleus at a time, perfectly accurate solutions of this form could be written down. Even when electronic interaction is allowed for, such functions have given surprisingly good results for approximations to atomic wave functions using only very few terms. However, it is well known that the evaluation of the general integrals in such cases has proved to be a singularly intractable problem, and the use of these functions cannot be considered unless some definite progress is made in the evaluation of these integrals.

The situation for atoms is much simpler. In this case the class of all linear combinations of functions $x^l y^m z^n \exp(-\alpha r)$ situated about the single nucleus is likely to give rapidly convergent approximations and all the necessary integrals can be evaluated. A first result using this method for beryllium is reported in a subsequent paper. Actually it is convenient to write the functions in the form

$$S^{lm}(\theta, \phi) \, r^{l+p} \exp(-\alpha r),$$

where S^{lm} is a spherical harmonic. The methods of evaluation of the necessary integrals are well known and the manipulation is particularly simple. The class can be easily shown to contain complete systems of functions since a system

$$\exp(-nkr), \ (n = 1, 2, \ldots)$$

is complete with respect to the radial variation, while the spherical harmonics are complete with respect to the angular variation. By considering different values of k we have infinite numbers of complete systems in our general class. The use of such functions for approximate wave functions consisting only of single detors has been made several times, the most systematic calculations being those of Morse, Young & Haurwitz (1935). However, the systematic use as a converging method by means of increasing numbers of detors has not previously been attempted.

The method which has been most extensively used for atoms is the Hartree-Fock method. The relation of this to our present considerations can be stated by saying that numerical functions of the type $f(r) \, S^{lm}(\theta, \phi)$ are used. In the ordinary case only a single detor has been used, and there is no attempt to obtain ultimate convergence. In the modification which is called 'superposition of configurations' more detors have been used, but actually, since all the integrals have to be evaluated numerically, it does not appear to be feasible to use more than two or three such terms. However, in principle this method can be regarded as a particular case of the procedure we have called variational selection, although in practice it is very dissimilar from the use of explicit functions.

In conclusion, the author wishes to state that, in his opinion, we shall ultimately be driven to the general method of variational selection of detors from one or other complete class of functions for more accurate data on the structure of atoms and molecules. Since the method using Gaussian class of functions for molecules would be laborious although possibly necessary, it appears best to develop and systematize the common aspect, the variation selection method. This can be done by some calculations for atoms while at the same time obtaining useful results. Numerical and theoretical results along these lines will be reported in the subsequent parts of this series of papers.

5. DISCUSSION

The value of the present treatment lies not so much in the fresh mathematical analysis, which is relatively elementary, but in the fact that it provides for the first time a systematic scheme by which the wave functions of the stationary states of the electrons in the field of any arrangement of nuclei can be evaluated. In general, the necessary computation would be laborious, but there are cases where such calculations provide the only hope of obtaining data otherwise almost inaccessible, and where long calculations might be worth while. On the other hand, it may be possible to improve the scheme either by modifications of the mathematical method, or by developments purely in the numerical procedure. For atoms the use of the variational selection method for detors from exponentials instead of Gaussian functions appears as if it will provide a powerful method without further modification.

An interesting aspect of the general method is that it has a certain heuristic value. By slightly specializing the most general method one is able to give an extremely compact statement of a procedure to which quantum mechanics reduces the general problem of predicting the energy and structure of any system of atoms and molecules. 'Consider Gaussian polynomial products situated around each nucleus of the system. Take orthogonal linear combinations of these and form the detors after combining these functions with the spin functions. Calculate the energy of a linear combination of these detors with adjustable coefficients. Choose these coefficients and the original parameters of the orthogonal functions to minimize the energy. As the number of functions considered is increased this energy will converge to the ground state. Alternatively, by minimizing a higher eigenvalue of the variational equation, we can converge to the energy of an excited state. All the necessary integrals can be evaluated by simple formulae.' The only errors which are not decreased indefinitely by taking larger numbers of detors are of the nature of relativistic corrections. It is the author's opinion that it is simpler to explain this general method than to explain many of the more approximate and restricted methods.

The relation of the present analysis to approximate theories, such as molecular orbitals, localized bonds, and modifications of these, is twofold. In the first place the integrals evaluated provide for the first time a possibility of applying these methods in a quantitative *a priori* manner for a general molecule without the necessity of the prohibitive numerical integrations over six dimensions. Previously, if calculations were attempted for any system more complicated than the simplest diatomic molecule, the only practical procedure was to derive the energy in terms of unknown integrals and then estimate these by comparison with experimental energies (Coulson 1947). In the second place an examination of the numbers of integrals which would be required for these approximate non-converging methods and for the variational selection of detors when using the same set of initial functions shows that the computation would not be very much greater in the general method. Hence it appears that in *a priori* calculations it will be most worth while to use the many detor procedure.

Conclusions

The methods developed above give for the first time a quantitative method of evaluating the stationary state wave functions and energy levels of all atoms and molecules to any required degree of accuracy. Direct application to complicated cases would involve very heavy computing but may be worth while in special cases. On the other hand, it may be possible to derive shorter modifications of the method. A related method, applicable only to atoms, appears to be of great practical value.

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The diffraction of blast. II.

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The head-on encounter of a plane shock, of any strength, with a solid corner of angle $\pi - \delta$ is investigated mathematically, when δ is small, by a method similar to that of part I. The incident shock is found to be reflected from each face as a straight segment, the two segments being joined by a shorter curved portion. Behind each straight segment is a region of uniform flow, the two regions being joined by one of non-uniform flow, bounded by arcs of a circle with centre at the corner, which expands at the local speed of sound, and by the shock, which is curved only where intersected by the said circle. The pressure is approximately equal in the two regions of uniform flow, but is less in the region of non-uniform flow between them; and it is found that if the deficiency of pressure therein, divided by the angle δ and by the excess of pressure behind the reflected shock over that of the atmosphere, be plotted at points along the solid surface, after the incident shock has travelled a given perpendicular distance beyond the corner, then the curve is independent of δ and of the precise angle of incidence of the shock, and changes remarkably little in the whole range of incident shock strengths from 0 to ∞ (see figures 5 to 8). It is suggested that some of the above qualitative conclusions may be true even if δ is not small.

The case $\delta < 0$, when the corner is concave to the atmosphere, is also considered. Shock patterns are found in cases when the incident shock has already been reflected from one, or both, walls before reaching the corner (figures 9 to 11).

1. Introduction

Let a plane shock, travelling horizontally into still air, encounter the corner of a building, which is assumed to extend indefinitely upwards and downwards for the purposes of the following analysis. Let the two faces of the building make angles δ_1 and δ_2 with the shock, so that the angle of the corner is $\pi - (\delta_1 + \delta_2) = \pi - \delta$. Choose