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Mathematical Problems in the Complete Quantum Predictions of Chemical Phenomena

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1. INTRODUCTION

At present, there is only one main method which provides practical procedures for the accurate calculation of many-electron wave functions and energies. It is often referred to as the method of configurational interaction or, as we call it in this paper, the polydetor method. In using this term, we imply a general expansion of the wave function as a linear combination of Slater determinants constructed from orthonormal single electron functions, the coefficients in the expansion being determined by the Ritz variation method. Very few wave functions of this general type have been calculated, but the stage has now been reached where all the essential procedures of calculation have been programed for high-speed electronic computing machines in a fully automatic way, and many more results are to be expected.

The development of the theory given here depends on two explicit assumptions: first, the validity of Schrödinger's many-particle equation and the antisymmetry condition and, second, the sufficiency of the Born-Oppenheimer approximation in which nuclear and electronic motions are separated. The solutions are determined completely by these assumptions which are generally accepted as the basic laws for atomic and molecular structure.

It is convenient to regard the calculation of a wave function as consisting of eight distinct stages. The solutions of several of these stages have involved considerable mathematical difficulty, but each stage presents a definite problem for which the accuracy of the solution can be specified and the significance of which can be understood quite independently of the detailed method of solution. It appears certain that this multiplicity of stages and these difficulties have obscured the essentially systematic nature of the whole problem and have given the impression that there may be ambiguities where, in fact, there are none. The aim of this account is to discuss the mathematical nature of these various stages, pointing out the difficulties, and indicating techniques of solution known at present. Such an account should be useful in enabling those not working directly in this field to understand the complexities of the problem. However, more important, the scheme as given should simplify considerably future accounts of the details of solution of the different problems by enabling their relation to the whole problem to be shown.

Since this account was commenced, fully automatic solutions have been obtained for the stages not previously solved. This has made it possible to discuss with certainty the determinate nature of the whole calculation and of each stage in it. It is important to realize that the only element of choice involved in the calculation is at the stage in which the single electron functions are selected. Thereafter, the calculation is as determinate in principle as if the results for all possible selections were tabulated. The automatic solutions emphasize this beyond all doubt.

Before examining further details, let us consider pos-

TABLE I. Unit operations in polydetor calculations (complexities relative to a $2n\times 2n$ eigenvector problem).

Operation	Computation	Program
A. Basic expansion functions ($\eta = xe^{-gr}$)	...	...
B. Single-electron integrals G, V, K	5	10
C. Electrostatic interaction integrals M	100	50
D. Choice of orthonormal functions and codetors	10	10
E. Assembly of G, V, K, and M matrices	3 to 15	20
F. Orthonormal transformation	10	2
G. Projective reduction	10	50
H. Eigenvector problem	8	2
I. Primary properties	5	5
J. Derivative properties (m arrangements)	$m\Sigma$ (A to I)	2
K. Primary induced properties	10	10
L. Interaction between q systems	$q^4\Sigma$ (A to H)	2

sible developments which could enable completely theoretical predictions to rival experimental measurements in several areas of chemical theory and, in certain cases, surpass them. Such a scheme can be represented as follows:

Limited polydetor variation calculation
+linear corrections for single electron functions
+linear corrections for "hypercorrelation."

To explain this scheme, it seems likely that the main framework of a fundamental quantitative calculation will consist of a polydetor variational calculation, the number and nature of the detors used being limited according to some theoretical criterion. In this calculation, it is hoped that the deviations of the initial single-electron functions from the "best" functions are sufficiently small so that corrections can be calculated according to some linear correction theory of a type completely different from the basic calculation. The limited variational calculation almost certainly would include a considerable amount of electronic correlation. The term "hypercorrelation" refers to correlation excluded at this stage, and it seems likely that a linear theory, having some similarities to perturbation theory, may be developed to calculate this hypercorrelation directly. Such a scheme may avoid the necessity of using the very large numbers of functions required in a full polydetor calculation to obtain sufficient accuracy but, in any case, the polydetor calculation remains as the basic calculation, and it is this that we now consider.

In Table I, brief headings are given for the division of a fundamental polydetor calculation into eight separate stages called $A, B, \ldots, H$. This is followed by four further stages, I, J, K, and L, which are considered to cover the predictions of all properties of arrangements of a finite number of atoms. The primary properties (I), which can be derived from the density kernel, are exemplified by the electronic density and the dipole moment. By "derivative" properties J, we mean those properties which can be calculated by examining the variation of a property of the system with different configurations of atomic nuclei. The simplest example is the calculation of force constants, but the most interesting is the calculation of potential energy barriers which control the rates of chemical reactions. It is shown later that induced properties K, such as polarizability and refractive index, can be fitted into the scheme. In L, we have written for completeness the interaction between two or more systems which, for the purposes of the present scheme, would be regarded as a single composite system.

The most important point of the table is that we consider all properties of molecules, atoms, and radicals to fall within a unified scheme and that the greatest part of any of the calculations is the basic polydetor calculation given by stages A to H.

In order to give most rapidly a sense of proportion about these problems, two columns of numbers have been included in the table. These are somewhat speculative and contain a considerable amount of subjective judgement; they are not to be regarded as numerically precise and they have been included to convey a useful idea of orders of magnitude. The first column measures the amount of computation necessary on an automatic computing machine. In order to make this independent of the particular machine, the figures are given in terms of the time taken to diagonalize a $2n\times 2n$ matrix, where n is the number of single-electron functions being used. These figures are based on actual machine programs with which we are familiar. Since these programs were constructed at very different stages of development, both of the general method and of automatic computers, the figures given have been modified to express our opinion in terms of current computer characteristics and the most recent developments in the mechanization of the complete calculation.

The figures in the second column, necessarily more subjective, are intended to provide some measure of the mathematical complexity of the particular stage and of the effort required to construct an automatic program for the stage, the figures again being relative to the diagonalization of a $2n\times 2n$ matrix.

The entry $m\Sigma(A$ to $I)$ opposite J is meant to indicate that derivative properties are just those for which m repetitions of the preceding stages A to I would be required, and hence the computation time is effectively multiplied by m. Further, the entry $q^4\Sigma(A$ to $H)$ is meant to show that, at present, for a composite system q times as large as a system treated before, the amount of computation increases as q^4. This appears as a severe limitation, but it need not be regarded as being in any sense permanent. In a following paper,[1] techniques where the increase is only linear in q will be discussed.

The sequence of mathematical stages in a polydetor calculation is examined systematically in Sec. 3. Of these stages, we single out for special discussion (Sec. 4)

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[1] S. F. Boys, Revs. Modern Phys. **32**, 296 (1960), this issue.

the projective reduction calculations by means of which the variational many-dimensional integrals are reduced to linear combinations of one- and two-electron integrals. This stage has been treated in particular problems in a manner dependent on physical considerations, but, in a general calculation, the mathematical difficulties become severe. For this reason, it has been considered worthwhile devoting a whole section (Sec. 2) to showing how projective reduction analysis occurs naturally in the variational solution of a simpler partial differential equation in many variables and how, in this simpler case, the projective reductions could be effected. It is shown that the calculation of the projective reduction coefficients could be carried out by a finite number of elementary operations. In practice, in quantum mechanical calculations, we use certain powerful analytical methods to obtain these coefficients; for example, in the case of atoms the most sophisticated use of vector coupling theory is made. It is most important to realize, however, that whatever detailed method is employed, essentially the same answer would be obtained. This exemplifies the fact that after stage *A*, the choice of the initial expansion functions, all stages of the calculation are fully determinate, no further physical assumptions being required and no ambiguities being present. This determinate nature has been emphasized recently by performing the whole of a polydetor calculation by automatic programs constructed for the EDSAC II in Cambridge, the starting point being simply a piece of tape with a coded form of the initial expansion functions punched on it.

We now proceed with a discussion of each of the stages listed in Table I, particular attention being devoted to projective reduction processes.

In order to appreciate the significance of the scheme as a whole, it is probably helpful to think in terms of particular problems which have been examined by the method and which show already that the possible applications are much wider than the investigation of stable molecules only. An exploration of the properties of the unknown CH_2 radical by Foster and Boys[2] can be taken as one example. For a reaction rate, one is limited to the simple case of the H_3 reaction examined by Shavitt and Boys,[3] although more complicated systems are being investigated at present.

2. ILLUSTRATION OF THE ESSENTIAL TECHNIQUE OF SOLUTION OF MANY-DIMENSIONAL WAVE EQUATIONS AND OCCURRENCE OF PROJECTIVE REDUCTION ANALYSIS

Converging quantum calculations for the properties of many-electron systems depend on the use of many-dimensional functions. For example, thirty space dimensions are required for the water molecule. An understanding of these calculations involves a familiarity with the construction, manipulation, and subsequent use of such functions. However, there is no necessity to attempt to visualize these functions physically since the many-dimensional character can be expressed solely in terms of coefficients and codes which specify, in a convenient form, the three-dimensional functions from which the many-dimensional functions are constructed.

In calculating the wave function by the variational polydetor method, only integrals of these many-dimensional functions are involved which factor into integrals of lower dimension. The wave function can be regarded solely as a mathematical intermediary from which numerical values of observable properties of the system can be calculated. In such calculations, integrals of the many-dimensional wave function are involved and these can be factorized in essentially the same way as those occurring in the calculation of the wave function itself.

Extremely complicated analysis does occur in quantum calculations (particularly for atoms and nuclei), but, from the logical point of view, this is not absolutely essential to the calculation. The value of this analysis is principally to reduce the amount of labor and the amount of data to be recorded at intermediate stages in the calculation. The same answer would be obtained by using simpler methods but in a much longer time. If this point can be realized, it may be very helpful in assessing the significance of different stages of reported calculations.

An understanding of this many-dimensional character is so important that this section is devoted to a mathematical treatment of a simpler problem which, however, exhibits many of the difficult features of a complete quantum calculation. Many-dimensional functions are not particular to quantum mechanics, and the method of solution of the given problem here is not without value in other physical situations. We have attempted to set out what might be called the product function variational method of solving a many-dimensional partial differential equation of eigenvalue type.

The problem which we examine here is one in which we suppose the value q_A of a property is given by the integral

$$q_A=\int d\tau\Psi^*Q_A\Psi, \tag{1}$$

where Q_A is a specified operator, and Ψ is the solution of the linear partial differential equation

$$D\Psi+W\Psi=0 \tag{2}$$

under certain given linear boundary conditions. In (2), W is an unknown real number (an eigenvalue) and D is an operator dependent, say, on coordinates x_1, x_2, $\cdots x_N$. The solution Ψ is therefore, in general, an N-dimensional function $\Psi=\Psi(x_1,x_2,\cdots x_N)$. Further, in (1), Q_A is an operator supposed dependent on N dimen-

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[2] J. M. Foster and S. F. Boys, Revs. Modern Phys. **32**, 305 (1960), this issue.

[3] S. F. Boys, G. B. Cook, C. M. Reeves, and I. Shavitt, Nature **178**, 1207 (1956).

sions and the notation $\int d\tau$ is used to denote integration over the appropriate range of each of the variables $x_1, x_2, \cdots x_N$. To make the present situation more analogous to a quantum mechanical problem, we should consider values $q_A, q_B, q_C, \cdots$ to be given by operators $Q_A, Q_B, Q_C, \cdots$ from the same function Ψ by means of equations like (1), one for each property.

Unless Eq. (2) is separable with respect to the coordinates $x_1, x_2, \cdots x_N$, there is little likelihood of obtaining an explicit solution, and there is only one generally satisfactory approach. Consider an approximation to Ψ given by

$$\Psi=\sum_r Y_r\Phi_r, \tag{3}$$

where the Φ_r are suitable N-dimensional functions satisfying the boundary conditions of the problem and the Y_r are coefficients to be determined. The Φ_r can be constructed from a set $\{\phi_i(x)\}$ of one-dimensional functions which are orthonormal and complete so that

$$\int dx\phi_i{}^*\phi_j=\delta_{ij}, \tag{4}$$

and, for any continuous function $f(x)$, a linear combination $\sum_{i=0}{}^m c_i\phi_i(x)$ can be found which approximates more and more closely to $f(x)$ in a mean-square sense as m is increased. The Φ_r are taken to be serial products of the ϕ_i as follows:

$$\begin{aligned}\Phi_1&=\phi_{11}(x_1)\phi_{21}(x_2)\phi_{31}(x_3)\cdots,\\ \Phi_r&=\phi_{1r}(x_1)\phi_{2r}(x_2)\phi_{3r}(x_3)\cdots,\end{aligned} \tag{5}$$

where ϕ_{kr} denotes the ϕ which is the kth factor of Φ_r. Each set ϕ_{kr} $(k=1, 2, \cdots N)$ is a particular permutation of N of the original ϕ_i and the Φ_r $(r=1,2\cdots)$ correspond to all such possible permutations. If the number of functions ϕ_i used is increased and all possible permutations are included in forming the Φ_r, the set of functions $\{\Phi_r\}$ so generated is complete in N dimensions in the limit, and the approximation (3) tends to Ψ in the mean-square sense. Considering, however, a finite number of terms in (3), the coefficients Y_r may be determined by the method of least squares in which the integral

$$I=\int d\tau[(D+W)\sum Y_r\Phi_r]^*[(D+W)\sum Y_s\Phi_s] \tag{6}$$

is minimized with respect to the Y_r. (This integral is always positive, and an exact solution would make it zero.) This minimization yields the set of equations

$$\sum_s Y_s\left\{\int d\tau(D\Phi_r)^*(D\Phi_s)+W\int d\tau\Phi_r{}^*D\Phi_s\right.$$
$$\left.+W\int d\tau(D\Phi_r)^*\Phi_s+W^2\int d\tau\Phi_r{}^*\Phi_s\right\}=0. \tag{7}$$

To emphasize the computational character of (7), we may write it as

$$\sum_s Y_s[(D^2)_{rs}+W(D_{rs}+D_{rs}{}^*)+W^2G_{rs}]=0, \tag{7$'$}$$

where Y_s and W are unknowns, and the other symbols are to be defined as equal to the quantities they replace in (7). These latter are integrals which can be evaluated numerically without any knowledge of the answer of the problem. If these values are inserted, then (7′) can be solved by computational procedures, which would be laborious without an electronic computer, but which could be performed by the systematic solution of sets of simultaneous equations. This is not discussed further, since when the Schrödinger Hamiltonian H replaces D there is an additional simplification which causes it only to be necessary to solve a standard eigenvector problem.

To obtain numerical values of the elements appearing in (7′), it would be necessary to evaluate the many-dimensional integrals in (7). Before discussing this, we may note that the evaluation of q_A requires the evaluation of similar integrals, for, if we substitute (3) into (1), dropping the suffix A, we obtain

$$q=\sum_{r,s} Y_r{}^*Y_s\int d\tau\Phi_r{}^*Q\Phi_s=\sum_{r,s} Y_r{}^*Y_sQ_{rs},\ \text{say.} \tag{8}$$

The evaluation of such a double sum is trivial when once numerical values of the many-dimensional integrals have been found. To take a particular instance and to keep the problem close to the quantum problem, let us assume that an operator Q has the form

$$Q=\sum_{\alpha,\beta} U(x_\alpha,x_\beta), \tag{9}$$

where $U(x_\alpha,x_\beta)$ is an operator which depends only on the coordinates x_α and x_β. Then a typical many-dimensional integral Q_{rs} in (8) is a sum of terms of the form

$$\begin{aligned}&\int d\tau\Phi_r{}^*U(x_1,x_2)\Phi_s\\ &=\int\int dx_1dx_2\phi_{1r}{}^*(x_1)\phi_{2r}{}^*(x_2)U(x_1,x_2)\\ &\qquad\times\phi_{1s}(x_1)\phi_{2s}(x_2)\int dx_3\phi_{3r}{}^*(x_3)\phi_{3s}(x_3)\cdots\\ &=C\int\int dx_1dx_2\phi_{1r}{}^*(x_1)\phi_{2r}{}^*(x_2)\\ &\qquad\times U(x_1,x_2)\phi_{1s}(x_1)\phi_{2s}(x_2).\end{aligned} \tag{10}$$

The coefficient C is either 1 or 0 since all the integrals following the double integral in (10) are either 1 or 0 by (4). All the other terms of Q_{rs} are similar so that the final result is of the form

$$Q_{rs}=\sum_{i,j,k,l} C_{ijkl}\int\int dx_1dx_2\phi_i^*(x_1)\phi_j^*(x_2) \times U(x_1,x_2)\phi_k(x_1)\phi_l(x_2). \tag{11}$$

Hence the many-dimensional integrals all collapse to linear combinations of two-dimensional integrals with coefficients C_{ijkl} equal to 1 or 0. It is the evaluation of these coefficients of which there are such a large number which is called the projective reduction calculation. Now two-dimensional integrals can always be evaluated either analytically or numerically, and hence we see that all stages in the evaluation of q in Eq. (8) can be performed.

The key point of the method is now reached. Generally the operator D is of the same general type as Q and, in such a case, a reduction similar to that leading up to Eq. (11) can be made for all the integrals appearing in (7). Thus the coefficients in (7′) only depend on integrals of a few dimensions, and after these have been evaluated by one means or another, the Y_s are obtained by solving Eqs. (7′). Assuming this solution to have been obtained, the Y_s are then used in an equation such as (8) for the determination of the properties of the system. It should be noted that, in the analysis outlined in the foregoing, it was not necessary to attempt to visualize physically a many-dimensional function.

When the many-dimensional complexities of the problem have been thus reduced, it can nearly always be shown that, because of symmetry or for some other reason, there are relations between the Y_s coefficients. Suppose, as often occurs in practice, that Y_r $(r=1,\cdots m)$ are all multiples of Y_1 so that

$$Y_r=B_{1r}Y_1 \quad (r=1,\cdots m).$$

It then follows that the approximation (3) with M terms may be written

$$\sum_{r=1}^{M} Y_r\Phi_r=\sum_{r=1}^{m} Y_1B_{1r}\Phi_r+\sum_{r=m+1}^{M} Y_r\Phi_r$$

$$=Y_1\bar{\Phi}_1+\sum_{r=m+1}^{M} Y_r\Phi_r,$$

where

$$\bar{\Phi}_1=\sum_{r=1}^{m} B_{1r}\Phi_r.$$

Thus a composite function $\bar{\Phi}_1$ can be introduced and, assuming similar combinations can be made for other terms, the approximation can be written

$$\Psi=\sum_{r=1}^{M'} Y_r\bar{\Phi}_r, \tag{12}$$

where M' may be very much less than M, i.e., a shorter expansion can be considered. If now we use (12) as our approximation function, the equations for the Y_s are just as in (7) but in terms of functions $\bar{\Phi}_r$. Consider one of the integrals which would now be required:

$$\int d\tau\bar{\Phi}_r^*D\bar{\Phi}_s=\sum_{t,u} B_{rt}^*B_{su}\int d\tau\Phi_t^*D\Phi_u. \tag{13}$$

The effect of introducing the $\bar{\Phi}$'s is, on the one hand, to reduce the size of the set of Eqs. (7) and, on the other, to increase the complexity of the integrals. In practice, this is very worthwhile since the new integrals can nearly always be evaluated by deductions from the special theory which established the relations between the Y's. The whole analysis may be very complicated but, once established, the total evaluation of the integrals involves very much less work. In quantum mechanics, the formation of new expansion functions $\bar{\Phi}$ is carried out because of the antisymmetry principle. The formation of such linear combinations, however, need not stop at one stage since, for example, in a molecule, new expansion functions which may be designated $\bar{\Phi}_r^b$ could be formed from the $\bar{\Phi}$'s to satisfy symmetry requirements.

Let us consider now the special features of the many-dimensional wave equation not exhibited by the example we have been considering. This equation can be written

$$(H-W)\Psi=0, \tag{14}$$

where the Schrödinger Hamiltonian operator H is defined in Sec. 3. First, H is a self-adjoint operator, and a variational theorem can be applied to show that an expression of the form (3) leads to the eigenvalue problem

$$\sum_s Y_s[(\Phi_r|H|\Phi_s)-W(\Phi_r|\Phi_s)]=0 \tag{15}$$

(where the usual quantum mechanical bracket notation has been employed), rather than the set of Eqs. (7). Second, associated with each electron, there is a set of four variables (x, y, z, v), where v denotes the discrete spin coordinate taking the values $\pm\frac{1}{2}$ only. The Φ's are now constructed as serial products of single-electron functions $\phi_i(x,y,z,v)$ rather than the one-dimensional functions $\phi_i(x)$. Third, owing to the antisymmetry postulate, it can be shown that the Φ_r occur in particular linear combinations of the type indicated in the previous paragraph. Such linear combinations are called Slater determinants and, when the single-electron ϕ's from which they are constructed are orthonormal, it is convenient to call them "detors." There are frequently high degrees of symmetry in the system, and linear combinations of these detors, called "codetors," are formed and used as expansion functions.

The great theoretical complexity of many-electron wave function calculations is bound up with the determination of the C_{ijkl} coefficients for the integrals $(\Phi_r|H|\Phi_s)$ where Φ_r and Φ_s are codetors. In principle, these could all be calculated by expansion in terms of more primitive functions but, for atoms, very powerful theory is available. In the future, it appears as if the projective reduction formulas will be worked out automatically on high-speed machines by a procedure which is likely to be intermediate in complexity between the most refined analysis used by hand and the direct but very lengthy method of using the simplest expansion functions.

It is interesting to note that the C_{ijkl} coefficients do not depend on the numerical values of parameters contained in the functions ϕ_i. For example, these coefficients would not depend on the value of g in an orbital specified as e^{-gr}. This property may enable a considerable economy to be effected in practice. For example, the same coefficients could be used in calculations for different internuclear distances in a radical such as BH and also for isoelectronic systems such as CH^+ or BeH^-.

The preceding account is an attempt to show the essential characteristics of many-dimensional problems and how the solution of these involves basically a large number of comparatively simple algebraic steps. The way in which mathematical analysis can reduce the number of steps by a large factor at the expense of complexity in formulation and manipulation has been indicated. The additional complexities of wave-mechanical problems have been pointed out. In the next two sections, the stages A to L involved in complete quantum calculations are examined in detail.

3. SEQUENCE OF MATHEMATICAL STAGES IN VARIATIONAL CODETOR CALCULATIONS

To give particulars of the calculations which are necessary for the stages listed in Table I, we consider the case where the elementary expansion functions are of the type $\eta_r\alpha$ and $\eta_r\beta$, where

$$\eta_r = x^a y^b z^c r^d e^{-gr}. \tag{16}$$

a, b, c, and d are positive integers or zero, and g is a positive number. α and β denote usual normalized spin wave functions with the values unity for $v=\frac{1}{2}$ and $v=-\frac{1}{2}$, respectively, and zero otherwise. For atoms, such a set of functions centered on one origin, the nucleus, would be used but, for molecules, functions of this general type centered on each of the nuclei and possibly on other points would be taken.

The methods to be described are limited to the circumstances, where the Born-Oppenheimer separation is sufficiently accurate so that the wave function is calculated for all electrons but with the nuclei in assigned positions. The following variational assumption is taken to be valid for the functions used. Let η_r be a complete system of three-dimensional functions such that a linear combination can be found to approximate indefinitely closely to any given continuous quadratically integrable function by choosing n sufficiently large. Let $\Phi_s = \Phi_s(x_1,y_1,z_1,v_1,\cdots,x_N,y_N,z_N,v_N)$, $(s=1, 2, \cdots)$ denote all the independent antisymmetric N-electron functions which can be constructed from serial products of the $\eta_r\alpha$ and $\eta_r\beta$. Then, it is assumed that for each electronic state, there is a solution $\{Y_s\}$, W of the eigenvalue problem

$$\textstyle\sum_s Y_s[(\Phi_r|H|\Phi_s) - W(\Phi_r|\Phi_s)] = 0, \tag{17}$$

where H is the Hamiltonian given in Sec. 3B, which converges to the electronic energy and for which

$$q = \sum_{r,s} Y_r^* Y_s(\Phi_r|Q|\Phi_s) \tag{18}$$

converges to the value of a property given by an operator Q. This assumption is equivalent to the statement that $\sum_r Y_r\Phi_r$ converges to the wave function, but it emphasizes that the latter is essentially a means of predicting observables. Rigorous proofs have so far not been obtained for this variational assumption, but it has appeared to be completely satisfactory in the instances in which it has been applied in practice.

A. Basic Expansion Functions

The first point to note about the choice of these functions η_r $(r=1, 2, \cdots n)$ is that this is, in principle, only a matter of computational economics. If these functions can be specified so that as $n\rightarrow\infty$, they form a complete system, then the same answer would be obtained irrespective of the particular functions chosen. In practice, the amount of work increases so rapidly with n that it is important to attempt to make a good choice. The usual procedures can be classified as (a) choice from trials on simpler systems, (b) choice from trials on similar systems, (c) choice by trials on the system being examined. A number of calculations have been made according to (a) by using parameter values given by Slater for the simplest type of exponential wave functions for atoms, and there have been some attempts at finding the "best" values of such parameters for molecules. Boys has used two or more exponential functions instead of a single Slater function (e.g., e^{-4r} and e^{-3r} instead of $e^{-3.7r}$ for Be), and this has been extended to molecules. While the choice in any particular problem is rather an open question, there is fortunately no doubt about the criterion which tests the quality of the choice. Once the η functions have been chosen, the whole calculation through to the final energy W is fully determinate, and the best choice is that for which W is lowest. If it were not for the rapid increase in labor as n is increased, it would probably be better to increase n than vary the parameters in the η_r; at present, some compromise between these considerations is necessary.

B. Single-Electron Integrals

It is convenient to write the Schrödinger Hamiltonian for a general molecular system as

$$H=\sum_i K_i-\sum_{i,I} Z_I V_{iI}+\sum_{i>j} M_{ij}$$
$$=-\tfrac{1}{2}\sum_i\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right)-\sum_{i,I}\frac{Z_I}{r_{iI}}+\sum_{i>j}\frac{1}{r_{ij}}, \quad (19)$$

where corresponding terms define K, V, and M. The suffix i numbers the electrons, I the nuclei, and Z_I is the atomic number of the Ith nucleus. The single-electron integrals which arise when the problem is treated as in Sec. 2 are $(\eta_r|G|\eta_s)$, $(\eta_r|V_I|\eta_s)$, and $(\eta_r|-\frac{1}{2}\nabla^2|\eta_s)$, where the first of these types of integral are the overlap integrals, the symbol G having been introduced into the bracket for future reference. The V_I integrals which involve three different nuclei require, in general, a method of numerical evaluation which is a much simplified version of the method used for the electrostatic integrals described in Sec. 3C. All the other integrals can be expressed as explicit formulas, but the organization of the evaluation of these is tedious owing to the number of different cases.

C. Electrostatic Interaction Integrals

These are conveniently denoted by

$$(\eta_i\eta_j:\eta_k\eta_l)=(\eta_i\eta_k|M|\eta_j\eta_l)$$
$$=\int\int d\mathbf{r}_1 d\mathbf{r}_2 \eta_i^*(\mathbf{r}_1)\eta_j(\mathbf{r}_1)\eta_k^*(\mathbf{r}_2)\eta_l(\mathbf{r}_2)/r_{12}. \quad (20)$$

The evaluation of these integrals constitutes one of the two most formidable problems in molecular quantum calculations. However, they constitute a definite mathematical problem, and there are various though difficult ways of obtaining these integrals to any desired accuracy. If the expansion functions η_r are formulated in terms of Gauss functions rather than exponential functions, this stage is simplified to the evaluation of explicit formulas for all types of electrostatic integral.[4]

D. Choice of Orthonormal Functions and Codetors

In principle, the calculation of a wave function could be carried out in terms of the η_r functions, but it is very advantageous to take linear combinations of these functions defined by $\phi_r=\sum_i X_i^r\eta_i$, such that the ϕ's are orthonormal, i.e., $(\phi_r|\phi_s)=\delta_{rs}$. The calculation is lengthened by stage F below, but stage G is shortened by a factor of about $1/N^3$, the net result generally being a large economy in calculation. There are an infinite number of choices of the coefficients X_i^r. One possibility is the Schmidt method and this has been used in practice. In principle, from these orthonormal functions all possible detors of the form

$$\Phi=\mathcal{A}\phi_1(\mathbf{r}_1)\mu_1(v_1)\phi_2(\mathbf{r}_2)\mu_2(v_2)\cdots\phi_N(\mathbf{r}_N)\mu_N(v_N) \quad (21)$$

are formed, where $\mathbf{r}$ has been used to denote (x, y, z) and μ denotes either the α or β spin wave function. $\mathcal{A}$ is the antisymmetry operator defined by

$$\mathcal{A}=\sum_u \sigma_u P_u,$$

where P_u is one of the $N!$ permutations of the suffixes $1,\cdots N$ and σ_u is 1 or -1 according as the permutation is even or odd.

It is nearly always possible to use linear combinations of detors to obtain a smaller eigenvector problem at the expense of mathematical complexity. This procedure depends on a group-theoretical analysis which is too extensive to be included here. The most feasible method is probably a compromise between the complexities of the most advanced theory and the heavy labor of the more direct approach.

In practice, it is found that, if the first detor or codetor is a reasonable approximation to the wave function, only a small proportion of the other possible Φ's have an appreciable effect on Ψ and W. This means that it is worthwhile making some special choice of the ϕ_r so that Φ_1 by itself is a reasonable approximation. This has been done in an intuitive way (see Boys[5]), but recently a first systematic way of making a good choice has been found and is described by Foster and Boys[2] in a subsequent paper. A dual system of orbitals, described as exclusive and oscillator, are defined in a way which suggests that only a small number of the Φ's appreciably affect the lowest energy level when this is a common type of singlet. Further investigations along these lines might be fruitful both in this and other circumstances. In the absence of other evidence, the contribution of each Φ to the lowering of the energy W should be estimated numerically. If the matrix H_{rs} is roughly diagonal, then the contribution of Φ_s is approximately

$$[(\Phi_1|H|\Phi_s)]^2/(\Phi_s|H|\Phi_s). \quad (22)$$

To conclude the discussion of this stage, it should be noted that, provided a full systematic calculation is made, these choices do not affect the final answer.

E. Assembly of the G, K, V, and M Matrices

This stage is not of fundamental mathematical significance but is often tedious and liable to error. It is concerned with sorting the G, V, K, and M integrals into the order required for the transformations at stage F. It is desirable to construct a fully automatic or semiautomatic scheme for generating these matrices. This has proved difficult on account of the considerable number of different procedures required for the various types of integral. Further, many elements of the matrix may be equal on account of symmetry and only one of these needs to be evaluated.

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[4] S. F. Boys, Proc. Roy. Soc. (London) **A200**, 542 (1950).

[5] S. F. Boys, Proc. Roy. Soc. (London) **A217**, 136 (1953).

F. Orthonormal Transformation

The following integrals which are required, since the subsequent calculation is to be performed in terms of the orthonormal ϕ's, are obtained by the transformations shown. This is an extremely tedious desk calculation but is reasonably straightforward to program for an automatic computer:

$$(\phi_r\phi_s:\phi_t\phi_u)=\sum_{i,j,k,l}(X_i{}^rX_k{}^t)^*X_j{}^sX_l{}^u(\eta_i\eta_j:\eta_k\eta_l), \qquad (23)$$

$$(\phi_r|K-\sum_I Z_IV_I|\phi_s)$$
$$=\sum_{i,j}X_i{}^{r*}X_j{}^s(\eta_i|K-\sum Z_IV_I|\eta_j). \qquad (24)$$

G. Projective Reduction Analysis

The object of the analysis is to find coefficients, designated B^{ij} and C^{ijkl} in the following, such that the many-dimensional integrals $(\Phi_r|H|\Phi_s)$, where Φ_r and Φ_s are codetors, are reduced to one- and two-electron integrals, numerical values of which are available from stages B, C, and F. Thus

$$(\Phi_r|H|\Phi_s)=\sum_{i,j}B_{rs}{}^{ij}(\phi_i|K-\sum_I Z_IV_I|\phi_j)$$
$$+\sum_{i,j,k,l}C_{rs}{}^{ijkl}(\phi_i\phi_j:\phi_k\phi_l). \qquad (25)$$

The calculation of these coefficients can be performed several ways and at different levels of abstract theory. The most advanced theory normally gives the briefest calculation but is probably not worthwhile except for specialists in the field. Once the B and C coefficients are tabulated and checked, the details of the derivation are not important. A general method which suffices for any vector-coupled functions of atoms has been given by Boys,[6] and an automatic method for molecules will be reported by Boys and Reeves. The latter method is restricted in form, and further development of automatic schemes is being examined.

H. Eigenvector Problem

This is the last numerical step in the energy and wave function calculation. The former is the most important observable property, and the latter is the key intermediary to the prediction of other observable properties. The values of the integrals obtained from stage F are substituted into the projective reduction formulas from stage G to give the eigenvector problem

$$\sum_s Y_s[(\Phi_r|H|\Phi_s)-W(\Phi_r|\Phi_s)]=0, \qquad (26)$$

which is solved numerically for the values of Y_s and W. The simple interative method of solution given by Boys[7] has been found very satisfactory.

I. Prediction of Primary Properties

A number of properties such as electronic density, electric dipole moment, etc., are given by integrals of the form

$$q=(\Psi|\sum_i Q(\mathbf{r}_i)|\Psi), \qquad (24)$$

where Q is a specified single-electron operator. By using the wave function $\Psi=\sum_r Y_r\Phi_r$, we have

$$q=\sum_{r,s}Y_r{}^*Y_s(\Phi_r|\sum_i Q(\mathbf{r}_i)|\Phi_s)$$
$$=\sum_{r,s,i,j}Y_r{}^*Y_sD_{rs}{}^{ij}(\phi_i|Q(\mathbf{r})|\phi_j)$$
$$=\sum_{i,j}D^{ij}(\phi_i|Q(\mathbf{r})|\phi_j), \qquad (28)$$

where the integrals of the form $(\Phi_r|\sum_i Q(\mathbf{r}_i)|\Phi_s)$ are reduced by an analysis precisely similar to that for the single-electron operator occurring in the Hamiltonian. The D^{ij} coefficients can be calculated as shown and used to predict a number of particular properties by combination with various integrals of the type

$$(\phi_i|Q|\phi_j)=\sum_{r,s}X_i{}^{r*}X_j{}^s(\eta_r|Q|\eta_s), \qquad (29)$$

which are generally easily evaluated.

The D^{ij} are frequently called the density matrix, and particular properties of this have been demonstrated. However, the fundamental calculation is direct without any further consideration of these properties. Other properties such as radiation strengths, between two states Ψ_1 and Ψ_2 are given by

$$q=(\Psi_1|\sum_i Q(r_i)|\Psi_2).$$

The evaluation differs from the preceding only by the first set of Y_r being taken from Ψ_1 and the second set from Ψ_2.

J. Prediction of Derivative Properties

Several physical properties of molecules are given by the rate of change of a primary property with a change in the configuration of the positions of the nuclei. Thus, the rates of change of energy for small changes of positions are the force constants of a molecule and these determine the frequencies of the infrared vibrational spectra. Again, the rates of change of dipole moment give the intensities of these bands.

The present scheme provides a straightforward method of predicting such properties by repeating the evaluation of the property for a number of distortions of the nuclear configuration. In an extensive calculation, the variation of the property would be fitted by a polynomial in the displacements, and exact derivatives (symbolically $\partial q/\partial R$) or finite alterations (symbolically $\Delta q/\Delta R$) could be evaluated as desired.

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[6] S. F. Boys, Proc. Roy. Soc. (London) **A206**, 489 (1951); **207**, 181, 197 (1951).

[7] S. F. Boys, Proc. Roy. Soc. (London) **A201**, 125 (1950).

It should be noted that, in using the word molecule in this section, any configuration of atomic nuclei is implied. Thus, in the prediction of chemical reaction rates, quantities of the form $\Delta q/\Delta R$ are particularly important.

K. Prediction of Primary Induced Properties

For the sake of completeness, the formula which predicts such induced properties as polarizability, magnetic susceptibility, etc., is given. In general, the rate of increase of some property q for unit increase in λ, where λF is some field applied to the system, is given by

$$-2\mathfrak{R} \sum_{r,s,t,u,v} Y_r{}^*Y_v(\Phi_r|Q|\Phi_s)(H-WS)_{st}{}^{-1} \times(\delta_{tu}-Y_tY_u{}^*)(\Phi_u|F|\Phi_v), \quad (31)$$

where $\mathfrak{R}$T denotes the real part of T. S denotes the matrix $S_{rs}=(\Phi_r|\Phi_s)$ and $(H-WS)^{-1}$ denotes the reciprocal matrix of $(H-WS)$. The reciprocal need not be calculated explicitly since quantities

$$X_s=E_t(H-WS)_{st}{}^{-1}Z_t$$

are given by the solution of

$$\sum{}_s(H-WS)_{rs}X_s=Z_t.$$

The preceding formula follows from perturbation theory, but no calculations for general atoms or molecules have yet been made. It seems certain that predictions will be made when fully automatic methods are in operation, but until then, the chief problem concerns the number of Φ's which must be included to obtain reasonable accuracy.

L. Interactions between Systems

This item has been included to make the list cover practically all physical phenomena which do not involve nuclear changes or macroscopic numbers of atoms. It merely indicates the obvious fact that the interaction of two or more systems can be predicted by calculations for the composite system. The direct labor of computation would increase as q^4 for a composite system q times as large as a system treated before, but there are some hopes of developing theories[1] to avoid this rapid increase.

COMMENT

It was most convenient to set out the calculation for electronic wave functions of molecules, although only small changes are necessary to convert this into the scheme for atomic or nuclear wave functions.

First, however, we consider what changes in molecular calculations occur if $\exp(-gr^2)$ is used in place of $\exp(-gr)$ in the expansion functions. The difficult stage C is simplified to the evaluation of explicit formulas and the labor is reduced by a factor of about 100. However, unless a much larger number of η functions is used, the accuracy is much diminished since the Gauss function is always a bad fit to an orbital while the exponential can be a good fit.

For atoms, stage D no longer presents a difficult obstacle and formulas for interaction integrals have been given by Boys.[7] Stage G becomes very abstract in practice but a completely general method appropriate to desk calculations has been given.[6] Stage J can be omitted, since there is no configuration of nuclei to be considered. Atomic calculations as a whole are much simpler.

In the nuclear case, the first difference to note is that at present, no Hamiltonian with two-particle interactions is known accurately. A number of possible forms of this type are known and these are complicated by the presence of spin interactions. For such a tentative H, a somewhat different problem has to be formulated at stage A to allow for the elimination of the center-of-mass motion. Expansion functions in which $\exp(-gr^2)$ replaces $\exp(-gr)$ are probably much more suitable and, for these, stage D would be laborious but not difficult. Because of spin interactions, stage G would become very complicated. A number of special cases have been analyzed in the literature, but no general method has been formulated yet.

4. PROBLEMS OF PROJECTIVE REDUCTION ANALYSIS

The essential problem is the calculation of the coefficients $C_{rs}{}^{ijkl}$ in the equation

$$M_{rs}=(\Phi_r|\sum_{i>j} M_{ij}|\Phi_s)=\sum_{i,j,k,l} C_{rs}{}^{ijkl}(\phi_i\phi_j:\phi_k\phi_l), \quad (32)$$

where Φ_r and Φ_s are codetors, together with the choice of the Φ's themselves so that the matrix M_{rs} contains as many zeros as possible and the calculation of the remaining C^{ijkl} is as simple as possible. The coefficients designated B^{ij} in the typical projective reduction formula given in G in the previous section can be derived from the C^{ijkl}. An ancillary problem of importance is the tabulation of the results, which, since the C's are independent of the ϕ's, can be used for repeated numerical calculations. Quite a considerable part of the latter problem is concerned with a description of the Φ_r themselves in terms of an unambiguous code; the need for this is pressing now that automatic methods are being considered. If this tabulation were possible, one piece of data could be used not only for different calculations but probably many times within the same calculation, since there are often elements M_{rs} which may be derived from each other by an interchange of ϕ's and others which could be described as degenerate cases of a particular key case.

Quite a large number of C coefficients have been reported in the literature for atoms and nuclei, but there has not been any general examination of the principles of the derivation and tabulation of these, particularly with reference to computing machines. The general procedure for atoms[6] is of a form requiring reference to previous tables and does not appear to be directly adaptable to machines. If these problems of mathematical analysis and of description and tabulation can be solved, presumably many man-years of work would be saved.

As an illustration of a possible method for automatic computing machines (but far too primitive for desk calculations), consider the case where the codetors are expanded explicitly as detors. Let

$$\Phi_r = \sum_i V_i^r \mathfrak{D}_i \tag{33}$$

so that

$$(\Phi_r|M|\Phi_s) = \sum_{a,b} V_a^{r*} V_b^s (\mathfrak{D}_a|M|\mathfrak{D}_b). \tag{34}$$

The rules for the evaluation of an integral $(\mathfrak{D}_a|M|\mathfrak{D}_b)$ are well known and simple. If the orbitals have been ordered to achieve maximum coincidence,

$$(\mathfrak{D}_a|M|\mathfrak{D}_b) = \sum_{i>j} Q_{ij} [(\phi_i^a \phi_i^b : \phi_j^a \phi_j^b) - (\phi_i^a \phi_j^b : \phi_j^a \phi_i^b)], \tag{35}$$

where $Q_{ij}=1$ if $\phi_k^a = \phi_k^b$ ($k \neq i$ or j) and zero otherwise. Hence, all the difficult labor is in the determination of the V_i^r. Whether this can be done sufficiently simply for functions of given symmetry merits further investigation, but a great deal depends on the discovery of adequate coded descriptions of the functions.

5. RELATION OF THE HARTREE, FOCK, KOOPMANS, AND ROOTHAAN METHODS TO THE POLYDETOR METHOD

The method associated with the names of these workers[8,9] is generally known as the self-consistent field method. In the framework of the present scheme it is possible to describe this as the approximation of using a single Φ and then adjusting some or all of the implicit parameters in this function to obtain a stationary value of the energy. This method cannot converge to the true solution of Schrödinger's equation. In the case of atoms, this introduction of a small finite error leads to a problem which can be solved efficiently by one-dimensional numerical integration. In the molecular case, however, most of the computation is concerned with the evaluation of molecular integrals (stages *B* and *C*) so that the self-consistent field calculation is comparable in computational effort with a polydetor calculation using the same η_r system. The real difference is that the answer is simpler to understand and that it is possible to perform the calculation without having to use the general theory of projective reduction (stage *G*).

The determination of the best single Φ can also be very useful as an intermediate in the clearest expression of a wave function in polydetor form, but then it can be regarded simply as an interesting step in the whole general calculation.

6. OTHER METHODS

In conclusion, it is important to state what other approaches to the general problem of finding the wave functions of many-electron systems have been made. None of these is at present applicable to a general molecule but, for one- and two-electron systems, they have given results of high accuracy for less labor than a polydetor calculation would involve. The outstanding examples are the wave functions for the helium atom determined by Hylleraas[10] and for the hydrogen molecule by James and Coolidge.[11] The methods employed in these calculations differ from those discussed here in that the functions used were not separable into orbitals, the interparticle distances being involved explicitly. Similar calculations have been attempted for nuclei using a Hamiltonian with two-body forces, but no general method is at present available.

7. DISCUSSION

The calculation of general many-electron wave functions for atoms and molecules by variational determinantal expansions has here been classified as consisting of eight distinct stages. From the wave function, it has been shown that it is possible to calculate any observable property by means of one or more of four further stages to an accuracy consistent with the assumption of the Born-Oppenheimer separation and with the omission of relativistic effects. It is generally known that, in principle, all molecular properties are calculable by such processes, but it is not always realized that these may be classified and reduced to so few different types of calculation.

It is considered that the classification provides a very useful mental picture of these complicated calculations and that this is particularly apposite now that it is possible to perform all the stages completely automatically by electronic computers. These different stages can all be specified as completely determinate calculations and, in fact, it is now possible to give tentative estimates of the effort involved in the programing and performance of these. The list in Table I appears to be the first explicit statement of this subdivision, but a limited number of calculations which are in accordance with this general scheme have already been reported. The earliest clear examples are probably the calculations for the Be, B, and C atoms by Boys,[5,7,12] although the calculation for the oxygen atom by Hartree and Swirles[13]

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[8] T. Koopmans, Physica **1**, 104 (1953).

[9] C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).

[10] E. Hylleraas, Z. Physik **54**, 347 (1929); **65**, 759 (1930).

[11] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

[12] S. F. Boys, Proc. Roy. Soc. (London) **A217**, 235 (1953).

[13] D. R. Hartree, W. Hartree, and B. Swirles, Phil. Trans. **A238**, 229 (1939).

combines a two-determinant treatment with a numerical integration process. For molecules, the calculations by Kastler[14] for HF and by Meckler[15] for O_2 are early examples.

Several of the stages involve considerable mathematical complexity, but it is the projective reduction processes which always appear to have caused the most intellectual difficulty. It is important to realize that, from the logical point of view, nearly all the complexities of this stage are not essential aspects of the quantum calculation. If the calculation were performed in a direct manner without the use of powerful theorems and relations (that is, by a variational expansion of simple determinants or, in the logical limit, of products), the same answer would be obtained but with much more computation. In particular, this is true for all the vector-coupling calculations for atoms and nuclei and, in fact, it may be shorter for those not performing series of calculations not to use the most advanced theory but to keep to simpler explicit expressions. At present, it is interesting to observe that there may be a return to simpler but somewhat more laborious methods in the future when automatic programs are constructed for all these problems. If the present analysis has shown how the projective reduction calculation can be separated from the actual quantum theory, with which it is so frequently mingled in the exposition of particular nonconvergent approximations, it will have served a useful purpose.

It is intended to report various mathematical and numerical methods for the efficient performance of the stages of Table I in the near future. It is also to be hoped that other contributions to the solutions of the more difficult of these stages may be developed. It is considered that the explanation of the significance of new developments may perhaps be made most briefly and informatively by a statement of the relation to the preceding classification.

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[14] D. Kastler, J. chim. phys. **50**, 556 (1953).

[15] A. Meckler, J. Chem. Phys. **21**, 1750 (1953).