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A Generalized Self-Consistent Field Method*

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A self-consistent field method is set up, general enough to be used in case we are treating configuration interaction between any number of states each represented by a single determinantal wave function. Thus it is more general than the Hartree-Fock method, which is limited to a single determinantal wave function. We cannot use a variation method, for if a sufficiently extensive configuration interaction is carried out, an equally good final value of the energy and wave function will be obtained irrespective of the one-electron functions used. Instead, we return to the original postulate of Hartree, that each electron is assumed to move in the averaged charge distribution of all other electrons, and all nuclei. It is shown that when this condition is properly interpreted, it leads to a unique potential for the self-consistent field, all the one-electron orbitals being solutions of the same Schrödinger equation, and hence orthogonal to each other. This field is somewhat different from that of Hartree, who did not literally follow this prescription for finding the potential. For the case where we are using a single determinantal function, the present method reduces to the simplification of the Hartree-Fock method recently proposed by the writer.

THE Hartree-Fock method, and the simplification of it recently suggested by the writer,[1] rest on the assumption that we are dealing with an n electron wave function given by a single determinant, or antisymmetrized product, formed from n one-electron orbital functions of coordinate and spin. Often, however, we wish to deal with a more general case, in which the wave function is approximated by a linear combination of such determinantal wave functions. The process of combining such determinants to get a better approximation than can be secured by one alone is generally called configuration interaction. In this note we shall examine the more general self-consistent field method to be used in such cases of configuration interaction.

If we start with a complete orthogonal set of one-electron spin-orbital functions u_i, then the products $u_j(x_1)u_k(x_2)\cdots u_p(x_n)$, where the indices j, k, $\cdots$, p are to take on all combinations of values, obviously form a complete orthogonal set of n electron functions coordinates and spin, and the antisymmetrized products or determinants $(n!)^{-\frac{1}{2}}\det\{u_j(x_1)u_k(x_2)\cdots u_p(x_n)\}$ form a complete orthogonal set of antisymmetric n electron functions of coordinates and spin. Thus the exact wave function of an n electron problem can be expanded as a linear combination of such determinantal functions, so that a proper treatment of configurational interaction can give an exactly correct solution and can yield a function which takes full account of the correlation between the motion of electrons, though of course it is well known that a single determinantal function by itself does not correctly describe this correlation. The expansion of a given wave function in terms of determinantal wave functions may be slowly convergent; studies of the problem of the ground state of helium by Taylor and Parr,[2] and by Green *et al.*[3] show that in this case the convergence is rather slow. On the other hand, the recent success of Meckler[4] in studying the oxygen molecule suggests that in at least some important cases the method of configuration interaction may converge well enough to be of practical value. It is well known that the Heitler-London and valence-bond methods can be regarded as examples of configuration interaction between a number of different configurations set up in terms of antisymmetrized products of molecular orbitals. Thus any advantages lying in those methods can surely be secured by using configuration interaction, between a relatively limited number of configurations. The case of oxygen studied by Meckler included enough configurations so that his treatment is more general than a valence-bond method, and the same thing is true of various other investigations under way in this laboratory.

Let us then consider the problem of determining the one-electron orbitals u_j by a self-consistent method. It is at once obvious that no variation method, like the Hartree-Fock procedure, can be used in this case, for that depends on choosing those u_i's which allow us to make the best single determinantal function. In the present case, no matter what orbitals we use, provided they form a complete orthogonal set, we can eventually get a precisely correct answer, by carrying the configuration interaction far enough. The only criterion which we can now use to determine the u_i's is that we wish the set in terms of which the process of configuration interaction will give a series which converges most rapidly. This is not a criterion which is readily expressed analytically. Accordingly we turn in quite a different direction for the determination of the u_i's and go back to something much more like Hartree's original intuitive argument for setting up the self-consistent field. We shall demand very simply that the u_i's be solutions of a Schrödinger equation representing the motion of an

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[1] J. C. Slater, Phys. Rev. 81, 385 (1951).

[2] G. R. Taylor and R. C. Parr, Proc. Natl. Acad. Sci. 38, 154 (1952).

[3] Green, Mulder, Ufford, Slaymaker, Krawitz, and Mertz, Phys. Rev. 85, 65 (1952).

[4] A. Meckler, Quarterly Progress Reports, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, July 15, 1952, p. 62; October 15, 1952, p. 19 (unpublished).

electron in the field of all nuclei, and in the field of all other electrons, averaged over the motions of these other electrons.

This very simple requirement leads to a perfectly unique Schrödinger equation. Let the wave function of all n electrons be $U(x_1, \cdots, x_n)$. This is an antisymmetric function, which may well be expressed as a linear combination of determinantal functions of the type we have just been discussing. The quantity $U^*(x_1\cdots x_n) \times U(x_1\cdots x_n)dx_1\cdots dx_n$ measures the probability that simultaneously electron 1 be in dx_1, $\cdots$electron n in dx_n (where we are including the spins with the coordinates). The electrostatic interaction energy between electron 1 and all other electrons is $\sum(j)e^2/r_{1j}$, where j goes from 2 to n, and r_{1j} is the distance from electron 1 to the jth electron. Thus

$$dx_1\int U^*(x_1\cdots x_n)\sum(j)e^2/r_{1j}U(x_1\cdots x_n)dx_2\cdots dx_n$$

can be considered as the probability that the electron 1 be in dx_1, times the average value of the electrostatic interaction energy as averaged over all positions and spins of the electrons $2\cdots n$. Since the probability that electron 1 be in dx_1, irrespective of the positions of other electrons, is $dx_1\int U^*(x_1\cdots x_n)U(x_1\cdots x_n)dx_2\cdots dx_n$, we see that the average potential energy of interaction between electron 1 and all other electrons, when electron 1 has coordinates and spin given by x_1, is

$$V_e(x_1)=\frac{\int U^*(x_1\cdots x_n)\sum(j)e^2/r_{1j}U(x_1\cdots x_n)dx_2\cdots dx_n}{\int U^*(x_1\cdots x_n)U(x_1\cdots x_n)dx_2\cdots dx_n}. \qquad (1)$$

If we add this to $V_n(x_1)$, the potential energy of an electron of coordinate and spin x_1 in the field of the nuclei, to get $V(x_1)$, then we see that $V(x_1)$ represents the average potential energy of the electron of coordinates and spin x_1, averaged over the motions and spins of all other electrons. We assume, then, that the correct generalization of the method of the self-consistent field is to set up a one-electron Schrödinger equation moving in this potential $V(x)$.

We have already mentioned (reference 1) the simplification of the Hartree-Fock method, by which a single Schrödinger equation was introduced in place of the Hartree-Fock equations, in the case where the wave function of the many-electron problem could be written as a single determinant. If we replace our function U by a single determinant, then it is easily shown that our Schrödinger equation reduces to that given in Eq. (7) of reference 1, so that the method of reference 1 is a special case of that which is now proposed. We can give the same interpretation to the potential V_e that was done in reference 1. That is, it is the potential energy of interaction of the electron with coordinates and spin x_1, with an electronic distribution of density

$$\frac{(n-1)\int U^*(x_1\cdots x_n)U(x_1\cdots x_n)dx_3\cdots dx_n}{\int U^*(x_1\cdots x_n)U(x_1\cdots x_n)dx_2\cdots dx_n}, \qquad (2)$$

with coordinates and spin given by x_2. This electronic distribution consists of a total charge equal to $(n-1)$ electrons, and its density goes to zero when x_2 equals x_1; that is, when electrons 1 and 2 have the same spin and are at the same position of space. That is just as if the electronic distribution consisted of the whole charge of n electrons, diminished by an exchange charge whose properties are like those discussed in reference 1. In other words, the qualitative discussion given in reference 1 is more general than the assumption made there that the wave function could be represented by a single determinant or a single configuration. In particular, the simplification introduced in Sec. 5 of reference 1, replacing the exchange potential by a value calculated from a free-electron gas, is as plausible a simplification in the general case of configuration interaction as it is for the single determinantal function, and is not tied in any way to the Hartree-Fock case.

One way to appreciate the useful features of the expression (1) for the potential V_e is to ask how to calculate the electronic repulsive interaction energy of the whole system. The average values of each term e^2/r_{ij} over the wave function are the same, on account of the antisymmetry of the wave function, and since there are $n(n-1)/2$ pairs, the total interaction energy will be just $n(n-1)/2$ times the integral for one term. Now if we multiply $V_e(x_1)$, as given in Eq. (1), by the denominator $\int U^*(x_1\cdots x_n)U(x_1\cdots x_n)dx_2\cdots dx_n$, and integrate over dx_1, the result will be just the value of $(n-1)$ interaction terms like e^2/r_{ij}. Thus the total interaction energy will be $n/2$ times as great as this. But $n\int U^*Udx_2\cdots dx_n$ is just the total charge density, in units of the electronic charge. Thus we see that the total electronic interaction energy can be written as

$$\tfrac{1}{2}\int\rho(x_1)V_e(x_1)dx_1, \qquad (3)$$

where $\rho(x_1)$ is the electronic charge density at the position and with the spin given by x_1.

The expression (3) is formally just like the interaction energy of a charge distribution with itself in classical electrostatics; only in the classical case, V_e would be related to ρ by Poisson's equation, whereas here it is not. The possibility of writing the electrostatic energy in this form, in the quantum theory, has been discussed by the writer,[5] using arguments closely related to those

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[5] J. C. Slater, Revs. Modern Phys. 6, 209 (1934).

of the present note. The reader should realize clearly that, if the exact wave function of the problem is used in calculating the potential $V_e(x_1)$ of Eq. (1), and in calculating the charge density, then Eq. (3) represents an exact result, including all exchange terms. The total electrostatic energy of the system of course includes in addition to (3) the interactions between electrons and nuclei, which can be computed from the charge density $\rho(x_1)$ alone, and the interactions between pairs of nuclei.

We have now seen that there is a straightforward method in principle for setting up a self-consistent field calculation for any atomic or molecular system. We set up the potential $V_e(x)+V_n(x)$, using Eq. (1) for $V_e(x)$. We solve Schrödinger's equation for the one-electron orbitals in this potential field. By general properties of Schrödinger's equation, these orbitals form a complete orthogonal set. We form from them a complete set of antisymmetrized products of n one-electron functions, and set up and solve the secular problem involved in finding those linear combinations of antisymmetrized products which make the energy of the n electron system stationary. One of the resulting solutions represents the state of the system in which we are particularly interested. We then take the antisymmetric wave function U representing this state, formed as a sum of the antisymmetrized products, and insert it in Eq. (1) to find a new V_e. Our condition of self-consistency implies that this final V_e should be identical with the original value.

The one-electron orbitals which we have obtained in this way are what are usually called molecular orbitals. Most writers, for instance Lennard-Jones[6] and Roothaan,[7] have derived molecular orbitals from the Hartree-Fock method. On account of the involved nature of this method, their discussions are necessarily somewhat complicated. In contrast, the present method, setting up a unique potential and Schrödinger equation of the usual sort, of which the molecular orbitals are eigenfunctions, makes a discussion much simpler. For instance, the potential V_e will usually have the same symmetry as the nuclear system, so that the application of the group theory to the discussion of the symmetry properties of the molecular orbitals follows very straightforwardly. Another advantage of the present method is that it gives us an infinite set of orbitals, in a much more direct way than the Hartree-Fock method, and the configuration interaction gives us (in principle) an infinite number of solutions, representing excited configurations. Since the one-electron orbitals are not chosen to make the problem self-consistent for these excited configurations, the process will presumably not converge as rapidly for these other configurations as for the ground state (if, as usual, it is the ground state which is made self-consistent), but the calculation of these excited configurations is on as firm a theoretical basis as that of the ground state.

The procedure which we have outlined is of course an idealized one which could never be carried through in practice, since we can neither solve the one-electron Schrödinger problem exactly to get the one-electron orbitals, nor carry out exactly the problem of configuration interaction. In an actual case, then, one must compromise, and our general discussion has been more with the aim of suggesting an ideal toward which one may aim in the calculation, than with the hope that it can represent a practicable program. We should ordinarily set up approximate solutions of the self-consistent problem in the form of linear combinations of atomic orbitals. We then note the following situation. If we are using a finite and very limited set of orbitals, and are solving the configuration interaction problem between all configurations which can be set up from these orbitals, as Meckler did in the work referred to, then we can equally well set the problem up in terms of any linear combinations of the orbitals. As Meckler has pointed out, the final result will be independent of what linear combinations we use. In such a case, it is useless extra labor to find those combinations of our orbitals which best represent solutions of the self-consistent field problem. This is the special case, for a limited number of orbitals, of the general statement that if we are completely solving the problem of configuration interaction, it makes no difference what complete orthogonal set of one-electron orbitals we use.

The difficulty with Meckler's procedure, however, is that as the number of electrons and orbitals goes up, the number of interacting configurations increases enormously. In such a case we can obviously handle interaction only between a limited number of configurations, normally those of lowest diagonal energy, and with largest nondiagonal matrix components of energy connecting them with the ground state. We may expect that in such problems, if we are using all configurations arising from N orbitals, then our results will be the more accurate, the more accurately we can write the N lowest molecular orbitals of the self-consistent field problem as linear combinations of these N orbitals. Our aim in setting up linear combinations of atomic orbitals, or other methods of setting up one-electron orbitals, must then be to have a set of unperturbed one-electron functions capable of approximating the lowest N molecular orbitals as accurately as possible.

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[6] J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 1 (1949), and later papers.

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