



# **The Calculation of Molecular Orbitals**

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# **THE CALCULATION OF MOLECULAR ORBITALS**

## Foreword

At the time of his sudden death in 1976 the manuscript of this book was found among Professor Slater's effects. It is essentially complete, having been finished just a few days before. The only addition that has been made is a list of references relevant to the discussion in the text.

This work represents the last in a series of books by Professor Slater, on the quantum theory of matter, consisting of seven volumes, published from 1960 to 1975. This monumental work covers all aspects of the modern theory of atoms, molecules, and solids. The present volume could be considered an addendum to this series, in that it is directed toward an unsolved problem of the quantum theory of matter, that is, how to solve exactly the self-consistent field problem.

In the last ten years of his life Professor Slater had been concerned with the local density form of the self-consistent field. His work, together with that of many collaborators, had resulted in the  $X\alpha$  method. Most of his publications during this time were concerned with the development of this method and its application to a wide range of problems. The usefulness of this model has been remarkable, and it has greatly helped in the understanding of complicated systems, for which more sophisticated methods are not applicable because of the limitations of present-day computers. However, the equations resulting from the  $X\alpha$  model have not yet been solved exactly. The applications so far have all involved approximations such as that of the "muffin-tin" potential, perturbation theory, the use of a limited basis set, and many other numerical methods. These approximations are not so severe as to invalidate the calculated results for many of the properties of molecules and solids. However, in certain cases, they have proved to be inadequate.

It was Professor Slater's purpose, in this book, to suggest a different scheme of solution of the equations. This scheme is essentially a revival of the cellular method, invented forty years ago but presented in the light of recent developments. The method as presented here is not complete in

all details but is simply an outline of the directions in which Professor Slater thought the research should proceed. It is indeed a great loss that he will not be around to continue the work. However, it is hoped that the publication of this book will encourage others to follow along the same lines and perhaps to complete the research to the end which Professor Slater intended.

JOHN W. D. CONNOLLY

*Washington, D. C.*  
*January 1979*

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# 1 Molecular orbitals and the self-consistent field

The concept of molecular orbitals is inextricably tied up with the idea of the self-consistent field. In a molecular system consisting of  $N$  electrons and many nuclei, the latter being assumed to be at rest, each electron will really move in the electric field produced by all  $N - 1$  other electrons and by all the nuclei. If  $N$  is greater than a very small number, this forms an impossibly difficult problem for rigorous solution in quantum mechanics, as it would be impossibly difficult in classical Newtonian mechanics. One recalls the very great difficulty of even the celebrated classical three-body problem,  $N = 3$ , in celestial mechanics.

Workers in the electronic problem of space charge in a vacuum tube encountered this difficulty many years ago, and overcame it by a very obvious device: they assumed that the effect of all  $N - 1$  other electrons could be approximated by averaging the density of these other electrons over their complex motions and finding the electric field arising from this continuous averaged density. They studied the motion of the one remaining electron in the field of these  $N - 1$  averaged charges. Then they demanded that the paths of the electrons, so computed, should lead to the same charge density that was assumed in the first place as that of the space charge.

The electric field so set up, produced by the electrons in their averaged motions and by any electrodes present (in the electronics problem) or by any nuclei present (in the molecule), is what we now call a self-consistent field. The name was introduced by D. R. Hartree in 1928. He was studying the electrons in an atom, moving around its nucleus. The same concept was applied at the same time by F. Hund, R. S. Mulliken, and J. E. Lennard-Jones to the molecular problem, and it formed the basis of theories of electrons in crystals set up around the same time by W. Heisenberg, F. Bloch, L. Brillouin, A. H. Wilson, and many others. We now apply the terminology of the self-consistent field to all these problems. The individual electrons then move in a fixed external field, and their wave functions, as found from the solution of Schrödinger's equation, are called orbitals—atomic orbitals for the atomic case, molecular orbitals for molecules or crystals.

The effect of this approximation is to reduce the many-body problem from a  $3N$ -dimensional one, in the three coordinates of all  $N$  electrons, to  $N$  separate three-dimensional problems, an enormous simplification. The Schrödinger equation for one of the molecular orbitals is still a difficult one. For the atom, Hartree's problem, it is quite simple, on account of the spherical symmetry. But in the molecule or crystal we no longer have this symmetry,



except in the neighborhood of one of the nuclei. A large part of our effort in this volume must go to examining adequate ways to handle the nonspherical problem of Schrödinger's equation in the molecule, making full use of our experience in solving the spherical atomic problem. But we must also investigate the total energy of the many-electron problem, as we compute it from the atomic orbitals determined self-consistently. We shall first look into this question of the interrelationship of the three-dimensional and  $3N$ -dimensional problems, and shall find that an approximation, the so-called  $X\alpha$  approximation, can be set up to overcome the larger part of the difficulty of the  $3N$ -dimensional problem. Then we go on to apply these methods to actual molecular calculations.

We start with Hartree's ideas. He was considering an atom or ion of  $N$  electrons, surrounding a nucleus at rest, with atomic number  $Z$ . Each electron, of course, is acted on electrostatically by the nucleus and all  $N - 1$  of the other electrons. He wished to replace the very complicated field exerted by the other electrons, which depends on just where these electrons are, by a single potential arising from the average positions of the other electrons. He then solved the Schrödinger equation for wave functions of a single electron moving subject to this averaged potential. If  $u_i$  is such a wave function or atomic orbital, normalized so that the integral over all space of  $u_i^* u_i$  is unity, he assumed that  $N$  of these wave functions represented occupied states in the atom and that  $u_i^* u_i$  represented the magnitude of the charge density (in units of the electronic charge) of the  $i$ th electron. The total charge density of all electrons would then be  $-\sum(i)u_i^* u_i$ , where the summation goes over the occupied orbitals and where we have used the minus sign to indicate that the electrons have a negative charge. We find it convenient to assign occupation numbers  $n_i$  to the states, unity for an occupied state, zero for an empty one. Then the total electronic charge density is

$$\rho = -\sum(i)n_i u_i^* u_i \quad (1-1)$$

where now the summation can go over all orbitals, both occupied and empty.

Hartree next set up the potential in which the  $i$ th electron moves. We use atomic units: the rydberg as a unit of energy, (although Hartree used 2 rydbergs as a unit, ordinarily called a hartree), and a unit of distance, now called the bohr, equal to the radius of the  $1s$  orbit of hydrogen in Bohr's atomic theory. In these units the potential arising from the nucleus, at distance  $r$ , is  $2Z/r$ . The potential arising from the charge located in all volume elements  $dv_2$ , at a point 1 distant from such a volume element by a distance

$r_{12}$ , is  $\int \rho(2)(2/r_{12}) dv_2$ , where the integral extends over all space and where  $\rho(2)$  is the charge density at point 2. However, Hartree naturally assumed that a given electron could not act on itself. Hence for an electron in the  $i$ th orbital, he omitted the quantity  $u_i^* u_i$  from the charge density as given in Equation 1-1. We can describe the situation by saying that the potential acting on the  $i$ th electron at position 1 is

$$V_i(1) = V_N(1) + V_e(1) + V_{Xi}(1) \quad (1-2)$$

where

$$V_N(1) = \frac{2Z}{r_1}, \quad V_e(1) = \int \rho(2) \left( \frac{2}{r_{12}} \right) dv_2,$$

$$V_{Xi}(1) = \int u_i^*(2) u_i(2) \left( \frac{2}{r_{12}} \right) dv_2$$

Thus  $V_N$  is the nuclear potential,  $V_e$  the electronic potential arising from all electrons, and  $V_{Xi}$  the correction term arising because the electron in one orbital does not act on itself.

Hartree then assumed that the electron moving in the  $i$ th orbital had a Schrödinger equation

$$-\nabla^2 u_i(1) - V_i u_i(1) = \varepsilon_i u_i(1) \quad (1-3)$$

where  $-\nabla^2$  is the kinetic energy in our atomic units,  $-V_i$  is the potential energy of the negative electron in the potential  $V_i$  of Equation 1-2, and  $\varepsilon_i$  is the one-electron energy. For the spherical symmetry found in the atom it is easy to solve Equation 1-3, as we show in detail in Chapters 3-5. The solutions, in spherical polar coordinates, are products of spherical harmonics of the angles and a function of the radius vector  $r$ . This radial function has an ordinary differential equation which can be easily solved by numerical methods. For certain discrete (negative) energies—the eigenvalues of the problem—we find functions—the eigenfunctions—that are regular both at the nucleus and at infinity. Hartree demanded for self-consistency that these eigenfunctions, normalized, should be identical with the functions  $u_i$  met in Equation 1-1.

This would not automatically happen, and Hartree devised a method of successive approximations, or iteration, to secure functions which had this property. Namely, he took the  $u_i$ 's resulting from solving Equation 1-3 at one stage of the process and substituted them in Equation 1-1 for setting up the next stage of iteration. After a number of iterations, he found that the initial and final  $u_i$ 's were identical. He gave the name self-consistent to the resulting

field, potential, and wave functions. He found that the self-consistent charge density from Equation 1-1 gave a very good approximation to the experimentally determined charge density in the atom. Furthermore, the difference between the energy values of an occupied state and an empty state gave a good approximation to the experimentally determined excitation energies. Ordinarily in the ground state of an atom it was found that the eigenfunctions of lowest energy should be occupied, the higher ones empty, although occasional cases did not fit in with this general rule.

At the same time Hartree was doing this work on atoms, we have mentioned earlier that Hund, Mulliken, and Lennard-Jones were considering simple molecules from essentially the same point of view, although the two sets of workers were at first independent of each other. The only difference in the formulation is that the nuclear potential  $V_N = 2Z/r_1$  of Equation 1-2 had to be replaced by a sum of such terms for the potential arising from all nuclei in the molecule. The equivalent Schrödinger equation, however, was felt almost impossibly difficult to solve directly, because it was not spherically symmetrical. Thus the results of this method of investigation of molecules were used only as a qualitative procedure until after World War II.

In 1930 it occurred to several workers that it ought to be possible to set up a many-electron wave function from the atomic orbitals  $u_i$  and to apply the variation method of quantum mechanics to this wave function. It is a fundamental principle of wave mechanics that if we have an approximate wave function and compute from it the average value of the many-electron Hamiltonian  $H$  over it, varying the approximate wave function to minimize the average value, the result will represent the closest approximation to the true wave function we can attain using the set of functions considered, and the average Hamiltonian must lie higher than the ground-state energy. If we set up a product function,  $u_1(1)u_2(2) \cdots u_N(N)$ , where  $u_1 \cdots u_N$  represent the  $N$  occupied orbitals and  $(1), \dots, (N)$  represent the coordinates of the  $N$  electrons, the product of this function and its complex conjugate is a product of quantities  $u_i^*(i)u_i(i)$  for the various electrons. This product would indicate that the electrons move independently of each other, which is at the foundation of Hartree's idea of self-consistency. The many-electron Hamiltonian for an atomic or molecular system, in the atomic units we are using, is

$$-\sum(i)\nabla_i^2 - \sum(i,a)\frac{2Z_a}{r_{ia}} + \sum(\text{pairs } ij, i \neq j)\frac{2}{r_{ij}} + \sum(\text{pairs } ab, a \neq b)\frac{2Z_a Z_b}{r_{ab}} \quad (1-4)$$

Here the indices  $i$  refer to the electrons; the indices  $a$  refer to the nuclei;  $r_{ia}$  is the distance between the  $i$ th electron and the nucleus  $a$ ;  $r_{ij}$  is the distance between electrons  $i$  and  $j$ , and  $r_{ab}$  is the distance between nuclei  $a$  and  $b$ . In this case, as in all others in the text, the nuclei are assumed to be at rest.

When this Hamiltonian was allowed to operate on the product wave function  $u_1(1) \cdots u_N(N)$ , multiplied by the conjugate of the wave function, and integrated over all values of the  $3N$ -dimensional space of the  $3N$  electronic coordinates, one had an expression for the total energy of the atom or molecule. If one of the orbitals was varied and the change in energy was computed, it was found that the energy minimum came precisely when the  $u$ 's satisfied Hartree's Equation 1-3. This thus formed a theoretical basis for the procedure Hartree had arrived at by intuition.

In the meantime, it had been found that the antisymmetry of the wave function when the coordinates (and spins) of two electrons were interchanged was an expression of Pauli's exclusion principle. One had to enlarge the meaning of the orbitals  $u_i$  to include dependence on spins, so that for each electron one could have both a spin-up and a spin-down orbital, hence called a spin orbital. To secure the required antisymmetry, it was necessary to write the many-electron wave function not in the form of a product  $u_1(1) \cdots u_N(N)$  but in the form of a determinant,

$$(N!)^{-1} \begin{vmatrix} u_1(1) & u_1(2) & \cdots & u_1(N) \\ u_2(1) & u_2(2) & \cdots & u_2(N) \\ \cdots & \cdots & \cdots & \cdots \\ u_N(1) & u_N(2) & \cdots & u_N(N) \end{vmatrix} \quad (1-5)$$

where the factor  $(N!)^{-1}$  gives a normalized function, if the spin orbitals  $u_i$  are orthonormal.

In this case, one can still vary one of the spin orbitals  $u_i$  to minimize the total energy. This total energy has the form

$$\begin{aligned} \langle EHF \rangle = & -\sum(i)n_i \int u_i^* \nabla^2 u_i dv - \sum(i)n_i \int u_i^* V_N u_i dv - \frac{1}{2} \sum(i)n_i \int u_i^* V_c u_i dv \\ & - \frac{1}{2} \sum(i,j)n_i n_j \delta(m_{s_i} m_{s_j}) \int u_i^*(1) u_j^*(2) \left( \frac{2}{r_{12}} \right) u_j(1) u_i(2) dv_1 dv_2 \\ & + \sum(\text{pairs } ab, a \neq b) \frac{2Z_a Z_b}{r_{ab}} \end{aligned} \quad (1-6)$$

where  $V_N = \sum(a)2Z_a/r_{1a}$ ,  $V_e$  is given in Equation 1-2, and  $\delta(m_{s_i}m_{s_j})$  indicates that one includes only those pairs of occupied orbitals  $i, j$  for which the spin quantum numbers  $m_{s_i}$  or  $m_{s_j}$  are the same or pairs of spin orbitals with parallel spins. When one varies one of the spin orbitals to minimize the total energy, the resulting one-electron Schrödinger equation is

$$-\nabla^2 u_i - (V_N + V_e)u_i - \sum(j) \delta(m_{s_i}m_{s_j}) \left[ \int u_j^*(2) \left( \frac{2}{r_{12}} \right) u_i(2) dv_2 \right] u_j = \varepsilon_i u_i \quad (1-7)$$

The self-consistent-field method using Equations 1-6 and 1-7 is called the Hartree–Fock method. Hartree and Fock both were able to develop the method into a practical form for solving atomic problems, and the results proved to be slightly closer to experiment than those obtained by the original Hartree method. The last term of Equations 1-6 and 1-7 is obviously much more complicated than the corresponding one in Equations 1-2 and 1-3. In connection with the Hartree–Fock equations it is generally referred to as the exchange term, which is why we have used the subscript  $X$  to refer to it. Its dependence on spin has led to many applications in magnetic problems. But its existence in the Hartree–Fock equations complicated the molecular problem so much that it seemed quite out of the question to make any straightforward calculation of molecular orbitals using the Hartree–Fock method, except for the very simplest molecules (in practice, for  $H_2$ ).

However, the interpretation of the Hartree–Fock method as one for minimizing the energy of Equation 1-6, with the Hamiltonian of Equation 1-4, suggested quite a different approach to the solution of the molecular orbital problem, which has been widely developed since World War II. This was based on the so-called LCAO, (linear combination of atomic orbitals) method, which had been used in a qualitative way since the earliest days of molecular orbitals. Approximate ways of computing molecular orbitals had shown that a linear combination of atomic orbitals, located on the various nuclei taking part in a chemical bond, gave quite a good first approximation. Furthermore, it had been shown that quite good approximations to atomic orbitals could be set up by use of functions  $\exp(-ar)r^n$  times a spherical harmonic of the angles. Linear combinations of such functions on each of the atoms concerned were then substituted for the  $u_i$ 's of Equation 1-6, with coefficients to be determined so as to minimize the energy. C. C. J. Roothaan, in 1951, formulated the required equations for the coefficients, which have been widely used. A great deal of effort was put into the determination of the

best constants  $a$  to use in the various basis functions  $\exp(-ar)r^n$ . When sufficiently large basis sets are used, very close approaches to Hartree-Fock molecular orbitals can be set up in this way.

It is, however, extremely demanding in the amount of computer time and capacity required. For this reason it was only in the 1960s that really good results began to be obtained by use of this method. An important improvement in technique arose from the discovery of S. F. Boys, during the decade of the 1950s, that if the orbitals were made up out of Gaussian functions of the form  $\exp(-ar^2)r^n$  instead of the functions  $\exp(-ar)r^n$ , the necessary integrals were much simpler to compute. Most of the present work is being done with the use of the Gaussian functions. But when one multiplies the exchange term of Equation 1-6 by the complex conjugate of one of the orbitals and integrates over  $dv_1$ , as is required to get the exchange terms in the total energy, one is dealing with a product of four orbitals. Each term leads to what is called a four-center integral, since the atomic orbitals of each of the molecular orbitals can be located on four separate nuclei. The experts in the use of this method, for instance E. Clementi, were speaking of literally billions of integrals which had to be computed and combined to get the complete result. For a large molecule, only the very largest computers sufficed, and the computing time required was quite colossal. As the 1960s led into the 1970s, it became quite obvious that this method was bound to lead to eventual trouble, since one was reaching the limit of what any computer in sight could do.

In the meantime, solid-state theory had been proceeding along quite a different direction. E. Wigner and F. Seitz, in 1933, had suggested what is now called a cellular method of handling the problem of computing the molecular orbitals of a simple crystal. These orbitals have eigenvalues  $\epsilon$  which form continuous bands, for which reason this type of theory is known as energy band theory. Furthermore, Wigner and Seitz had made very valuable observations about the simplification of the exchange terms. They had used corresponding terms developed earlier by Dirac and Bloch for studying the magnetic properties of an electron gas.

Unfortunately, the quantum chemical theorists were almost completely unaware of these developments. However, the author, interested in both the molecular and the solid-state theory, realized from 1933 that the general methods introduced by Wigner and Seitz and developed during the 1930s into practical methods for calculating energy bands should be equally

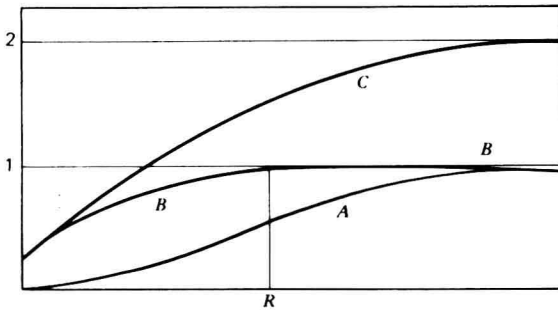
adaptable to the molecular problem. For a variety of reasons, it has taken up to the present decade to get these methods into a form adaptable for molecular calculations.

In the *MS-X $\alpha$*  method of K. H. Johnson and F. C. Smith, Jr., (*MS* refers to multiple scattering; *X $\alpha$*  to an exchange term with a parameter alpha), we have a method of calculation going back in spirit to the original calculations of Hartree, using a straightforward solution of the one-electron Schrödinger equation, rather than the LCAO schemes which lead to the great computational difficulties. Results of these newer methods, on quite complicated molecules, show accuracy which is in most cases better than the best Hartree-Fock calculations done by the LCAO method, with computer times in many cases a thousand times less than for the conventional methods. There are some features in which this *MS-X $\alpha$*  method is not completely rigorous and satisfactory. But outgrowths of this method, which are described in the following chapters, give promise of overcoming the unsatisfactory features, while retaining the computational advantages of the method.

## 2 The X alpha method

At the end of the preceding chapter it was mentioned that Wigner and Seitz had made use of earlier work by Dirac and Bloch in setting up a simplified form for the exchange term. Dirac and Bloch had been considering a perfect gas composed of  $N$  electrons. The one-electron wave function  $u_i$  of an electron in a perfect gas is of the nature of a plane wave, expressed in exponential form as  $\exp(ik \cdot r)$ , where  $k$  is a so-called wave vector,  $r$  the radius vector. One can set up the determinantal many-electron function for  $N$  electrons in the form of Equation 1-5. If  $N\uparrow$  of the electrons have spins pointing up and  $N\downarrow$  have spins pointing down, the determinant factors into two terms, one a determinant formed from the  $N\uparrow$  electrons with spin pointing up, the other formed from the electrons with spin pointing down.

If we now fix our attention on an electron with spin up, at a given position in space, we can answer from the wave function the question, what is the



**Figure 2.1** Density of charge near an electron, plotted against distance from a given electron. Curve *A* for another electron of same spin, *B* of opposite spin, *C* for both spins combined. One unit of density represents maximum allowable value for electron of one spin. Integrated deficiency of charge, for curves *A* and *C*, 1 electron unit; for *B*, zero. From Slater, *Rev. Mod. Phys.*, 6, 209 (1934).

density of other electrons of spin up in the neighborhood of the one electron at the given position? We find that at a large distance from the fixed electron, the density is just the average value we should expect to find in the perfect gas. Near the given electron, however, there is a deficiency of charge, as indicated in Figure 2.1. The density of other electrons of the same spin falls to zero at the position of the fixed electron, and the integrated deficiency of electronic charge amounts to exactly one electron. This electron deficiency is called the Fermi hole.

The meaning of the Fermi hole is obvious. There are only  $N\uparrow - 1$  other electrons of spin up, aside from the electron at the fixed position. Thus the Fermi hole represents the sphere of influence, so to speak, from which one electron is removed, so that the remaining charge density will integrate to  $N\uparrow - 1$  electrons. There is no corresponding Fermi hole for electrons of spin down, near an electron of spin up. There are  $N\downarrow$  electrons of spin down, and to the approximation in which the electrons are represented by a perfect gas, they have a uniform unperturbed density in the neighborhood of an electron of spin up. Wigner and Seitz, however, realized that an electron of spin up would repel an electron of spin down electrostatically, and that this would tend to keep them apart. They concluded that the probability of finding an electron of spin down near an electron of spin up would be given by a curve similar to that of curve *B* in Figure 2.1, whereas the probability of finding the electron of spin up is given by curve *A*. This additional effect, a result of electrostatics rather than of the antisymmetry of the wave function, is



generally called the correlation effect. Its importance is rather small compared to the effect of the Fermi hole.

Dirac and Bloch studied the effect of the Fermi hole on the total energy of the electron gas. They pictured a free electron gas as consisting of  $N$  electrons, which, of course, would carry a very large negative charge, plus a uniformly distributed positive charge, just enough to cancel the negative charge. This positive charge was supposed to take the place of the nuclei. Then an electron would feel no electrostatic effect whatever, since all electrostatic charge was neutralized, except for its interaction with the positive charge left unneutralized because an electron was removed from the Fermi hole. In other words, the electron had a potential energy as if it were at the center of a positive charge distribution, arising from a single positive charge distributed as in the Fermi hole.

We can use a simple argument to get the dimensional form of the resulting energy term. Let us suppose that the density of electrons of spin up is  $\rho \uparrow$ . If we replaced the Fermi hole by a sphere, such that within this sphere of radius  $r$  there was no electronic charge of spin up, whereas outside the sphere the density was  $\rho \uparrow$ , we can calculate the radius of the sphere. The volume of the sphere is  $4/3 \pi r^3$ , so that we have the condition that this volume times the density of charge must equal one electron. That is,

$$\frac{4}{3} \pi r^3 \rho \uparrow = -1 \quad (2-1)$$

where the minus sign comes in because we are treating the electronic density as negative. Hence we have  $r = (-3/4\pi\rho\uparrow)^{1/3}$ . But the potential energy of an electron at the center of a uniformly charged distribution of this sort can be shown by electrostatics to be  $-3/r$  in our atomic units. Thus we should find that the energy of the electron was

$$\text{energy} = -3 \left( \frac{-4\pi\rho\uparrow}{3} \right)^{1/3} \quad (2-2)$$

This argument is oversimplified, because, actually, the Fermi hole is like that shown in Figure 2.1, rather than being a spherical hole with a sharp edge. But the simple argument has shown correctly that the energy arising from the Fermi hole should be proportional to the  $\frac{1}{3}$  power of the electron density of spin up. The only correction that is needed is in the value of the constant coefficient. It is this term that takes the place of the  $V_{X_i}$  of Equation 1-2 or