

# Self-Consistent-Field $X\alpha$ Cluster Method for Polyatomic Molecules and Solids\*

J. C. Slater

*Department of Physics, University of Florida, Gainesville, Florida 32601*

and

K. H. Johnson

*Department of Metallurgy and Materials Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

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This paper describes a practical self-consistent-field (SCF) method of calculating electronic energy levels and eigenfunctions, adapted for polyatomic molecules and solids. The one-electron Schrödinger equation is set up for a so-called "muffin-tin" approximation to the true potential, spherically symmetrical within spheres surrounding the various nuclei, constant in the region between the spheres, spherically symmetrical outside a sphere surrounding the molecule. The method of solving this equation is a multiple-scattering method, equivalent to the Korringa-Kohn-Rostoker (KKR) method often used for crystals. Once the eigenfunctions and eigenvalues of this problem are determined, one assumes that the orbitals of lowest eigenvalue are occupied, up to a Fermi level. From the resulting charge densities, one can compute a total energy, using a statistical approximation for the exchange correlation. This approximation has an undetermined factor  $\alpha$  (whence the name  $X\alpha$  method). The spin orbitals and occupation numbers are varied to minimize this total energy, resulting in one-electron equations. The value of  $\alpha$  for an isolated atom is determined by requiring that the total energy, using the statistical approximation, should equal the precise Hartree-Fock energy. This leads to very accurate spin orbitals. In a molecule or crystal, one uses the  $\alpha$ 's characteristic of the various atoms within the atomic spheres, and a suitable average in the region between. The computer programs for making these self-consistent calculations, for such radicals and polyatomic molecules as  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{MnO}_4^-$ , and  $\text{SF}_6$  have been worked out and calculations made. They are more than 100 times as fast as comparable programs using the LCAO (linear-combination-of-atomic-orbitals) method, and the results appear to be in better agreement with experiment than such LCAO results. For calculating the frequencies of optical transitions, one must make a self-consistent calculation, not for the initial or final state, but for what we call the transition state, in which occupation numbers are halfway between the initial and final states. Then it can be proved that the differences of eigenvalues of the  $X\alpha$  method are more accurate than Hartree-Fock energy values, in that they take account of the modification or relaxation of the orbitals in going from the initial to the final states. These transition states, for a crystal, involve a localized perturbation at the site of the excited atom. The multiple-scattering method is adapted to the use of such perturbed crystals, as well as to isolated molecules, and to perfect crystals. It results, in such problems as x-ray absorption, in the use of localized orbitals rather than bandlike functions. The method is adapted to the calculation of magnetic problems, by use of a spin-polarized version of the method. The method can also be used for calculations of cohesive energy of crystals, and has been used successfully for several types of metals. Unlike most other SCF methods, long-range correlation is automatically included, so that the energy of a system as a function of internuclear positions automatically reduces to the proper values at infinite internuclear distances.

## I. INTRODUCTION

The method which we are presenting in this paper goes back to papers by the two authors, in 1965<sup>1</sup> and 1966,<sup>2</sup> respectively. The method has developed so far since that time, and gives indication of being so useful in the treatment of both polyatomic molecules and solids, that it seems worthwhile describing its main points in a unified way, tying together the many papers which have treated isolated aspects of it, which have been published in a number of journals.<sup>3-19</sup> Two review articles by the authors<sup>20,21</sup> are in preparation, as well as

a number of articles by the authors and others bearing on the subject.

The method is a self-consistent-field (SCF) one, making use of the so-called  $X\alpha$  statistical exchange. In the one-electron equations determining the spin orbitals, we approximate the one-electron potential by the so-called muffin-tin approximation. That is, we surround each atom by a sphere, such that ordinarily these spheres touch but do not overlap, and inside each of these spheres we replace the exact potential by a spherical average. This region of atomic spheres we denote as region I. In the region between the spheres we replace the potential by a

constant, the average of the exact potential over the interatomic region, which we denote by II. For an isolated molecule, we surround the entire molecule by a sphere, the extramolecular region outside this sphere being denoted by region III, and in this region we replace the exact potential by a spherical average. In a crystal, we replace region III by the assumption that the wave functions must satisfy a Bloch condition in going from one unit cell to another.

The necessary computational procedures for implementing the method have now been worked out in enough detail so that applications to fairly complicated molecules can be easily made. Examples are the  $\text{SO}_4^{-2}$  and  $\text{ClO}_4^-$  ions, the  $\text{MnO}_4^-$  ion, and the  $\text{SF}_6$  molecule.<sup>9, 22-25</sup> Calculations of spin orbitals and excitation energies for these molecules and radicals have given values in quite good agreement with experiment, better than provided by linear-combination-of-atomic-orbitals (LCAO) methods, and in  $\frac{1}{100}$ th or less of the computing time required for the LCAO method. Thus the self-consistent calculations for the cases mentioned above take only a few minutes on the IBM 360/65 computer for such a molecule. Applications have also been made to crystals, such as the elements Cs and V, and the compound TiC.<sup>26-28</sup> Not only do the resulting energy levels agree well with energy-band experiments, but calculations of the cohesive energy of Cs and V have been made, which show good agreement with experiment.<sup>26, 27</sup> Further applications are visualized to much more complicated molecules, including molecules of biological interest,<sup>24</sup> and to various problems of great importance in the theory of solids. These include the chemical shift of x-ray levels, the nature of excitons, and the calculation of ferromagnetic and antiferromagnetic exchange integrals of the Heisenberg type. We shall mention the methods to be used in these applications in later sections. First, however, we take up the main features of the calculational methods.

## II. MULTIPLE-SCATTERING METHOD

In carrying through a self-consistent calculation, we may imagine that we start with an assumed potential, solve the one-electron equation for that potential, finding certain spin-orbitals  $u_i$  with eigenvalues  $\epsilon_i$ , then decide by use of suitable criteria which spin orbitals will be occupied. We then take the charge density arising from these occupied spin orbitals, as well as the nuclei, determine the potential arising in this way, carry out the averaging required by the muffin-tin method, and use the resulting potential as the starting point of the next iteration. In the present section we describe very briefly the computational method used for solving the one-electron Schrödinger equation. This is the

multiple-scattering method, described in Refs. 2-11.

Inside each of the atomic spheres in region I we have a spherically symmetrical potential. Consequently we can expand the solution of Schrödinger's equation as a linear combination of products of spherical harmonics of the angles, and radial functions depending on the azimuthal quantum number  $l$  and the energy  $\epsilon$ , which are numerically determined solutions of the radial Schrödinger equation within the sphere. In region II, outside the spheres, we have a constant potential (ordinarily taken for convenience to be zero). Thus we have the wave equation, whose solutions can be taken to be products of spherical harmonics of the angle, and radial functions which are spherical Bessel or Neumann functions of the argument  $\sqrt{\epsilon}r$ , where  $\epsilon$  again is the energy, negative for the bound states which are occupied in the ground state. Thus we deal with spherical Bessel or Neumann functions of an imaginary argument. We must use the combination of these called the spherical Hankel function of the first kind, which falls off exponentially like  $e^{-\sqrt{-\epsilon}r}$ , in order to get a solution falling off properly as we go away from an atom.

Surrounding each atom of the crystal, we have a number of these spherical Hankel functions of the first kind, representing in a way the exponentially decreasing tails of the atomic orbitals associated with this atom, as we go away from the atomic sphere. The equations which have to be satisfied, to get a solution of Schrödinger's equation, are those which demand that the superposition of all these exponentially decreasing tails from all the atoms should join continuously and with continuous derivative onto the solution inside each of the atomic spheres. This leads to a secular equation in which the unknowns are the amplitudes of the various spherical Hankel functions of the first kind, surrounding each of the atoms. The equations have nonvanishing solutions only for certain values of  $\epsilon$ , the eigenvalues.

These equations have been programmed very efficiently for the digital computer, and can be solved very rapidly. The expansion of the wave function converges very rapidly: Not many of the spherical Hankel functions are required for each atom. It is this rapid convergence which is one of the features leading to the rapid program for the computer. Yet we see that the final wave function has the physical features of a LCAO, but analytic properties of the spherical Hankel functions lead to efficient methods of dealing with them. It should be stated that region III, outside the molecule, is treated without difficulty by expanding the wave function in that region as a linear combination of spherical harmonic functions of the angle and radial solutions of the spherically symmetrical problem in that region, which are regular at infinity.

There is nothing which has to be done in the way of artificially introducing hybridization of orbitals, or of deciding whether to introduce certain  $l$  values into the wave functions. The programs carry the sum over  $l$  far enough to get a required degree of convergence in the result. For a crystal rather than a molecule, the application of the Bloch conditions instead of the boundary conditions over the sphere bounding region III leads directly to the KKR (Korringa-Kohn-Rostoker) formalism. The method can be adapted to the determination of excited spin orbitals, either in the molecule or the solid, as well as to the occupied spin orbitals found in the ground state. These excited spin orbitals have positive energy, so that the spherical Hankel functions in region II have a sinusoidal rather than a decreasing exponential form, and in the case of a crystal, the Ewald method must be used in carrying out the required summations.

### III. $X\alpha$ POTENTIAL METHOD

The one-electron Schrödinger equation used for determining the spin orbitals  $u_i$  is derived by the variation principle from an approximate expression for total energy, much as suggested by Gaspar, Kohn, and Sham.<sup>29,30</sup> As a first step in setting up the energy,<sup>18,20</sup> we require occupation numbers  $n_i$  for the various spin orbitals. These numbers are zero for empty spin orbitals, unity for occupied spin orbitals, though we require in some cases the use of fractional values of  $n_i$  between zero and unity. From these occupation numbers and the spin orbitals we can set up a charge density

$$\rho(1) = \sum_i n_i u_i^*(1) u_i(1). \quad (1)$$

Each spin orbital is assumed to be associated with either the spin-up or spin-down Pauli function, so that the charge density of Eq. (1) can be separated into  $\rho_+(1)$  associated with spin up and  $\rho_-(1)$  associated with spin down.

The Hamiltonian is assumed to consist of a sum of one-electron operators  $f_i$ , consisting of the kinetic and potential energies in the field of the nuclei, a sum of two-electron operators  $g_{ij}$ , Coulomb interactions between pairs of electrons; and the internuclear repulsions, which can be treated as a constant in our case where the nuclei are assumed to be fixed, and which we shall henceforth not write down, but must assume to be added to the total energy at the end of the calculation. We shall then express the expectation value of the total energy in the form

$$\begin{aligned} \langle E \rangle = & \sum_i n_i \int u_i^*(1) f_i u_i(1) dv_1 \\ & + \frac{1}{2} \int \rho_+(1) \left[ \int \rho(2) g_{12} dv_2 + U_+(1) \right] dv_1 \\ & + \frac{1}{2} \int \rho_-(1) \left[ \int \rho(2) g_{12} dv_2 + U_-(1) \right] dv_1. \quad (2) \end{aligned}$$

The first term, the average of the one-electron

operators, does not require further comment. The remaining terms are the interactions of the electrons with the electron clouds. These interactions are different for spin-up and spin-down electrons, because of the exchange effects, so that we write these terms separately for the two spins.

Each term is one-half the integral of the charge density, multiplied by an effective potential energy acting on the electron of the appropriate spin. This potential energy for spin up is made up of the Coulomb interaction  $\int \rho(2) g_{12} dv_2$ , which includes the self-interaction of an electron with itself, and of the term  $U_+(1)$ , a negative term which removes the self-interaction and also takes account of all exchange terms. Up to this point the formulation is exact, since the exact potential energy of interaction can be expressed, in terms of the first-order and second-order density matrices, in the form of Eq. (2) with a suitably chosen  $U_+(1)$ .

At this point we introduce the statistical approximation for the term  $U_+(1)$ , which we shall call the exchange-correlation potential. If we use units in which the energy is measured in rydbergs (rather than Hartree atomic units), the assumption which we make<sup>18,20</sup> is that

$$U_{X\alpha}(1) = -9\alpha \left[ \frac{3}{4\pi} \rho_+(1) \right]^{1/3}, \quad (3)$$

where  $\alpha$  is a constant to be determined, as we shall describe later. The functional dependence of  $U$  on the density, being determined as a constant times the  $\frac{1}{3}$  power of the density, is a consequence of the simple concept of the Fermi hole. Thus, if one determines the potential energy acting on an electron of spin up as the total Coulomb interaction  $\int \rho(2) g_{12} dv_2$ , minus the potential energy of a spherical distribution of uniform charge density, holding one electron, centered on the point symbolized by (1), and having a charge density equal to  $\rho_+(1)$ , it is easily proved that we should have instead of Eq. (3) an exchange-correlation potential

$$U_+(1) = -3 \left( \frac{4}{3} \pi \rho_+(1) \right)^{1/3}, \quad (4)$$

which would correspond to  $\alpha = 0.87$ . We shall see that instead of this value we require a somewhat smaller value of  $\alpha$ , which corresponds to a Fermi hole somewhat more spread out than the uniform-charge-density case just considered.

When we write the total energy in the form of Eq. (2), supplemented by Eq. (3), we see that it is a function of the occupation numbers  $n_i$ , and a functional of the spin orbitals  $u_i$ . We vary the  $u_i$ 's in the familiar way, to minimize the total energy at fixed occupation numbers, and find that the one-electron Schrödinger equations are

$$\left[ -\nabla_1^2 + V_C(1) + V_{X\alpha}(1) \right] u_i(1) = \epsilon_i u_i(1). \quad (5)$$

Here  $-\nabla_1^2$  is the kinetic energy in the units we are using, and  $V_C(1)$  is the electrostatic potential en-

ergy at position 1 of the complete charge, electronic and nuclear, computed classically. The quantity  $V_{X\alpha}(1)$  is different for spin-up and spin-down spin orbitals, and it is given by

$$V_{X\alpha\uparrow}(1) = \frac{2}{3} U_{X\alpha\uparrow}(1) = -6\alpha[(3/4\pi)\rho_1]^{1/3}, \quad (6)$$

with a similar value for spin down. This value is equal to that suggested by the author<sup>31</sup> in 1951, provided  $\alpha=1$ , and is equal to that suggested by Gaspar<sup>29</sup> and Kohn and Sham<sup>30</sup> provided  $\alpha=\frac{2}{3}$ . As we shall see in Sec. IV, a value between these two extremes is better than either limiting value.

#### IV. CHOICE OF PARAMETER $\alpha$

The criterion which we use in a choice of the parameter  $\alpha$  is that it should give as good a description as possible of the separated atoms. This has been discussed by Slater and Wood.<sup>18</sup> One notes first that, owing to the linear dependence of  $U_{X\alpha\uparrow}(1)$  on  $\alpha$ , given in Eq. (3), the total energy  $\langle E_{X\alpha} \rangle$  of Eq. (2) in which Eq. (3) is used has a linear dependence on  $\alpha$  (if we disregard the effect of  $\alpha$  on the spin orbitals), and consequently by choice of  $\alpha$  one can make the energy  $\langle E_{X\alpha} \rangle$  vary over very wide ranges. There is no minimum principle associated with the dependence of  $\langle E_{X\alpha} \rangle$  on  $\alpha$ . One can, however, choose  $\alpha$  so that the energy  $\langle E_{X\alpha} \rangle$  agrees exactly with the Hartree-Fock energy of the same atom (if the atom is a closed-shell case in which a single determinant is appropriate), or with the average energy of all multiplet levels determined from the ground-state configuration (if it is an open-shell atom). These energies have been determined for all atoms by Mann,<sup>32</sup> so that this is a convenient criterion to use. One can see, furthermore, by the following argument, that it results in very close agreement between the spin orbitals and the Hartree-Fock spin orbitals [or what we call the hyper-Hartree-Fock<sup>17</sup> (HHF) spin orbitals for the open-shell atom].

The argument for the accuracy of the spin orbitals arising from this choice of  $\alpha$  is the following. It can be proved<sup>33,34</sup> that the virial theorem is exactly satisfied by the energy  $\langle E_{X\alpha} \rangle$  of Eqs. (2) and (3), for any value of  $\alpha$ . The virial theorem is also exactly satisfied for the Hartree-Fock (or HHF) method. Since for isolated atoms the virial theorem states that the kinetic energy is the negative of the total energy, this then means that if the criterion which we have outlined in the preceding paragraph is used, the kinetic energy as computed from Eq. (2) will be precisely equal to that found from the Hartree-Fock or HHF method from the Hartree-Fock orbitals. The kinetic energy is a very sensitive test of the accuracy of the orbitals. A change of the orbitals will result in a first-order change in the kinetic energy, though only a second-order change in the total energy, if we are making small

variations in the orbitals with respect to those found by a variation method. Thus we should expect very accurate spin orbitals from use of this criterion. Numerical examination of calculations made in special cases verifies this expectation. Essentially this same method of determining  $\alpha$  has been suggested by Berrondo and Goscinski<sup>35</sup> and by Sham.<sup>34</sup>

Calculations of  $\alpha$  made by this method for most of the lighter elements have been given by Schwarz.<sup>36</sup> They vary rather smoothly with atomic number, showing slight discontinuities as one goes from one outer shell of electrons to another. For two-electron atoms the values are about 0.77, decreasing rapidly as the atomic number increases to about 0.70 for 3d transition elements. A few individual calculations which have been made for heavier elements indicate a gradual decrease, perhaps to about two-thirds (the value of Gaspar, Kohn, and Sham).

The reasons for the variation of  $\alpha$  with atomic number have been investigated by Lindgren and Schwarz.<sup>37</sup> They have shown that a single choice of  $\alpha$  for an atom does not give equally good fits for each spin orbital, and does not handle the self-interaction and exchange parts of the exchange-correlation term equally well. The values of  $\alpha$  determined by Schwarz represent a sort of compromise between these varying values of  $\alpha$ . The high value of 0.77 for two-electron atoms results from the 1s spin orbitals, which require a considerably larger  $\alpha$  than some of the outer spin orbitals. In spite of this range of  $\alpha$ 's which would be required to handle all spin orbitals equally well, the single  $\alpha$  recommended by Schwarz leads to quite good spin orbitals even for those cases for which it is not an ideal value, and the convenience of having a single value of  $\alpha$  for each atom far outweighs the slight improvement which could be secured by using different  $\alpha$ 's for different spin orbitals.

There is quite a different method of determining  $\alpha$  which might be used. This method, originally suggested by Lindgren,<sup>38</sup> takes the spin orbitals found by the  $X\alpha$  method, using Eq. (5), and then inserts these into the Hartree-Fock expression for total energy, which amounts to finding the exact energy of the single determinantal function formed from the spin orbitals (if we are dealing with a closed-shell atom for which the single determinant is appropriate). This energy shows a minimum principle as the value of  $\alpha$  is varied, and we might use this value. Unfortunately the resulting minimum is a very shallow one as a function of  $\alpha$ , and it is very hard to find the best  $\alpha$  in this way. Kmetko<sup>39</sup> has calculated  $\alpha$ 's by this method for all the atoms, but his calculated values show a rather random type of variation as we go through a shell of electrons, in contrast to the smooth variation found by Schwarz.<sup>36</sup> If we use the spin orbitals

determined by Schwarz, and compute from them the Hartree-Fock expression for total energy, the resulting energies are very good, indicating that the spin orbitals are very close approximations to the Hartree-Fock or HFF spin orbitals. This has been examined by Schwarz and Connolly,<sup>40</sup> who conclude that the  $X\alpha$  spin orbitals are approximately as good as the so-called double- $\zeta$  spin orbitals of Clementi,<sup>41</sup> which have proved to be good enough for quite accurate calculations on molecules.

For a molecule or crystal, we find that a satisfactory method of choosing  $\alpha$  is to use inside each atomic sphere the value of  $\alpha$  found by Schwarz for the corresponding atom, and to use in interatomic region II a suitably chosen average of the values for the various atoms. No computational difficulties arise from the discontinuities of  $\alpha$  on the various spheres. As the internuclear distances change when the atoms are separated to infinity, we use spheres which change their radii in the same proportion as the internuclear distances. As the atoms go to infinite distance from each other, the atomic spheres thus become infinite, and the problem inside a single atomic sphere reduces precisely to that of an isolated atom. As we shall point out later in Sec. VIII, this is an important feature favoring the use of the energy expression of Eqs. (2) and (3). It means that if the  $X\alpha$  method is accurate for the equilibrium distance, then, since it is adjusted to be correct for the isolated atoms, we may expect that this energy expression will give an adequate approximation to the whole form of the curve giving energy as a function of internuclear distances, leading to the cohesive energy, compressibility, and so on.

This supposition has been tested by Averill<sup>26</sup> in calculations on the cesium crystal as a function of internuclear distance. The resulting cohesive energy and curve for pressure as a function of volume agree well with experiment. Similar calculations of Hattox<sup>27</sup> on vanadium are satisfactory, though not quite as good as for cesium. Further tests of the applicability of Eqs. (2) and (3) to calculations of the total energy of molecules and crystals are in progress. So far the calculations are using the muffin-tin approximation. It is likely that, particularly in cases of small coordination numbers, it will be found necessary to make corrections to the muffin-tin approximation in the computation of total energy. This can be done without undue difficulty.

Various writers<sup>42,43</sup> have suggested more complicated forms of the statistical exchange than the simple proportionality to the  $\frac{1}{3}$  power of the charge density which we are employing. Some of these involve the theory of the free-electron gas with small perturbations superposed on constant density or a constant potential. Slater and Wood<sup>18</sup> have

pointed out that the forms involving derivatives of the density, as well as the density itself, do not seem to improve the accuracy of the agreement of the quantity  $U_{X\alpha}(1)$  of Eq. (3) with the Hartree-Fock value. It is the view of the authors that the charge density within an atom, which is what we are dealing with, is so far from a small perturbation of a constant density that these supposed improvements in the theory are really not of any practical value. We feel that the use of the simple  $X\alpha$  method is as accurate as would be found by these more elaborate methods, and do not recommend their employment.

#### V. EIGENVALUES IN $X\alpha$ METHOD AND TRANSITION STATE

So far we have been considering the eigenfunctions or spin orbitals  $u_i$  of the  $X\alpha$  method and the resulting charge density. We now consider the eigenvalues  $\epsilon_{iX\alpha}$  met in Eq. (5). These are found to be appreciably different from the eigenvalues of the Hartree-Fock or HFF method, the differences increasing as we go to the inner orbitals of the atom. The explanation of this fact was given by Slater and Wood,<sup>18</sup> who also quoted other writers who had noticed the explanation. The point is that the relation between the eigenvalue and the total energy of Eq. (2) is different in the  $X\alpha$  and Hartree-Fock methods. In the Hartree-Fock method, the eigenvalue is given by

$$\epsilon_{i\text{HF}} = \langle E_{\text{HF}}(n_i = 1) \rangle - \langle E_{\text{HF}}(n_i = 0) \rangle \quad (7)$$

or the difference between the energy computed by the Hartree-Fock method when the  $i$ th spin orbital is occupied and when it is empty. The calculations are supposed to be made keeping the spin orbitals fixed, not modifying those of the ion ( $n_i = 0$ ) with respect to those of the atom ( $n_i = 1$ ). On the other hand, in the  $X\alpha$  method, the eigenvalue is

$$\epsilon_{iX\alpha} = \frac{\partial \langle E_{X\alpha} \rangle}{\partial n_i} \quad (8)$$

or a first derivative. If the energy is not a linear function of the occupation number  $n_i$ , the finite difference of Eq. (7) will not equal the derivative of Eq. (8), and this discrepancy explains why we would get different eigenvalues by the two methods, even in cases where the eigenfunctions given by the  $X\alpha$  method were identical with those of the Hartree-Fock method.

This formula for eigenvalue, Eq. (8), has several important consequences, respects in which the use of the  $X\alpha$  method is different in a qualitative as well as a quantitative way from the more familiar Hartree-Fock method. The first point is that one can arrive uniquely at the ground state of a system by moving electrons from states with higher eigenvalues  $\epsilon_{iX\alpha}$  to states with lower eigenvalues, since each such

transfer reduces the energy according to Eq. (8). This can be accomplished in the course of the iterations used in getting self-consistency. At each stage of iteration, one not only varies the spin orbitals to minimize the energy, by solving Eq. (5), but after this one adjusts the  $n_i$ 's for the next stage of iteration so that all lower spin orbitals are occupied and higher ones are empty. When self-consistency is achieved, we shall have lower states occupied up to a Fermi energy  $\epsilon_F$ , and higher states empty. As a matter of fact, it is easy to show that the condition of Eq. (8) is just what is required for the Fermi statistics to be rigorously applicable to the system. This is discussed in Ref. 20. In Ref. 17 there was a treatment of a number of cases in which the order of energy levels is different in the  $X\alpha$  and Hartree-Fock methods, and in which the  $X\alpha$  method leads to the proper assignment of occupation numbers, while the Hartree-Fock method does not.

A second consequence of Eq. (8) is found when one wishes to find the frequency of an optical transition in an atom, molecule, or crystal. The use of the Hartree-Fock eigenvalue, as in Eq. (7), is not a very accurate way to get at this frequency. The reason is that if the same spin orbitals are used for the excited or ionized states as for the ground state, the excited state will not be handled as accurately as the ground state, since the spin orbitals are determined by variation procedures of the ground state. To get a more accurate calculation, one should make a separate self-consistent calculation of the energy of the excited or ionized state, allowing the spin orbitals to be modified in the excited state with respect to the ground state, or as one sometimes states it, using spin orbitals which have relaxed. This will reduce the energy  $\langle E_{HF}(n_i=0) \rangle$ , and therefore will make the energy difference between ground and excited states slightly smaller in absolute value. With calculations of the accuracy which are now being attained, this correction is appreciable.

There is a device which can be used to get the ionization or excitation energy directly from the  $X\alpha$  method, without the necessity of computing energy differences of total energy, as in Eq. (7). This is by the use of a concept introduced in Refs. 19 and 20, called the transition state. It was shown in those references that if one solves an  $X\alpha$  self-consistent problem, not for the ground state of a system but for a transition state, in which the occupation numbers of each spin orbital are halfway between those of the ground state and of the excited state, then the excitation energy is given very accurately by the difference of  $\epsilon_{iX\alpha}$  eigenvalues between the initial and final states, computed from the SCF appropriate to this transition state. It was shown that if it is legitimate to express the en-

ergy  $\langle E_{X\alpha} \rangle$  as a power series in the occupation numbers, which proves to be sufficiently accurate if terms up to third power are used, then the contribution of the leading nonlinear term, the quadratic term, is eliminated by use of the transition state. Use of this method takes account of the effect of relaxation of orbitals, except for small third-power deviations, which are estimated in Ref. 20 in actual cases, and shown to be very small.

One can understand how the transition-state method works by considering a simple example, an ionization of an atom. Here, if we regard the occupation number of the spin orbital which is to be removed as an abscissa and the total energy  $\langle E_{X\alpha} \rangle$  as ordinate, the ionization energy will be the difference between the values of the curve at occupation numbers 1 and 0. This is the slope of the chord connecting these two points on the curve. The transition state will correspond to having this occupation number equal to  $\frac{1}{2}$ , and the eigenvalue of Eq. (8) at this point will be the slope of the tangent to the curve at this point with occupation number  $\frac{1}{2}$ . But it is a simple mathematical theorem that for a parabola the slope of the chord of a curve equals the slope of the curve itself at the midpoint. Thus in this case, except for the third-power corrections to the parabola, the value of  $\epsilon_{iX\alpha}$  measures the negative of the ionization energy of the  $i$ th electron from the atom. The resulting values, calculated for atoms by the  $X\alpha$  method, are in good agreement with the experimental x-ray energies.

In two of the calculations of molecular clusters which have been made by the  $X\alpha$  method, namely the  $\text{SF}_6$  molecule<sup>25</sup> and the  $\text{MnO}_4^-$  ion,<sup>24</sup> calculations of energy differences have been made using the transition-state method. The results are in remarkably good agreement with experiment. The results are much poorer if one uses differences of eigenvalues obtained from an  $X\alpha$  calculation for the ground state. It appears, therefore, from the evidence so far in hand, that this use of the transition state is well suited to getting accurate excitation or ionization energies of molecules as well as atoms. It should be pointed out that the programs for computing eigenvalues of Eq. (5) are much less difficult than those for finding total energy, using Eq. (2). Thus in practice it is much more convenient to use the transition-state method, even though one must carry through a separate self-consistency calculation for the transition state corresponding to each transition, than it is to make calculations of total energy and subtract.

## VI. TRANSITION STATE FOR CRYSTALS

The optical transitions of crystals corresponding to large oscillator strength are ordinarily rather localized transitions, in which orbitals concentrated on one atom or a small cluster of atoms have a

transition to another rather concentrated orbital. The transition state in such a case corresponds to a case in which there is then a localized perturbation of the charge density and potential in the neighborhood of this excited atom or cluster. The reason is that it corresponds to a crystal in which half an electron has been removed from one localized orbital and has been inserted in another orbital in the same general region of space. We must then solve the self-consistent equation, Eq. (5), for such a perturbed periodic potential. The multiple-scattering method described in Sec. II can easily be adapted to this problem, though this has not yet been done in detail. It is more conveniently adaptable to such problems than are the earlier methods of Wannier<sup>44</sup> and of Koster and Slater,<sup>45</sup> which have been adapted to such problems in the past.

There is one characteristic which this type of problem has, no matter which technique is used for solving it. For a small perturbation on a given atomic site, there is no modification of the energy-band structure of the crystal. As the perturbation increases, however, a critical point is reached at which a discrete energy level breaks out of the energy band and approximates the energy level which an electron in an isolated perturbed atom would have. As the perturbation grows greater, so that the discrete level is further and further from the band, the eigenfunction of the discrete state shrinks in linear dimensions so that it is almost entirely concentrated on the perturbed atom. At the same time, the eigenfunctions associated with the energy band avoid the perturbed atom more and more completely.

It is the discrete levels which are concerned in the optical excitation, for it is transitions between them which have large oscillator strength. To find the frequencies and oscillator strengths of these transitions, we need consider only the discrete states and their eigenfunctions. The energy differences will then be very closely the same as for the transition state of the atom which is having the transition, approximately disregarding the presence of the rest of the crystal. Calculation of the eigenfunctions by the multiple-scattering cluster method, however, will give the deviations from the behavior of the isolated atom. It is clear to those familiar with the theory of the exciton that we are here sketching the type of exciton theory which the  $X\alpha$  method leads to. For an x-ray ionization or excitation, the process on this view will be almost completely localized on the atom which is losing its x-ray electron. However, as we consider transitions involving smaller and smaller energy differences, the perturbation of potential met in the transition state will decrease, and at the same time the energy bands will become broader. Finally, for low-energy optical excitation, the perturbation

involved in the transition state will not result in the formation of a discrete level, the excited orbitals will extend over a large volume or essentially the whole crystal, and we shall be led to something very close to the conventional energy-band theory of optical absorption, in which an electron goes from one energy-band orbital to another.

#### VII. TRANSITION STATE AND HEISENBERG EXCHANGE INTEGRAL

Very interesting applications of the  $X\alpha$  method arise when one considers magnetic problems. In a magnetized molecule or crystal there are different charge densities  $\rho$ , and  $\rho_s$ , and hence different potentials, eigenfunctions, and eigenvalues for spin up and spin down. The spin-up eigenvalues will be lower than the spin down (assuming that the magnetization corresponds to spin up), so that more spin-up than spin-down spin orbitals will have energies below the Fermi energy. This allows a self-consistent situation with a net magnetization. Studies of the magnetization of iron, cobalt, and nickel<sup>46,47</sup> show that one can get a general interpretation of ferromagnetism in this way.

One asks next, however, how does one discuss the Curie temperature and the Heisenberg exchange integral which is closely connected with it? We note, in the first place, that the energy difference between spin-up and spin-down eigenvalues of the magnetic atoms has no direct connection with this problem. One can see this directly from the magnitude of the energy differences involved. The spin-up and spin-down eigenvalues differ by several tenths of a rydberg in some cases, while the magnitude of the Curie temperature, converted to energy units, can well be of the order of magnitude of  $10^{-3}$  Ry, orders of magnitude smaller. The energy separation between spin-up and spin-down eigenvalues can be shown to be connected with the energy difference between the multiplets of highest multiplicity, and those of next-highest multiplicity, in the spectrum of the magnetic ion. The contrast between this quantity and the Curie temperature is even more striking in such a ferromagnetic crystal as EuS, in which the Curie temperature is only of the order of  $10^{-4}$  Ry, while the energy separation between spin-up and spin-down eigenvalues is of the order of 0.4 Ry.

The complete study of the low-lying energy levels of a magnetic crystal is very complicated. However, we can get an idea of the order of magnitude of the Curie temperature by considering an excited state in which one atom out of the crystal has its magnetic moment reversed in orientation with respect to the rest of the crystal. Since the completely magnetized state is the ground state, this reversal of the magnetic moment of one atom will increase the energy, and one can connect this en-

ergy difference with the Heisenberg exchange integral. Let us then ask how we should use the transition-state method to find the energy of this excited state, and hence to compute the Heisenberg exchange integral. The transition state would be one whose occupation numbers are halfway between those of the ground state and of the state with one atom with reversed magnetic moment. But this means that on the atomic site where we are producing the reversed magnetization, the transition state will have no magnetization whatever. We must solve the spin-polarized self-consistent  $X\alpha$  problem for this transition state and find the energy difference between the  $\epsilon_{iX\alpha}$ 's corresponding to initial and final states.

This is a problem not very different from the exciton-state problems which we were considering in Sec. VI. In the ordinary atoms of the crystal, the spin-up orbitals correspond to a much lower potential energy than the spin-down orbitals, since the quantity  $U_{X\alpha}(1)$  is a much larger negative quantity than  $U_{X\alpha}(1)$ . In the excited atom, however, we have  $U_{X\alpha}(1)$  and  $U_{X\alpha}(1)$  the same, approximately the average of the spin-up and spin-down values found on the other atoms. Consequently we shall have a set of eigenfunctions localized on the atom, and a continuum of energy-band eigenfunctions avoiding this excited atom. We must find the energy difference between spin-up and spin-down eigenvalues of the discrete set of orbitals localized on the excited atom. This difference would vanish, except that the exponentially decreasing tails of the eigenfunctions on the excited atom overlap the neighboring atoms, which have different potentials for spin-up and spin-down. Consequently there will be an energy difference between the spin-up and spin-down eigenvalues for the transition state, depending on the overlap between the orbitals on neighboring atoms, and vanishing in the limit as the atoms get far apart.

One can show that this energy difference between the spin-up and spin-down eigenvalues of the transition state is of the same order of magnitude as the Curie temperature, translated into energy values. Consequently it is not surprising that it is small compared to the energy difference between the spin-up and spin-down bands of the crystal as a whole. For the larger part of the latter effect is an intra-atomic effect, an interaction between the spin orbitals and the large difference between spin-up and spin-down potential in the typical atoms of the crystal. On the other hand, for the Heisenberg exchange integral and the Curie temperature, we have only the interaction between neighboring atoms, since the transition state has no difference between spin-up and spin-down potentials.

Calculations of this type have not yet been carried out. However, they are entirely practical using the

multiple-scattering cluster method and the spin-polarized  $X\alpha$  procedure. It is to be hoped that this will at last make it possible to calculate these important magnetic quantities from microscopic first principles, a type of calculation that has been almost impossibly difficult with existing methods of treatment which were based on the LCAO method.

We have described the ferromagnetic case. However, a good deal of work<sup>48-58</sup> has been done on the theory of antiferromagnetic, helimagnetic, and other types of crystals. It has been found possible to correlate the features of their energy-band structure with their antiferromagnetism in such a way as to indicate that a proper treatment of the antiferromagnetic ground state, by the  $X\alpha$  method, would indicate that it had a lower total energy than a ferromagnetic structure. We could then start from this antiferromagnetic or helimagnetic ground state and find the increase of energy when the magnetic moment of a single atom was reversed. This problem would be very similar to that of the ferromagnetic case, and it would lead in the same sort of way to a study of the Heisenberg exchange integral and the Néel temperature. It should be equally simple to incorporate into the theory.

#### VIII. DISCUSSION

In the preceding sections we have indicated a few of the many types of calculations which are made possible by the SCF- $X\alpha$  cluster method which we have been discussing in this paper. The preceding paper by Johnson and Smith sketches some of the types of molecules and other substances to which the method seems readily adaptable. Many of the applications which we have taken up refer to calculations which have not yet been made. We refer to them, however, to indicate the possibilities inherent in the method. The calculations are practical, by computer programs which in most cases are already worked out. In all cases where we have been able to make calculations, or to ask what would be expected to be the result of the method, it seems to lead to reasonable results.

Before we close, we should mention problems in which it will be necessary to go beyond the limitations of any SCF method. This method is a one-electron method, and as such it cannot give a complete description of atomic multiplets. A certain amount of information is given about multiplets by the spin-polarized  $X\alpha$  method, but this does not go far. Just as with atomic theory, we shall have to start with spin orbitals determined from a self-consistent method, and then set up determinantal functions, and linear combinations of them, to describe the multiplets. This will be required when one comes to describe crystal and ligand field problems using the present procedure. One can start with the discrete spin orbitals found in the transi-

tion state by the present method. These already contain within themselves a good approximation to the crystal field splitting, which is a self-consistent one-electron phenomenon. But one must use them as basis functions for further calculations of multiplet theory.

We should also mention one point which seems to bother some readers: the question of correlation energy. There are two types of correlation effect commonly met in molecular theory. First is the short-range correlation, inside an individual atom, required to get an exact value of the energy of the individual atom. This is a quite small effect for heavy atoms, as has been pointed out by Slater,<sup>59</sup> and would be expected to change only slightly as the atom is bound into a molecule. Consequently it is not very important in studying chemical binding. Second, however, is the long-range correlation. This is the type of error met in the well-known molecular-orbital theory of the H<sub>2</sub> molecule, in which a determinantal wave function made up from two electrons, one of each spin, in the lowest 1σ<sub>g</sub> molecular orbital, goes into a state which is half composed of neutral atoms, half from positive and negative ions, at large internuclear distance. This results in a quite wrong behavior of the total energy as computed by the Hartree-Fock method, as a function of internuclear distance. Consequently the Hartree-Fock method cannot be used directly to compute cohesive energy and such problems. If one wishes to modify a Hartree-Fock calculation to take this into account, one has to make a very extensive linear combination of determinantal functions

containing excited orbitals. As Matheiss<sup>60</sup> has shown in the case of a ring of six hydrogen atoms, this linear combination becomes very complicated even for a six-atom molecule, and by the time we have many more atoms it is entirely unmanageable.

The whole object of this linear combination is to obtain a curve of total energy which not only behaves properly at the equilibrium distance, but also goes properly to a collection of neutral atoms as the atoms go far apart from each other. We meet such difficulties in every case except those of crystals composed of atoms or ions which are closed-shell configurations, such as crystals of inert gases. But we have seen in Sec. IV that the expression for total energy in the Xα method automatically goes to the energy of the separated atoms at infinite distance. Thus, with no further complication, it takes care of this long-range correlation, which has been such an impossible feature of the Hartree-Fock method using configuration interaction. As we mentioned in Sec. IV, this fact is one of the strong points of the Xα method. It should help dispel the thought which many workers have that the object of the statistical exchange-correlation correction is merely to approach the Hartree-Fock method as closely as possible. It is only with the case where a single determinant is appropriate that we should aim for this. In the general case, which includes all molecules or crystals composed of partially filled shells of electrons, the Xα method is definitely superior to the Hartree-Fock method, not merely an approximation to it.

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