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Nonintegral Occupation Numbers in Transition Atoms in Crystals*

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We consider the implications of a nonintegral occupation number of $3d$ and $4s$ electrons in a $3d$ transition element or compound, in a configuration such as $3d^{n+x}4s^{2-x}$, where x is a variable. In the energy-band problem, such fractional occupation numbers are common, but we pay particular attention to the atomic problem. We apply Hartree–Fock procedures to such a problem, using the formula for the average energy of all multiplets associated with the configuration, and vary not only the orbitals but the occupation numbers to minimize the energy. We consider both the non-spin-polarized and spin-polarized cases. This procedure, which is more general than the ordinary Hartree–Fock procedure, we shall call the hyper-Hartree–Fock method (HHF). We have carried through HHF calculations for fractional occupation numbers in the Co and Ni atoms, and have also treated these atoms by several schemes involving approximate statistical exchanges. We compare the results with the atomic spectra of these atoms. We find that the condition for minimum energy, in the HHF scheme, can be put in a form stating that one-electron energies E_i' of the $3d$ and $4s$ orbitals must be equal; these quantities E_i', which we call modified one-electron energies, are different from the ordinary one-electron energies E_i of Hartree–Fock theory, involving only one-half the self-energy correction met with in HF theory. These quantities E_i', rather than the ordinary one-electron energies E_i, are the quantities which have the properties desired for one-electron energies in energy-band theory and Fermi statistics: The change in the total energy of the system, when an infinitesimal fraction of the electrons shifts from one orbital to another, rigorously equals the net change in the quantities E_i' for the electrons which have made the shift. We show that the ordinary one-electron eigenvalues of the Kohn–Sham statistical exchange method form fairly good approximations to these HHF quantities E_i', which explains why energy-band calculations using that exchange have had considerable success in studies of transition-element crystals and compounds. Preliminary mention is made of calculations under way by one of the authors (TMW) on the antiferromagnetic crystals MnO and NiO, in which an exchange potential set up according to the ideas presented here leads to energy bands describing correctly the electrical, magnetic, and optical behavior of these crystals, including the insulating properties and the crystal-field splitting of the $3d$ orbitals into the e_g and t_{2g} components.

I. INTRODUCTION

In energy-band calculations involving $3d$ transition atoms, two sources of uncertainty make the problem particularly difficult. It is well known that, with these atoms, the energy levels are very sensitive to the precise self-consistent field used in the calculations. This field involves the approximation used for handling the exchange, which has been discussed in detail in an earlier paper.[1] But furthermore, the potential, both Coulomb and exchange, depends strongly on the assumed occupancy of the energy bands arising from the atomic $3d$ and $4s$ energy levels. Should one use an occupation $3d^n4s^2$, or $3d^{n+1}4s$, or some nonintegral value between these cases, or even outside this range? It is this second question which we shall take up in the present paper, but, as we shall see, it is closely interrelated with the other question of the exact exchange approximation to use. By studying these matters, we hope to throw additional light on the whole problem of the use of a one-electron approximation in dealing with the many-electron problem of an atom or a crystal.

Various writers have investigated the effect of different assumptions regarding the occupation numbers of $3d$ and $4s$ bands on the resulting energy bands. Most recently, Snow and Waber[2] have carried through a study of the energy band of all the $3d$ transition elements, in bcc and fcc structures, using potentials determined from the two occupation numbers $3d^n4s^2$ and $3d^{n+1}4s$, and the exchange assumption suggested by the senior author in 1951.[3] Snow and Waber give references to various earlier writers who have looked into similar problems, and for that reason we shall not give references to all that earlier work here. Their general conclusion is that the occupation $3d^{n+1}4s$ leads to energy bands in better agreement with experiment than $3d^n4s^2$, but they leave open the question as to whether a nonintegral occupation might not be even better.

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[1] J. C. Slater, T. M. Wilson, and J. H. Wood, Phys. Rev. **179**, 28 (1969). The reader's attention is also called to the interesting paper of A. Rosen and I. Lindgren, Phys. Rev. **176**, 114 (1968), which appeared too late to be considered in connection with our work.

[2] E. C. Snow and J. T. Waber, Acta Met. **17**, 623 (1969).

[3] J. C. Slater, Phys. Rev. **81**, 385 (1951); **82**, 538 (1951).

As a general rule, as the number of *3d* electrons increases and the number of *4s* decreases, the *3d* band moves rapidly upward with respect to the *4s* band, making a considerable change in the energy bands and the Fermi surface.

One must realize that it is really not a matter of hypothesis to determine the proper occupation numbers; they should be found from a self-consistent calculation. The potential depends sensitively on the occupation numbers, and one should find that particular set of occupation numbers which leads to energy bands such that, if they are filled up to the Fermi energy, they will in turn result in the assumed occupation numbers. Since in a *3d* transition metal both *3d* and *4s* bands are only partially filled, the resulting fractional numbers follow directly from a self-consistent calculation. Such calculations have been made for ferromagnetic nickel by Connolly,[4] and for nickel and several other cases by Wakoh and Yamashita.[5] Their results in general verify the occupation numbers which lead to energy bands in agreement with observed Fermi surfaces.

However, there is one very uncertain feature in these calculations. It is a fundamental postulate of the energy-band theory that electrons will occupy the lowest possible energy bands, and that if we consider the ground state, with partially filled *3d* and *4s* bands, the energies of the topmost occupied *3d* and *4s* levels must each equal the Fermi energy and hence must equal each other. But different assumptions regarding exchange lead to quite different one-electron energies, and thus to different conclusions regarding the ground state. This was brought out particularly in Ref. 1, in which it was shown that very significant differences in one-electron energies arise from different assumptions regarding exchange, which may give equally good descriptions of the electronic wave functions. This sensitivity to the exchange was found in the work of Connolly, Wakoh, and Yamashita, in Refs. 4 and 5, as well as in other papers quoted in Ref. 2.

It is not a foregone conclusion that is is possible to set up a one-electron model of a crystal such that the energy change when an electron is shifted from one band to another equals the difference in one-electron energy between the two bands. It is such questions which we shall encounter in the present paper. One finds similar problems in a simpler form in studying isolated atoms. In either the Hartree–Fock calculations for isolated atoms,[6] or the calculations of Herman and Skillman[7] using the statistical exchange assumption of Ref. 3, one finds one-electron energy levels of the atoms which show remarkable agreement with the x-ray levels. On the other hand, there is one difficulty which arises in treating the *3d* transition atoms and other transition series. It is an essential feature of the self-consistent field treatment of atoms, as of energy bands, that electrons should go into the lowest possible energy levels. By and large they do, and the success of Bohr's theory of the periodic table is based on this fact. But in the *3d* and the other transition groups, there are discrepancies which appear to be closely related to the difficulties we have mentioned in the energy-band theory.

These difficulties come from the one-electron energies of the *3d* and *4s* atomic levels. There is every reason to think, as a result of knowledge of the observed spectra of these atoms, that in their ground states they generally contain two, or in some cases one, *4s* electron per atom, with a partially filled *3d* shell. In other words, they correspond to the configurations $3d^n4s^2$ or $3d^{n+1}4s$, which we have mentioned earlier. On the other hand, from either the Hartree–Fock or the Herman-Skillman method, the *3d* one-electron energies lie well below the *4s*, so that we should expect no occupied *4s* levels until the *3d* levels are filled. Thus the electrons are not filling the levels in the correct order. As in the energy-band case, going from the $3d^n4s^2$ to the $3d^{n+1}4s$ and $3d^{n+2}$ configurations results in a considerable raising of the *3d* level with respect to the *4s*, but not enough to bring the *3d* above the *4s*. However, change of the assumption regarding exchange has an equally great effect on the energy difference between the two. We shall now go on to examine this interrelation.

II. THE HYPER-HARTREE–FOCK METHOD

Let us start our discussion by following the Hartree–Fock method as closely as possible; later we shall come to the various approximations used for studying exchange. It is a characteristic of atomic problems with partially filled shells that many multiplets arise from such a configuration, and there is no single determinantal wave function which represents the state of the atom in a satisfactory way. The Hartree–Fock method, as defined literally, arises when we can set up a wave function which is a single determinant formed from a definite set of spin orbitals. In the present more complicated situation, for these transition elements, we can use instead the formula for the weighted mean energy of all the multiplets arising from the configuration. We can vary the orbitals to minimize this averaged energy, thereby getting orbitals which should be satisfactory for representing the whole set of multiplets arising from this configuration, though they might not be quite the best possible ones for investigating the lowest multiplet of the configuration. The senior

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[4] J. W. D. Connolly, Phys. Rev. **159**, 415 (1967).

[5] J. Yamashita, M. Fukuchi, and S. Wakoh, J. Phys. Soc. Japan **18**, 999 (1963); J. Yamashita, *ibid.* **18**, 1010 (1963); S. Wakoh and J. Yamashita, *ibid.* **19**, 1342 (1964); S. Wakoh, *ibid.* **20**, 1894 (1965); S. Asano and J. Yamashita, *ibid.* **23**, 714 (1967); J. Yamashita, S. Wakoh, and S. Asano, in *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P.-O. Löwdin (Academic Press Inc., New York, 1966), p. 497.

[6] J. B. Mann, Los Alamos Scientific Reports LA-3690, 1967, LA-3691, 1968 (unpublished); available from Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Va.

[7] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

author[8] has set up formulas for this average energy of a configuration, in terms of the various atomic integrals. These formulas are based on pioneer work by Shortley, referred to in Ref. 8. One of the present authors (JBM) has programmed the resulting problem of finding orbitals to minimize the average energies, and has made calculations for all the atoms in the periodic table, using this method.[6] Since this use of the average energy of a configuration is an important method, and is not identical with the Hartree–Fock method, it seems desirable to have a name for it. We propose the name hyper-Hartree–Fock, abbreviated HHF, a name which does not seem to have been applied to any other procedure.

An essential feature of our problem is that it is mathematically useful to consider configurations with nonintegral occupation numbers, as $3d^{n+x}4s^{2-x}$, where x is a continuous variable which can run from zero to 2. For the atomic problem we ordinarily give physical meaning only to the integral values of x, but in the energy-band problem we run into continuously variable occupation numbers in transition-element energy-band problems. The formulas of Ref. 8 for average energy in terms of such parameters as x are derived for integral occupation numbers, but mathematically they are functions of a continuous variable x, being defined for fractional as well as integral values of x. In Sec. V, Eqs. (14) and (15), we shall write down these formulas, and it will be seen that the energy is a quadratic function of x, the coefficients depending on integrals over the spin-orbitals. We can then regard the HHF problem as one in which the energy is a functional of the atomic spin-orbitals and a function of the occupation parameters such as x; the energy can be minimized separately with respect to each of these quantities. When we minimize with respect to the occupation numbers, we get a theoretical minimum energy for certain fractional occupation numbers.[9] The simplest interpretation of this, for the atomic problem in which physical meaning is given only to the integral occupation numbers, is that there may be several configurations (such as $3d^n4s^2$ and $3d^{n+1}4s$ in our case) having low energies, the minimum of the mathematical energy function coming for nonintegral occupation numbers close to these integral values. This question will be discussed further in Sec. VI.

The determination of the minimum with respect to the orbitals leads to the ordinary one-electron equations similar to the Hartree–Fock equations, which we may call the HHF equations, and which Mann has solved for certain assumed integral values of x.[6] These will be written down later in Eq. (4). But the determination of the minimum with respect to occupation numbers leads to a quite different sort of condition, which we can interpret as the requirement that certain modified one-electron energies of the orbitals in question (in our case the $3d$ and $4s$) should be equal for the state of minimum energy. These modified one-electron energies are similar to, but by no means equal to, the ordinary one-electron energies for the Hartree–Fock method. They resemble instead the one-electron energies met in the theory of the Fermi liquid, as described by Landau, and also the electronegativity as met in chemistry.[10] We shall denote them by E_{3d}' and E_{4s}', to to distinguish them from the ordinary one-electron energies E_{3d} and E_{4s}. Like the quantities E_{3d} and E_{4s}, we find that E_{3d}' and E_{4s}' are quite sensitive to the occupation numbers, E_{3d}' rising with respect to E_{4s}' as x, or the occupation number of $3d$ electrons, increases. But E_{3d}' and E_{4s}' differ enough from E_{3d} and E_{4s} so that they are in fact equal to each other for the value of occupation number which leads to the minimum energy, though E_{3d} is well below E_{4s} at this point. In other words, these quantities E_{3d}' and E_{4s}' form a mathematical model for the one-electron energies of the energy-band theory, such that electrons go into the states of lowest E_i' in order to lead to the lowest energy of the system. They form the correct model to use for these one-electron energies, which the ordinary quantities E_i of the Hartree–Fock procedure do not.

In the next section we shall set up the mathematical formulation of the HHF method, and of these modified one-electron energies E_i', so as to furnish the detailed justification for the general remarks which we have been making in the present section. Later we shall take up the relation of the various approximate treatments of exchange to the quantities E_i', and shall show that the procedures which various workers have empirically found to lead to calculations of energy bands in good agreement with experiment apparently have the effect of getting one-electron Schrödinger equations whose eigenvalues, though they do not agree with the ordinary quantities E_i of the Hartree–Fock method, agree fairly well with the modified quantities E_i' which are needed to justify a one-electron model.

III. MATHEMATICAL FORMULATION OF THE HHF METHOD

Let us consider an atom with a number of electron shells (such as $1s$, $2s$, $2p$, $3s$, etc.) denoted by an index i.

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[8] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., New York, 1960), Vols. 1 and 2. See particularly Chap. 14, Vol. 1.

[9] For early calculations using such nonintegral occupation numbers see J. T. Waber and A. C. Larson in *Rare Earth Research II* (Gordon and Breach Science Publishers, Inc., New York, 1964); J. T. Waber, D. Liberman and D. T. Cromer in *Proceedings of the Fourth Conference on Rare Earth Research* (Gordon and Breach Science Publishers, Inc., New York, 1965); E. A. Kmetko and J. T. Waber in *Plutonium 1965* (Chapman and Hall Ltd., London, 1967).

[10] L. D. Landau, Zh. Eksperim. i Teor. Fiz. **30**, 1058 (1956); [English transl.: Soviet Phys.—JETP **3**, 920 (1957)]. The authors are indebted to P. W. Anderson for pointing out the resemblance of the arguments of the present paper to Landau's work. As for the electronegativity, we are indebted to J. P. Dahl for pointing out the close resemblance of our work to chemical thinking in this field. An equation essentially equivalent to our Eq. (12) appears in R. S. Mulliken, J. Chem. Phys. **46**, 497 (1949). See particularly Eqs. (122) and (144), p. 537. For a good review of literature in the field of electronegativity and chemical bonding, with many references, see R. Ferreira, Advan. Chem. Phys. **13**, 55 (1967).

Such a shell with azimuthal quantum number l_i could hold $4l_i+2$ electrons if it were filled. However, let it hold only q_i electrons, where q_i may take on any value from zero to $4l_i+2$. It is then easy, using methods which are taken up in Ref. 8, Vol. 1, Sec. 14-2, to set up a formula for the energy of the atom, averaged over all multiplet states found in the configuration in question. This formula is

$$E_{\text{av}}=\sum_i \left[q_iI(i)+\tfrac{1}{2}q_i(q_i-1)(i,i)\right] + \sum_{\text{pairs } i,\,j,\,i\neq j} q_iq_j\,(i,j), \quad (1)$$

where the sums are over shells, and where

$$I(i)=I(n_il_i),$$
$$(i,i)=F^0(n_il_i;\,n_il_i)-\sum_{k\neq 0}\frac{c^k(l_i0;\,l_i0)}{4l_i+1}F^k(n_il_i;\,n_il_i),$$
$$(i,j)=F^0(n_il_i;\,n_jl_j)-\sum_k\frac{c^k(l_i0;\,l_j0)}{[(4l_i+2)(4l_j+2)]^{1/2}}G^k(n_il_i;\,n_jl_j). \quad (2)$$

In these formulas, the symbols have their usual meanings as defined in Ref. 8. That is, $I(n_il_i)$ is a one-electron integral involving the kinetic energy and the potential energy in the field of the nucleus. The quantities $F^k(n_il_i;\,n_jl_j)$ and $G^k(n_il_i;\,n_jl_j)$ are the standard integrals involving Coulomb and exchange interactions between the orbitals, and the c^k's are the coefficients arising from the products of three spherical harmonics. The first summation in Eq. (1) is the sum of one-electron integrals followed by the sum of interactions between the $q_i(q_i-1)/2$ pairs of electrons in the ith shell, and the last is the sum of interactions between the q_iq_j pairs of electrons in which the first is in the ith shell, the second in the jth. Equation (1) is derived on the assumption that all orbitals in the ith shell have the same radial functions, independent of the quantum numbers m_l and m_s, and that the angular dependence is given by a spherical harmonic of the angles in the usual way. We postpone the spin-polarized case, or use of different orbitals for different spins, until Sec. VII.

We now wish to minimize the energy expression of Eq. (1) by varying the radial functions involved in the spin-orbitals, keeping the occupation numbers q_i constant, and preserving the normalization and orthogonality of the spin orbitals, which are required to make the expression of Eq. (1) valid for the energy. To do this, we shall vary the expression

$$E_{\text{av}}-\sum_i q_iE_i\int u_i^*u_i dv-2\sum_{\text{pairs } i,\,j} q_iq_jE_{ij}\int u_i^*u_j dv \quad (3)$$

in which the quantities E_i, E_{ij} are undetermined Lagrange multipliers, and in which $E_{ij}^*=E_{ji}$. The nondiagonal Lagrange multipliers E_{ij} are different from zero only between radial functions associated with the same azimuthal quantum numbers, since in other cases the orthogonality automatically results from the functions of angles.

We vary this expression by varying the radial wave function associated with the ith spin orbital u_i, which we write as $R_{n_il_i}(r)=P_{n_il_i}(r)/r$. When we do this, as indicated in Ref. 8, Vol. 2, Eq. (17–57), the result is

$$\left[-\frac{d^2}{dr_1^2}-\frac{2Z}{r_1}+\frac{l_i(l_i+1)}{r_1^2}+\sum_j q_j\frac{2}{r_1}Y_0\left(n_jl_j;\,\frac{n_jl_j}{r_1}\right)-\frac{2}{r_1}Y_0\left(n_il_i;\,\frac{n_il_i}{r_1}\right)-\frac{(q_i-1)}{4l_i+1}\sum_{k\neq 0}c^k(l_i0;\,l_i0)\frac{2}{r_1}Y_k\left(n_il_i;\,\frac{n_il_i}{r_1}\right)-E_i\right]$$
$$\times P_{n_il_i}(r_1)=\sum_{k,\,n_jl_j\neq n_il_i}\left[\frac{q_jc^k(l_i0;\,l_j0)}{[(4l_i+2)(4l_j+2)]^{1/2}}\frac{2}{r_1}Y_k\left(n_il_i;\,\frac{n_jl_j}{r_1}\right)+E_{ij}\right]P_{n_jl_j}(r_1). \quad (4)$$

In these equations, energies are expressed in terms of Ry, and distances in multiples of the Bohr radius. It is Eq. (4) which Mann (Ref. 6) has solved. The functions Y_k have their usual significance; that is,

$$Y_k\left(n_il_i;\,\frac{n_jl_j}{r_1}\right)=r_1^{-k}\int_0^{r_1}P_{n_il_i}(r_2)P_{n_jl_j}(r_2)r_2^k dr_2 + r_1^{k+1}\int_{r_1}^{\infty}P_{n_il_i}(r_2)P_{n_jl_j}(r_2)r_2^{-k-1}dr_2. \quad (5)$$

As mentioned earlier, we shall refer to Eq. (4) as the hyper-Hartree–Fock equation.

Mann in his calculations of Ref. 6 adopted the usual procedure of assuming integral occupation numbers q_i for the various shells, in accordance with our usual interpretation of the filling of the shells in the ground state of the atoms in the periodic system. He then has solved for the radial functions $P_{n_il_i}(r)$ for the occupied orbitals, which agree well with our usual assumptions regarding the wave functions. The energies E_i agree well with the negatives of the x-ray ionization energies. The nondiagonal energy parameters E_{ij}, which are required to insure the orthogonality of the radial wave functions, are different from zero only for the case where i and j refer to two shells of the same l value. They are tabulated by Mann, and prove to be small enough so that for many purposes they can be neglected.

The one-electron energies E_i can be found from Eq. (4), by multiplying on the left by $P_{n_il_i}(r_1)$ and integrating over r_1, taking advantage of the orthonormal properties of the P's. The result is

$$E_i=I(i)+(q_i-1)(i,i)+\sum_{j\neq i}q_j(i,j). \quad (6)$$

This is equivalent to Eq. (17-58) of Ref. 8, Vol. 2. It can be equally well derived by finding the energy of the ion lacking one electron in the ith shell, from Eq. (1), using the same equation but with q_i-1 substituted in place of q_i, and by subtracting the energy of the ion so found from the energy of the atom given in Eq. (1).

In the $3d$ transition elements and in many other important cases, we have but two partly filled shells, such as the $3d$ and $4s$. Let us therefore see how the results of the preceding discussion work out in this case. We assume that the partly filled shells are numbered 1 and 2. Let there by N electrons in the two shells taken together. Let the values of q_1 and q_2 be

$$q_1=q=n+x,\quad q_2=N-q=N-n-x, \tag{7}$$

where n is a fixed constant, and x is the variable which allows us to change the occupation numbers. In the $3d$ transition group q could be taken to represent the number of $3d$ electrons, and $q_2=N-q$ the number of $4s$. We shall often take n to be the value of q for which $q_2=2$, and $N=n+2$, so that we are considering a configuration $3d^{n+x}4s^{2-x}$ as before. Sometimes, however, particularly in Sec. V, we shall find it convenient to use other values of n.

We can now consider the other part of our minimizing process: the variation of occupation numbers to make the energy a minimum, subject to fixed orbitals. In this case in which N remains constant, we can vary E_{av} with respect to x, and the condition for minimum energy will be $\partial E_{\text{av}}/\partial x=0$. In the expression of Eq. (1), E_{av} will depend on x through the dependence on q_1 and q_2, each of which is a function of x by Eq. (7). Hence we shall have as the condition for minimum energy

$$\partial E_{\text{av}}/\partial x=0=\partial E_{\text{av}}/\partial q_1-\partial E_{\text{av}}/\partial q_2. \tag{8}$$

Let us define

$$\partial E_{\text{av}}/\partial q_i=E_i', \tag{9}$$

where the differentiation is to be carried out keeping all q's except q_i fixed, and also keeping all orbitals and integrals fixed. Then the condition for minimum energy is, from Eq. (8),

$$E_1'=E_2'. \tag{10}$$

In other words, the quantities E_i' defined by Eq. (9) are the quantities referred to in the preceding section; the condition for minimum energy is the equality of the E_i''s for two energy levels such as $3d$ and $4s$ which are capable of interchanging electrons.

Let us look more closely at the significance of the quantities E_i'. From Eq. (1) we have

$$E_i'=I(i)+(q_i-\tfrac{1}{2})(i,i)+\sum_{j\neq i} q_j(i,j) \tag{11}$$

$$=E_i+\tfrac{1}{2}(i,i) \tag{12}$$

in which Eq. (12) follows from Eq. (6). In other words, we verify our earlier statement that the modified one-electron energies E_i' are similar to the one-electron energies E_i of the HHF method, but are not identical: they are larger by the amounts $\frac{1}{2}(i,i)$.

Let us correlate these relations with our knowledge of the behavior of the self-consistent field method. We ordinarily consider an electron to move in the potential field of the nucleus and of all electrons including itself, diminished by the repulsive interaction of the electron with itself. The one-electron energy of an electron moving in the potential of the nucleus and of all electrons including itself would be $I(i)+q_i(i,i)+\sum_{j\neq i} q_j(i,j)$. We see that E_i of Eq. (6) differs from this by having the interaction (i,i) subtracted from it. This then stands for the self-interaction correction, in this form of writing the relations. When we compare with Eq. (11), we then see that to find E_i' we use only half the self-interaction correction used in the HHF calculation. There is, in other words, a large difference between E_i' and E_i, and, on account of the quite large positive form of (i,i), the one-electron energy E_i' is a good deal more positive than E_i.

We can even see from this in a qualitative way how the difference $E_{3d}'-E_{4s}'$, which will be the value of $\partial E_{\text{av}}/\partial x$ for the transition elements according to Eq. (8), will behave. We know that E_{3d} is considerably more negative than E_{4s}. However, the $3d$ orbital is a good deal more concentrated than the $4s$, and as a result the self-energy term $(3d,3d)$ is larger than $(4s,4s)$. The difference $E_{3d}'-E_{4s}'$ is greater than $E_{3d}-E_{4s}$ by $\frac{1}{2}[(3d,3d)-(4s,4s)]$. Consequently it is considerably more positive than $E_{3d}-E_{4s}$. It is this fact which makes it possible for $E_{3d}'-E_{4s}'$ to be zero, leading to the energy minimum for a reasonable occupation number in the transition elements, even though $E_{3d}-E_{4s}$ is strongly negative throughout that series of elements. But at the same time we can understand why, if we use one of the various approximate treatments of exchange and replace $E_{3d}-E_{4s}$ by the corresponding difference in eigenvalues of the approximate Schrödinger equation, we can arrive at quite different results.[1] We preceed in the next section to specific calculations which we have made for the cases of Co and Ni, and a few for Cu, to illustrate these facts.

IV. CALCULATIONS FOR COBALT AND NICKEL

To test the phenomena we have been discussing, one of us (JBM) has made HHF calculations for the Co atom in the configurations $3d^{7+x}4s^{2-x}$ and for the Ni atom in the configurations $3d^{8+x}4s^{2-x}$ with x equal to 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0, 1.5, 1.8, and 2.0; calculations have also been made for Cu in the configurations $3d^94s^2$ and $3d^{10}4s$. In Fig. 1, we show the average energy E_{av} of Eq. (1), for each case of Co and Ni, as a function of q, the number of $3d$ electrons, resulting in very similar curves for each atom and leading to a minimum energy at $q=7.464$ for Co, 8.517 Ni. We tabulate the values of E_{av} for these cases in Table I. We find that the computed points can be fitted well by a cubic function of x, which we give in Eq. (13):

$$\begin{aligned} E_{\text{av}}&=-2762.6171-0.1677(q\text{-}7)+0.1917(q\text{-}7)^2\\ &\qquad-0.0157(q\text{-}7)^3\ \text{Ry}\quad\text{for Co}\\ &=-3013.6318-0.1971(q\text{-}8)+0.2029(q\text{-}8)^2\\ &\qquad-0.0157(q\text{-}8)^3\ \text{Ry}\quad\text{for Ni.} \end{aligned} \tag{13}$$

The deviations between the computed points and those given by these cubic equations are of the order of magnitude of 0.0001 Ry.

One can find the one-electron energies E_{3d}, E_{4s}, and the modified one-electron energies E_{3d}', E_{4s}' from the integrals computed in connection with the HHF calculation. Alternatively one can find $E_{3d}'-E_{4s}'$ as a function of x(equal to q-7 for Co, q-8 for Ni) by differentiating the average energy E_{av} of Eq. (13) with respect to x. This procedure follows from Eq. (8), except that it is only at the minimum of the curves of Eq. (13) or Fig. 1 that $\partial E_{\mathrm{av}}/\partial x$ equals zero. We find that the two determinations of $E_{3d}'-E_{4s}'$ agree to the accuracy of our calculation. In Fig. 2 we show the quantities $E_{3d}-E_{4s}$ and $E_{3d}'-E_{4s}'$ as functions of q for Co; the case of Ni is similar. We see the way in which $E_{3d}-E_{4s}$ is negative for all values of x from zero to 2, verifying our earlier statement that the one-electron energies of the HHF method place the $3d$ level below the $4s$ for all possible occupation numbers. On the other hand, as we have mentioned, $E_{3d}'-E_{4s}'$ goes through zero at the value of x equal to 0.464 which corresponds to minimum energy according to Fig. 1 or Eq. (13). In other words, the HHF method would predict an occupation for these atoms about half-way between $4s^2$ and $4s$, or would imply that both of these configurations lead to low-lying energy levels. We shall consider the agreement between this fact and experiment in Sec. VI.

Before we come to this comparison with experiment, let us describe other calculations which we have made. The HHF calculations are more difficult than those carried out with various forms of approximate exchange, and they were not in fact available until we had examined the approximate exchanges quite thoroughly. One of us (JHW) carried out calculations for both Co and Ni, at occupations corresponding to $x=0$, 0.2, 0.4, $\cdots$, 1.8, 1.99, using two different forms of exchange. One of these was the so-called XKSG method (Ref. 1), in which one follows Kohn and Sham in using an exchange proportional to the $\frac{1}{3}$ power of the charge density but $\frac{2}{3}$ as large as that suggested by another of us (JCS) in Ref. 3. The other was the so-called Xα method, in which, again following Ref. 1, one uses an exchange equal to α times that of Ref. 3, varying α to get a minimum energy in the self-consistent calculation. The parameter α was varied for each value of x, and the optimum parameters are given in Table 2. In addition to these calculations, Herman and Skillman have made calculations using the original exchange of Ref. 3 (referred to as XS in Ref. 1, arising from using the factor $\alpha=1$), for Co $3d^7 4s^2$, and for Ni for $3d^8 4s^2$ and $3d^9 4s$ (see Ref. 7), and Snow and Waber (Ref. 2) have given values also for Co $3d^8 4s$ (indicated graphically

TABLE I. Energies of Co, Ni, and Cu in various configurations, by HHF method. Energies in Ry.

Cobalt		Nickel		Copper	
$3d^7 4s^2$	−2762.61713	$3d^8 4s^2$	−3013.63190	$3d4s^2$	−3277.90066
$3d^{7.2}4s^{1.8}$	−2762.64300	$3d^{8.2}4s^{1.8}$	−3013.66322	$3d^{10}4s$	−3277.92775
$3d^{7.4}4s^{1.6}$	−2762.65444	$3d^{8.4}4s^{1.6}$	−3013.67912		
$3d^{7.5}4s^{1.5}$	−2762.65494	$3d^{8.5}4s^{1.5}$	−3013.68157		
$3d^{7.6}4s^{1.4}$	−2762.65209	$3d^{8.6}4s^{1.4}$	−3013.68043		
$3d^{7.8}4s^{1.2}$	−2762.63664	$3d^{8.8}4s^{1.2}$	−3013.66777		
$3d^{8.0}4s^{1.0}$	−2762.60877	$3d^{9.0}4s^{1.0}$	−3013.64187		
$3d^{8.5}4s^{0.5}$	−2762.49002	$3d^{9.5}4s^{0.5}$	−3013.52380		
$3d^{8.8}4s^{0.2}$	−2762.38915	$3d^{9.8}4s^{0.2}$	−3013.42047		
$3d^{9.0}$	−2762.31088	$3d^{10.0}$	−3013.33987		

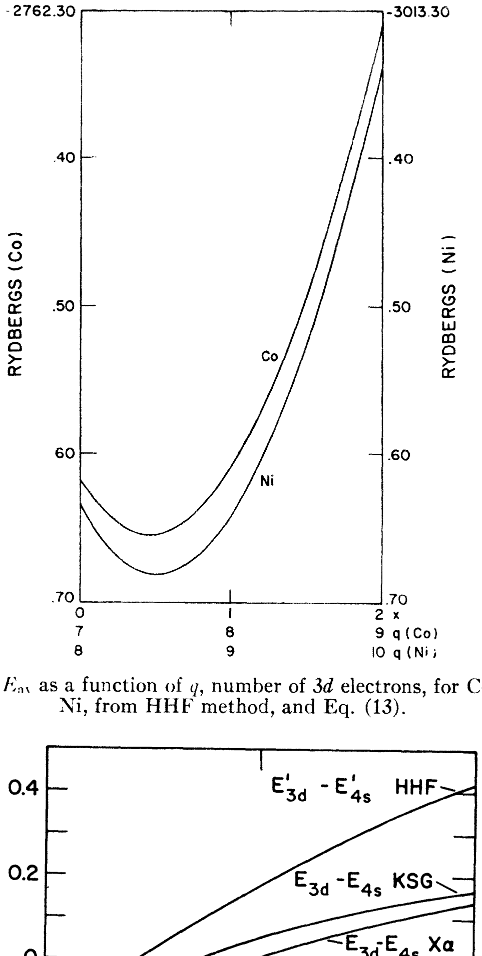

FIG. 1. E_{av} as a function of q, number of $3d$ electrons, for Co and Ni, from HHF method, and Eq. (13).

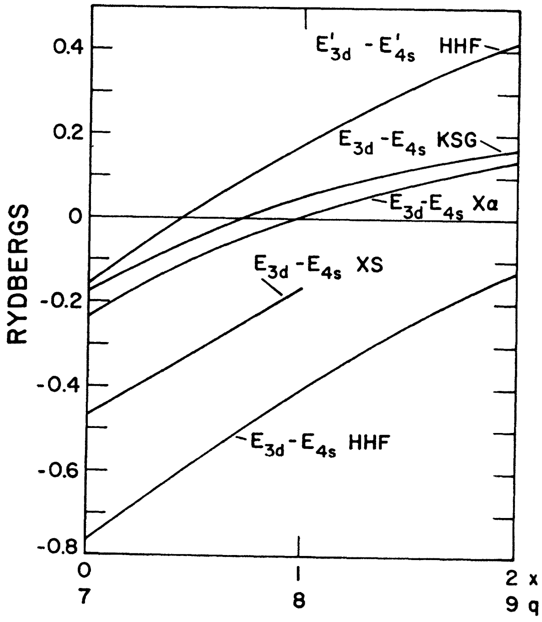

FIG. 2. Quantities $E_{3d}'-E_{4s}'$ and $E_{3d}-E_{4s}$ from HHF method, and $E_{3d}-E_{4s}$ from XKSG, Xα, and XS methods, for Co, as function of q, number of $3d$ electrons.

TABLE II. Summary of best α values for Co and Ni as function of number of s electrons ($V_{X\alpha}=\alpha V_{XS}$)[a].

No. s electrons	α(Co)	α(Ni)
2.0	0.735	0.736
1.8	0.738	0.739
1.6	0.745	0.745
1.4	0.745	0.745
1.2	0.750	0.751
1.0	0.754	0.756
0.8	0.757	0.759
0.6	0.761	0.763
0.4	0.764	0.767
0.2	0.765	0.767
0.01	0.765	0.768

[a] In these calculations, the Latter potential (Ref. 7) has been used at large values of the radial coordinate r.

on their Fig. 2). In Fig. 2 we show the difference of eigenvalues of the differential equations for the $3d$ and $4s$ levels, found by these various methods, as functions of q or of $x=q-7$, for Co, for comparison with the HHF values. Curves for Ni are very similar.

The comparison of the differences of eigenvalues $E_{3d}-E_{4s}$ for each of these methods—HHF, XS, Xα, and XKSG—follows the general behavior of the eigenvalues found in Ref. 1. There it was found that the Hartree–Fock one-electron eigenvalues lay lowest, then the XS followed by the Xα, while the XKSG lay highest, just as we find here for the energy differences between $3d$ and $4s$. The reasons for the differences were discussed in Ref. 1, in which we also discussed another assumed exchange, denoted XLSW, which gave results in rather close agreement with the Hartree–Fock values. We have not used this method, which is considerably more complicated in practice, in investigating the nonintegral occupation number problem. It was indicated in Ref. 1 that the higher eigenvalues found for the Xα and XKSG methods were a result of rather accidental features connected with the potentials used in those methods. But it was suggested also that study of the nonintegral occupation number problem, such as we are now giving, threw a different and more fundamental light on these methods.

From study of Fig. 2 we can see what this new light is: the eigenvalue differences $E_{3d}-E_{4s}$ found for the XKSG method and to a lesser extent for the Xα method, though they are far above the HHF differences $E_{3d}-E_{4s}$, begin to approach rather closely the differences of the modified one-electron energies, $E_{3d}'-E_{4s}'$, which we are discussing in the present paper. In other words, if one merely used the XKSG method, and used the difference of eigenvalues, $E_{3d}-E_{4s}$, determined by this method rather than the HHF quantity $E_{3d}'-E_{4s}'$, one would not be far from the correct HHF values. We could use XKSG eigenvalues as one-electron energies, and determine the ground state by letting the electrons go into the lowest one-electron states, and we should end up with occupation numbers which are not far from those resulting from the HHF values. In fact, as we shall point out in Sec. VI, it seems that the results of this very simplified treatment agree better with experiment, in the matter of the relative energies of different configurations or occupation numbers, than do the HHF results. This appears to us to be the reason why it is found in practice that the use of an exchange corresponding to a value of α considerably less than unity gives energy bands much closer to experiment for these $3d$ transition elements than does the original value $\alpha=1$ of Ref. 3. We give references to some of the calculations which have led to this result in Ref. 11.

One can define one-electron energies E_i' for all of the orbitals of the atom, and later in Sec. VIII we point out some of their properties. It is only the $3d$ and $4s$ energies which we use in the present connection, but it is interesting to see that in all of these cases the eigenvalues of the Schrödinger equations derived from the various approximations to the exchange potential agree much better with the E_i''s than with the E_i's of the HHF method. This is illustrated in Table III. in which we compare the values of E_i and E_i', as determined by the HHF method, with the eigenvalues E_{XKSG}, $E_{\text{X}\alpha}$, and E_{XS} found with the approximate exchange, for all the orbitals of the Ni atom, in the configuration $3d^84s^2$. We also give experimental x-ray term values, as well as certain other quantities explained in the table. Similar results are found for other atoms and occupation numbers.

We shall not attempt to answer the question as to whether the reason for the approach to similarity between the values of E_{XKSG} and E'_{HHF} is more than accidental. One must realize that in the original derivation of the XKSG method[12] the authors have used a variation method which reminds one of that employed in the present paper. They did not, however, separate the variations in the charge density and in the energy produced by varying the orbitals, and by varying the occupation numbers, as we are doing in the present paper. For that reason we cannot regard the derivation of the XKSG method given in Ref. 12 as being more than suggestive. However, it is certainly interesting that there is at least a resemblance between the eigenvalues found by that method and the quantities E_i' found by our present more realistic scheme.

In Sec. VI we go into the question as to the agreement between the nonintegral occupation numbers found by minimizing the energy, and by experiment. Before we do this, however, there is one rather complicated point which we wish to discuss. It is well known, and was shown in Ref. 1, that if one takes the wave functions resulting from the XKSG, Xα, or XS methods, and uses the integrals arising from them to compute the average energy of the atom, and the one-electron energies, the resulting values agree fairly well with those obtained by **HHF** methods. In that reference, we de-

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[11] See references of Connolly (Ref. 4), of Yamashita *et al.*, (Ref. 5). See also P. D. DeCicco and A. Kitz, Phys. Rev. **162**, 486 (1967); E. C. Snow, *ibid.* **171**, 785 (1968); and L. F. Mattheiss, *ibid.* **133**, A1399 (1964).

[12] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965); R. Gaspar, Acta Phys. Acad. Sci. Hung. **3**, 263 (1954).

TABLE III. Total and one-electron energies of Ni $3d^8 4s^2$ determined by different methods, in Ry.[a]

	HHF	XKSG	Xα	XS	Exp.
Total energy	−3013.6319	−3013.5054	−3013.5382		
1*s* E	− 611.2537	− 595.697	− 597.3477	−603.7	−604.66
ϵ	− 611.2537		− 611.5378		
E'	− 594.1117		− 594.4158		
2*s* E	− 75.8529	− 70.723	− 71.0181	− 72.57	− 72.37
ϵ	− 75.8529		− 76.5591		
E'	− 72.1913		− 72.9171		
2*p* E	− 65.9006	− 61.731	− 62.1633	− 63.86	− 62.52
ϵ	− 65.9006		− 65.7994		
E'	− 61.8391		− 61.7335		
3*s* E	− 9.7871	− 7.914	− 8.0261	− 8.500	− 7.93
ϵ	− 9.7871		− 9.8450		
E'	− 8.5838		− 8.6422		
3*p* E	− 6.5661	− 5 201	− 5.3066	− 5.756	− 4.87
ϵ	− 6.5661		− 6.6254		
E'	− 5.4605		− 5.5125		
3*d* E	− 1.3942	− 0.7114	− 0.7859	− 1.1151	− 0.28
ϵ	− 1.3942		− 1.4390		
E'	− 0.4516		− 0.5088		
4*s* E	− 0.5536	− 0.4951	− 0.5095	− 0.5831	
ϵ	− 0.5536		− 0.5758		
E'	− 0.2567		− 0.2822		
$3d-4s$					
E	− 0.8406	− 0.2163	− 0.2764	− 0.5320	
ϵ	− 0.8406		− 0.8632		
E'	− 0.1949		− 0.2266		

[a] Total energies determined by Eq. (1) from integrals computed by each method. E, eigenvalues of the differential equations, for HHF, XKSG, Xα, and XS methods. ϵ, one-electron energy determined from integrals by Eq. (6.) For the HHF method, this automatically equals the eigenvalue E, but this is not true in other cases. However, ϵ in each case forms a good approximation to HHF value. E', modified one-electron energy of Eq. (11), computed from integrals. Experimental value from K. Siegbahn *et al.*, *Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy* (Almqvist and Wikselboktryckeri AB, Uppsala, 1957), Nova Acta Regiae Societatis Scientiarum Upsaliensis Ser. IV, Vol. 20. Corrected by methods of Ref. 7 to remove the relativistic effect.

noted the one-electron energies computed in this way as ϵ_{XKSG}, $\epsilon_{\mathrm{X}\alpha}$, and ϵ_{XS}. They are quite different from the eigenvalues of the differential equations, which were denoted in Ref. 1 as E_{XKSG}, $E_{\mathrm{X}\alpha}$, and E_{XS}; it is only in the HHF method that the two sorts of one-electron energies agree with each other. These facts can be seen in Table III, in which we have given $\epsilon_{\mathrm{X}\alpha}$ for Ni, as well as $E_{\mathrm{X}\alpha}$. We discuss these quantities in the next section, and show that it is not as straightforward as we should suppose to compute them and that in fact the values given in Table III must be properly modified before they can be compared with those from the HHF method.

V. CALCULATION OF ENERGIES FROM APPROXIMATE WAVE FUNCTIONS

As a preliminary to the discussion which we shall give in this section, we shall carry further our treatment of the HHF method. In the course of our calculations of the Co and Ni atoms with ten different sets of occupation numbers, enumerated at the beginning of Sec. IV, we have found ten different sets of orbitals and the resulting integrals of the one- and two-electron operators, though the last case, for $3d^9$ or $3d^{10}$, lacks the integrals involving the $4s$ orbital, which is missing in this case. We then have a number of different complete sets of integrals $I(i)$, (i,i), and (i,j), of the type mentioned in Eqs. (1), (2), and later equations. There is nothing to prevent our using the set of orbitals and integrals computed by minimizing the energy for one value of q, the number of $3d$ electrons, to calculate values of the energy for other values of q. We need merely substitute the one set of integrals and the other set of q_i's into Eq. (1). But for any set of q_i's, we shall find that the lowest energy E_{av} comes from the set of integrals which were found by solving the HHF equations for that set of q_i's, because the HHF equations are equivalent to varying the orbitals to minimize the energy, at constant occupation number.

It is interesting nevertheless to carry out these calculations with the wrong integrals, for it gives us insight into the sort of results which we shall find by using wave functions which are not proper solutions of the HHF method for the occupation numbers in question. It points the way to the method of handling the orbitals and integrals found by the approximate exchange methods, which are not derived by a method of varying orbitals to minimize the energy. As a first step toward this discussion, we rewrite the expression of Eq. (1) for E_{av}, in the form appropriate to our present problem. We take the q_i's of the $3d$ and $4s$ orbitals to be given by Eq. (7); that is, we have the configuration $3d^{n+x}4s^{N-n-x}$, where N is the total number of electrons in the $3d$ and $4s$ levels. In most of our previous work, we have taken n to equal the number of $3d$ electrons in a configuration with two $4s$ electrons, which implies that $n=N-2$. In the present case, however, we shall choose n to be that nonintegral number of $3d$ electrons for which the integrals are to be computed from our HHF calculations. Since the expression of Eq. (1) is quadratic in the q_i's, and therefore in x, and since we are taking the integrals to be constant, we shall find an energy which is a quadratic function of x, as we mentioned in Sec. I.

Let us define the average energy computed for a configuration with $n+x$ $3d$ electrons, but computed using the integrals derived from a HHF calculation with n $3d$ electrons, as $E_n(x)$. We then find by straightforward substitution of the expressions of Eq. (7) into Eq. (1), the result

$$E_n(x)=E_n(0)+x[E_{3d}'(n)-E_{4s}'(n)]+x^2A(n), \quad (14)$$

where

$$A(n)=\tfrac{1}{2}[(3d,3d)(n)+(4s,4s)(n)]-(3d,4s)(n), \quad (15)$$

the quantity $E_n(0)$ is the value of E_{av} computed when $x=0$, or when $n=q$, so that it is computed for the correct integrals corresponding to its occupation number. The quantities E_{3d}', E_{4s}', $(3d,3d)$, $(4s,4s)$, and $(3d,4s)$ are likewise to be computed from the HHF calculations for $q=n$, or $x=0$. This is the reason for writing them as functions of n. As we see from Eq. (14), we then find for any particular value of n that $E_n(x)$ is given by a parabola as a function of x, or of q.

In Fig. 3, we show four parabolas for the case of Co, corresponding to the cases $n=7.0$, 7.5, 8.0, 8.5. We also show the envelope of this family of parabolas. For any given value of q, each parabola gives a different energy, and the lowest value is found from that which is tangent to the envelope curve at the value of q. That is, a parabola must be tangent to the envelope at $q=n$. Furthermore, since each point on the envelope gives the energy derived from those particular integrals which minimize the energy for that value of q, the envelope must be identical with the energy curve of Fig. 1, approximated by Eq. (13).

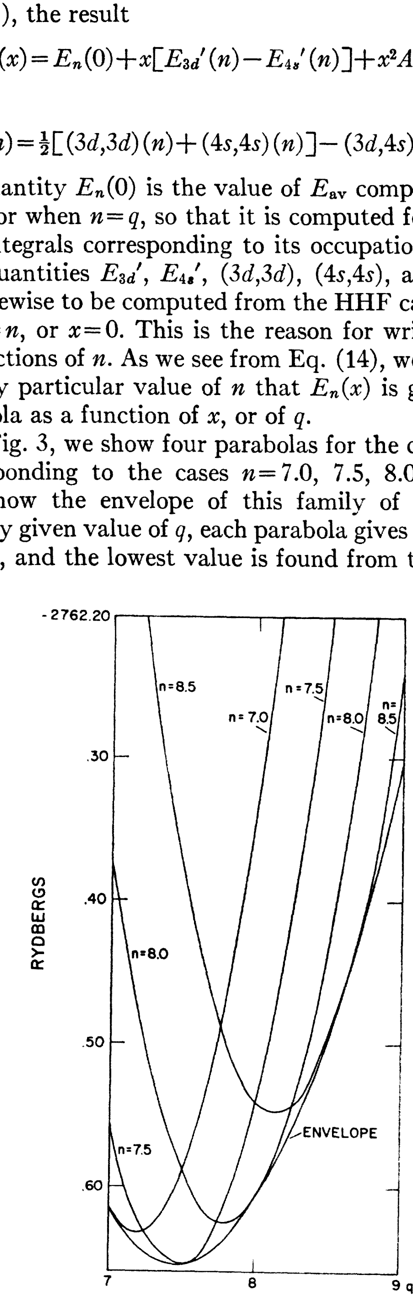

FIG. 3. Envelope curve, or E_{av} of Eq. (13), and parabolas, for Co, as function of q, number of $3d$ electrons, from HHF calculations and Eq. (16). The quantity n is the value of the number of d electrons for which the HHF calculation is made. Each parabola represents $E_n(x)$ as a function of $q=n+x$ for the particular set of orbitals determined by HHF equation for case of n $3d$ electrons. For the envelope, identical with curves of Fig. 1, optimum orbitals are used for each value of q.

The tangency of the parabolas to the envelope curve at $x=0$, or $q=n$, is shown mathematically from the fact that when $q=n$, or $x=0$, the parabola has a value of $E_n(x)$ given by the curve $E_n(0)$. Furthermore, the slope of the parabola at this point, from Eq. (14), is $E_{3d}'-E_{4s}'$, which as we have already seen is the slope of the curve of Fig. 1, a fact which follows from Eqs. (8) and (9). In the HHF method, the energy E_{av} of Eq. (1) is to be computed for each set of q_i's from the orbitals satisfying the HHF equations for those q_i's. The partial derivatives $\partial E_{\text{av}}/\partial q_i$ computed for fixed orbitals are defined as the E_i''s. Thus $\partial E_{\text{av}}/\partial x=E_{3d}'-E_{4s}'+$additional terms coming from the change of E_{av} with changes in the orbitals arising from changing the q_i's. But since we are dealing with a solution of the HHF equations, the derivative of E_{av} with respect to change of orbitals is zero, and we are left with $\partial E_{\text{av}}/\partial x=E_{3d}'-E_{4s}'$. Hence the parabola has the same slope as the envelope at $x=0$, as is required for tangency.

We can now combine the results of Eqs. (13) and (14), giving $E_n(x)$:

$$\begin{aligned}E_n(x)=&-2762.6171-0.1667(n\text{-}7)+0.1917(n\text{-}7)^2\\&-0.0157(n\text{-}7)^3+x[-0.1667+0.3834(n\text{-}7)\\&-0.0471(n\text{-}7)^2]+x^2[0.4410-0.0169(n\text{-}7)\\&-0.0013(n\text{-}7)^2](\text{for Co}). \quad (16)\end{aligned}$$

In setting up Eq. (16), the term $E_n(0)$ comes from Eq. (13), the term in x comes by differentiating the first term, and we have approximated $A(n)$ as a quadratic function of n, which we find to be justified to a sufficient approximation. The corresponding function for Ni is

$$\begin{aligned}E_n(x)=&-3013.6318-0.1971(n\text{-}8)+0.2029(n\text{-}8)^2\\&-0.0157(n\text{-}8)^3+x[-0.1971+0.4058(n\text{-}8)\\&-0.0471(n\text{-}8)^2]+x^2[0.4766-0.0151(n\text{-}8)\\&-0.0001(n\text{-}8)^2]. \quad (17)\end{aligned}$$

We now have sufficient understanding of the problem of minimizing the energy by varying the orbitals, or integrals, as well as by varying the occupation numbers, so that we can proceed to the calculations based on the eigenfunctions and integrals derived from the XKSG or the Xα methods. From either of these cases we have a set of eigenfunctions and integrals determined from a family of calculations.[13] Each of these calculations is

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[13] In the Xα and XKSG calculations, a modification of the Herman–Skillman program was used (Ref. 7). The integrals were computed using a modified form of the program described by R. N. Zare [R. N. Zare, Report No. 80, Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, Colorado, 1966, (unpublished)].

made for a particular set of occupation numbers, or a particular n. From each of these sets of integrals, we can compute quantities E_{av}, E_{3d}', E_{4s}', and A, using Eqs. (1), (2), (12), and (15). If we identify these quantities with $E_n(0)$, E_{3d}', E_{4s}', and A of Eq. (14), we can then find a parabola, representing the energy computed as a function of occupation number, using the integrals found from the XKSG or Xα method. These parabolas resemble those found for the HHF case in Fig. 3. We can draw an envelope curve tangent to the parabolas, and the arguments we have given earlier indicate that, for any value of occupation number q, the energy will be lower for the envelope curve than for any of the parabolas except for that parabola tangent to the envelope at this q, so that the envelope represents the best approximation to the true energy that we can find from this restricted set of variation functions.

However, we must remember that these functions are not true solutions of the HHF problem. Thus our argument that the slope of the parabola at $x=0$, where $E_n(x)$ equals $E_n(0)$, must equal the slope of the curve giving the computed average energy E_{av} as a function of $q=n+x$ breaks down. Since the average energy computed from these functions does not satisfy the HHF equations, we find that $\partial E_{\mathrm{av}}/\partial x=E_{3d}'-E_{4s}'$ + (additional terms which do not vanish in this case). If we interpret $E_n(0)$ as being the value of E_{av} computed for $q=n$ by using the integrals found from the XKSG or Xα method, as we are doing, the slope of the parabola intersecting this curve at a given q will not exactly equal the slope of the curve $E_n(0)$. Thus the parabolas will cut through this curve, and it will not be the envelope which will necessarily lie lower.

The consequence of this is that the point of tangency between one of the parabolas and the true envelope curve will not come at the value of q for which the eigenfunctions were determined. For instance, one set of eigenfunctions for Co was found by assuming the configuration $3d^7 4s^2$, and by using the XKSG method. That is, the program (essentially the Herman–Skillman program of Ref. 7) takes the orbitals resulting from one stage of the calculation, computes from them a charge density using the assumed occupation numbers, derives a Coulomb potential from this charge density, and an exchange potential found by the XKSG assumption, and iterates until the orbitals found by solving the Schrödinger equation for this potential are identical with the original orbitals, to a predetermined tolerance. When this is carried through, it is in fact found that the resulting parabola is tangent to the true envelope curve, not at $q=7$, but approximately at $q=7.4$. In other words, these orbitals and integrals, which were intended to be used for the configuration $3d^7 4s^2$, prove to be even better approximations for the configuration $3d^{7.4}4s^{1.6}$ than the orbitals which were determined by carrying through the analogous procedure for that occupation number.

We have carried through these calculations not only for the XKSG exchange, but also for the Xα exchange, as mentioned earlier. We had supposed that the envelope curve derived from the Xα exchange would lie below that for the XKSG exchange, since the parameter α was varied to minimize the energy calculated by Eq. (1) from the orbitals of the Xα method, while the orbitals of the XKSG method lead to a considerably higher energy with fixed occupation numbers. But when the calculations are made, we find that the Xα method leads to a lower energy only for q less than about 7.4, while the envelope found from the XKSG method crosses the other at this point, and corresponds to lower energy for larger q's. However, the parabolas found by the Xα method are tangent to the envelope at different values of q from those found by the XKSG method. For instance, the parabola found by the Xα method by solving the Schrödinger equation with the Xα exchange for the configuration $3d^{7.2}4s^{1.8}$ proves to be tangent to the envelope at approximately $q=7.4$. This means that we have two functions, that determined by the XKSG method for $q=7$, and that determined by the Xα method for $q=7.2$, both of which are tangent to envelopes at approximately 7.4, at which both envelopes correspond to the same energy. It would seem reasonable, then, that these two wave functions must be very similar. They prove to be, when one intercompares them by comparing the various integrals, or the orbitals themselves.

We may well ask how it can be that the use of different exchange values (different α's) and different occupation numbers, can lead to approximately the same wave functions. In Ref. 1, we found that when we had good agreement between different procedures for computing orbitals, the reason could be traced back to good agreement between the potentials used in the corresponding Schrödinger equations. We have not traced through this agreement in detail in the present case, but it is inherently plausible that the same situation would be found here too. It would be of interest to find the coulomb and exchange potentials arising in these two cases, and see whether they agree fairly well, as we suspect they will.

Since the wave function giving the lowest envelope is presumably the best, from the point of view of the variation method, we have fitted a composite envelope to those determined from the Xα and XKSG methods, and have found values of the various integrals from the wave functions giving the parabolas tangent to the envelope at each occupation number. We then can find equations, like Eqs. (16) and (17), expressing the best values which we have found from the statistical exchange approximation method. These equations are:

$$\begin{aligned}\text{Co}: E_n(x)=&-2762.5320-0.1532(n\text{-}7)+0.1893(n\text{-}7)^2\\&-0.0123(n\text{-}7)^3+x[-0.1532+0.3786(n\text{-}7)\\&-0.0369(n\text{-}7)^2]+x^2[0.4290-0.0184(n\text{-}7)\\&-0.0080(n\text{-}7)^2],\end{aligned}\qquad(18)$$

$$\begin{aligned}\text{Ni: } E_n(x) = &-3013.5390-0.1799(n\text{-}8)+0.1940(n\text{-}8)^2\\ &-0.0106(n\text{-}8)^3+x[-0.1799+0.3880(n\text{-}8)\\ &-0.0318(n\text{-}8)^2]+x^2[0.4620-0.0080(n\text{-}8)\\ &-0.0120(n\text{-}8)^2]. \quad (19)\end{aligned}$$

It will be seen that aside from the fact that the HHF method gives energies almost 0.1 Ry lower than the best calculations using statistical exchange, the agreement between these equations and those of Eqs. (16) and (17) describing the HHF method is quite good. The values of the quantities $E_{3d}'-E_{4s}'$ found by differentiating these functions derived from the statistical exchange agree well enough with those found from the HHF method so that the differences would hardly be noticeable in a graph such as Fig. 2. Similarly we can find values of the one-electron energies ϵ_i and the values $\epsilon_{3d}-\epsilon_{4s}$ are in good agreement with those found by the HHF method.

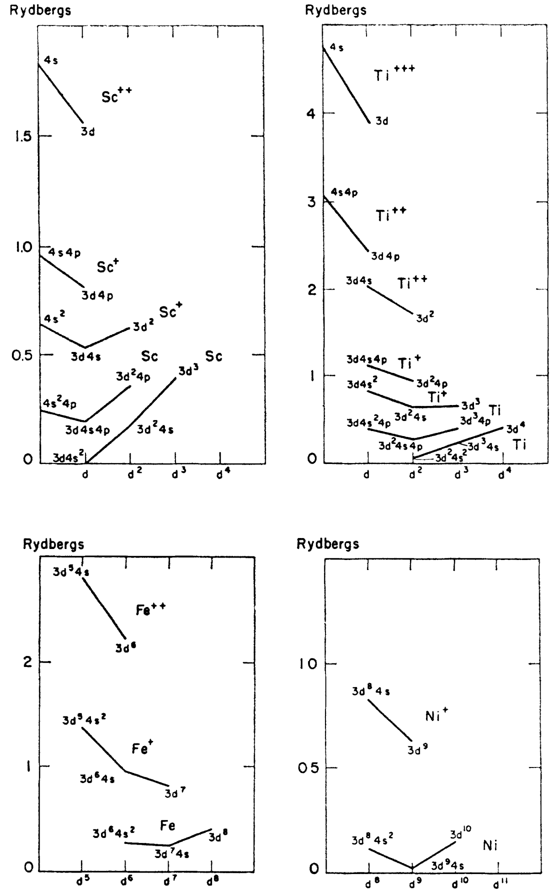

FIG. 4. E_{av} for a number of configurations of atoms and ions of Sc, Ti, Fe, and Ni, as a function of number of d electrons, computed from experiment. From Ref. 8, Vol. 1, p. 381.

VI. COMPARISON OF NONINTEGRAL OCCUPATION NUMBERS WITH EXPERIMENT

We now understand the calculations which have been made well enough so that we can start comparing the results with experiment. As a preliminary, and for general interest, we show in Fig. 4 a figure prepared by the senior author a number of years ago[14] to illustrate the experimental situation regarding the average energies E_{av} found in the $3d$ transition atoms. Experimental energy levels were described as well as possible by fitting to them values of E_{av} and of the various atomic integrals involved in the multiplet separations, regarded as empirical parameters, using methods described in Ref. 8. As one will see from Fig. 4, this was done for a number of configurations of several transition-group atoms and ions, and E_{av} was plotted as a function of the parameter which we are calling q in the present paper. Calculated points of course correspond only to integral values of q, and in Fig. 4 they are connected by straight lines, rather than being fitted to smooth curves.

Theoretical curves were not available when Fig. 4 was prepared, with which to make comparison. Now, however, curves of E_{av} as a function of q, such as we have in Fig. 1, represent theoretical curves to compare with the particular cases of the configurations $3d^{n+x}4s^{2-x}$ shown in Fig. 4. If the theory agreed perfectly with experiment the calculated points found for integral values of $q=n+x$ in Fig. 1 would agree with the values shown in Fig. 4 (or in corresponding figures for the atoms not included in Fig. 4). It is clear that in a general way the calculations agree with experiment, the theoretical curves of E_{av} as a function of q having minima between the configurations $3d^n4s^2$ and $3d^{n+1}4s$ in Fig. 1, which seems to agree with the experimental behavior of the curve for Ni shown in Fig. 4 although Fig. 4 indicates that the minimum of the experimental Ni curve lies closer to $3d^94s$ than to $3d^84s^2$.

Though we have not made detailed calculations for any atoms except Co and Ni, still we can make estimates regarding the behavior of the earlier members of the $3d$ transition series. From Fig. 4, it would appear that the minimum of the curve for E_{av} as a function of x should move to the left as we go to the lighter atoms, passing to the left of $x=0$ by the time we get down to Sc and Ti. We can investigate this point from Mann's calculations for the configurations $3d^n4s^2$, from Ref. 6 and from the results of the present paper. From those calculations we can find $E_{3d}'-E_{4s}'$ for these occupation numbers. Since this quantity measures the initial slope of the curve of $E_n(x)$ versus x, of Eq. (14), at $x=0$, we should expect that, as we go to the lighter atoms, the quantity would change from the negative value which we have for Co and Ni, indicating that the envelope curve is sloping downward at $x=0$, to a positive value, indicating an upward slope, leading to a minimum of the curve corresponding mathematically to negative values of x. A tabulation to test this hypothesis is

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[14] J. C. Slater, Ref. 8, Vol. 1, p. 381. We also call the attention of the reader to the interesting paper on a similar subject by C. R. Claydon and K. D. Carlson, J. Chem. Phys. **49**, 1331 (1968), which appeared too late to be considered in our discussion in the present paper.

given in Table IV, in which we list values of E_{3d}, E_{4s}, E_{3d}' and E_{4s}', as found from Mann's integrals, for each of the configurations for which he has made calculations, including those reported in the present paper and in Ref. 6.

TABLE IV. One-electron energies E_i and E_i', from Eqs. (6) and (11), for the $3d$ and $4s$ orbitals of elements from Sc to Zn, determined from calculations of Mann in Ref. 6 and from present work. Integrals are computed by the HHF method for the configurations tabulated. Energies in Ry.

		E_{3d}	E_{4s}	E_{3d}'	E_{4s}'
Sc	$3d4s^2$	−0.6874	−0.4202	−0.1455	−0.1918
Ti	$3d^24s^2$	−0.8116	−0.4438	−0.2013	−0.2035
V	$3d^34s^2$	−0.9224	−0.4649	−0.2504	−0.2139
Cr	$3d^54s$	−0.6450	−0.4151	0.0144	−0.1793
Mn	$3d^54s^2$	−1.1223	−0.5027	−0.3372	−0.2322
Fe	$3d^64s^2$	−1.2157	−0.5203	−0.3769	−0.2407
Co	$3d^{7.0}4s^{2.0}$	−1.3061	−0.5372	−0.4149	−0.2488
	$3d^{7.2}4s^{1.8}$	−1.2094	−0.5204	−0.3303	−0.2378
	$3d^{7.4}4s^{1.6}$	−1.1157	−0.5037	−0.2489	−0.2268
	$3d^{7.5}4s^{1.5}$	−1.0700	−0.4953	−0.2095	−0.2214
	$3d^{7.6}4s^{1.4}$	−1.0251	−0.4869	−0.1709	−0.2160
	$3d^{7.8}4s^{1.2}$	−0.9379	−0.4701	−0.0965	−0.2053
	$3d^{8.0}4s^{1.0}$	−0.8540	−0.4534	−0.0259	−0.1948
	$3d^{8.5}4s^{0.5}$	−0.6610	−0.4116	0.1325	−0.1694
	$3d^{8.8}4s^{0.2}$	−0.5578	−0.3870	0.2138	−0.1551
	$3d^{9.0}$	−0.4948		0.2616	
Ni	$3d^{8.0}4s^{2.0}$	−1.3942	−0.5536	−0.4516	−0.2567
	$3d^{8.2}4s^{1.8}$	−1.2931	−0.5361	−0.3622	−0.2451
	$3d^{8.4}4s^{1.6}$	−1.1949	−0.5185	−0.2761	−0.2336
	$3d^{8.5}4s^{1.5}$	−1.1469	−0.5097	−0.2342	−0.2279
	$3d^{8.6}4s^{1.4}$	−1.0997	−0.5009	−0.1932	−0.2222
	$3d^{8.8}4s^{1.2}$	−1.0077	−0.4832	−0.1138	−0.2109
	$3d^{9.0}4s^{1.0}$	−0.9190	−0.4653	−0.0380	−0.1997
	$3d^{9.5}4s^{0.5}$	−0.7131	−0.4203	0.1341	−0.1723
	$3d^{9.8}4s^{0.2}$	−0.6014	−0.3929	0.2244	−0.1563
	$3d^{10.0}$	−0.5324		0.2786	
Cu	$3d^94s^2$	−1.4804	−0.5695	−0.4871	−0.2643
	$3d^{10}4s$	−0.9825	−0.4770	−0.0497	−0.2044
Zn	$3d^{10}4s^2$	−1.5651	−0.5850	−0.5217	−0.2718

From Table IV we first note that E_{3d} lies below E_{4s} in each case, verifying the difficulty which we pointed out in Sec. I that if we use the Hartree–Fock criterion the electrons will go into the state of lowest E_i. On the other hand, E_{3d}' lies above E_{4s}' in Sc $3d4s^2$ and Ti $3d^24s^2$, so that the initial slope of the envelope curve for these cases, equal to $E_{3d}'-E_{4s}'$, will be positive, indicating that the minimum will come for negative x as in Fig. 4, or for q less than n. As we get to heavier atoms with configuration $3d^n4s^2$, the quantity $E_{3d}'-E_{4s}'$ changes sign and becomes increasingly negative, indicating that the minimum of the curve moves to larger positive x values.

The case of Cr is an exception in the table, since for this atom we have calculations only for the configuration $3d^54s$, or $3d^{n+1}4s$, so that the energies are computed for this configuration. For this case, $E_{3d}'-E_{4s}'$ is positive, but this now indicates the slope of the curve at the configuration $3d^54s$, so that the minimum energy comes at a value of q less than that appropriate for this configuration, but presumably greater than for the configuration $3d^44s^2$. We note that the case of Cr $3d^54s$ shows a behavior similar to Co $3d^84s$, Ni $3d^94s$, and Cu $3d^{10}4s$, shown in Table IV.

The general behavior of the curves, then, is in agreement with experiment, but when we come to examine the results more quantitatively, the situation is not as good. Thus, from Mann's calculation, as given in Table I, we find that E_{av} for Co $3d^84s$ lies 0.0084 Ry above E_{av} for $3d^74s^2$. We can find experimental values of E_{av}. The calculations used in constructing Fig. 4 were part of a rather extensive study of the experimental energy levels of the multiplet states of the $3d$ transition atoms, which was never published in detail, but in that study it was found that the experimental value of E_{av} for Co $3d^84s$ was in fact 0.0534 Ry below $3d^74s^2$. Hence there is a discrepancy of $0.0084+0.0534=0.0618$ Ry between theory and experiment, the calculated energy of $3d^84s$ lying too high in comparison with $3d^74s^2$ to agree with experiment. A similar situation is found for Ni, where the value of E_{av} for $3d^94s$, as computed by Mann from the HHF method, lies too high in comparison with the $3d^84s^2$ by the amount 0.0703 Ry, if we accept the experimental values. In each case, the experimental values indicate that a curve, like Fig. 1, giving E_{av} as a function of q, should have its minimum at considerably greater values of q than are found from the HHF calculation, for agreement with experiment.

It need not trouble us very much that we do not have better agreement. It is a well-known fact that the simple theory of multiplet separations, based on computing the various integrals from the HHF method and computing the positions of the various multiplets from these integrals by the methods outlined in Ref. 8, does not give results which are in very good quantitative agreement with experiment, though qualitatively it is quite good. The reason of course is that the HHF method is only a first approximation, to be corrected by some hypothetical discussion of correlation energy, and these correlation corrections are large enough to modify the multiplet separations quite strongly. It need not surprise us that similar difficulties should appear in the matter of E_{av}.

The reader might well ask, are these discrepancies of the order of 0.06 or 0.07 Ry of significant size? To answer this question, we give in Figs. 5 and 6 comparison of the experimental and computed multiplets for the configurations being considered, for Co and Ni, respectively. Calculated values are plotted as abscissas, experimental values as ordinates, so that if there were agreement between theory and experiment, the points would lie on a straight line with 45° slope. The calculated F and G integrals concerned in the multiplet separations are taken from the calculations by the HHF method, though the integrals would be very nearly the same if calculations from the XKSG or Xα method were used instead. But the calculated value of E_{av} for the configuration with a single $4s$ electron is arbitrarily

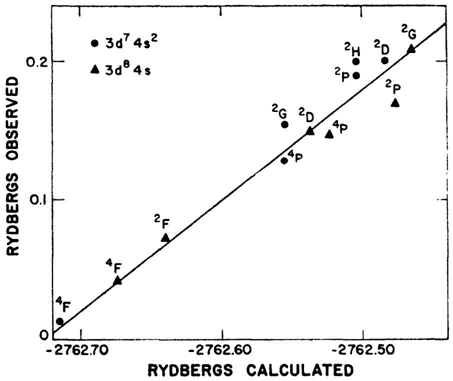

FIG. 5. Observed energies of multiplets in $3d^74s^2$ and $3d^84s$ configurations of Co, as ordinates, plotted against calculated energies of same multiplets, computed from HHF integrals appropriate to $n=7.63$, as in Fig. 8.

decreased by the amount 0.0618 or 0.0703 Ry, respectively, to make the difference of calculated E_{av}'s for the two configurations agree with experiment.

It is clear that though there is considerable scatter of the calculated points, they still tend to lie fairly close to a straight line. The straight line has a slope around 0.80, rather than unity, a common feature of such calculations. It indicates that the values of the F and G parameters required to fit the experiments are only about 0.80 times the calculated values, the discrepancy being a measure of the correlation corrections which were mentioned earlier. But the essential point here is not the slope of the curve but whether the points representing the multiplets arising from the two configurations $3d^74s^2$ and $3d^84s$, or $3d^84s^2$ and $3d^94s$, respectively, fall on a single curve or not. If E_{av} were given the HHF value, rather than the modified value which we have used in constructing Figs. 5 znd 6, the points representing the configurations $3d^84s$ or $3d^94s$, respectively, shown by crosses in the figures, would be shifted to the right in the diagram by amounts corresponding to 0.06 or 0.07 Ry. This would clearly be of such magnitude that it would cause the points representing the two configurations to lie on two quite distinct lines, rather than falling fairly satisfactorily on the same line, as they do in Figs. 5 and 6. In other words, comparison between theory and experiment is capable of deciding on the correct energy differences between the E_{av}'s of the two configurations with an accuracy great enough to show that the HHF calculations must be corrected, even though the spread of the multiplets arising from either configuration is a good deal greater than the difference between the average energies of the two.

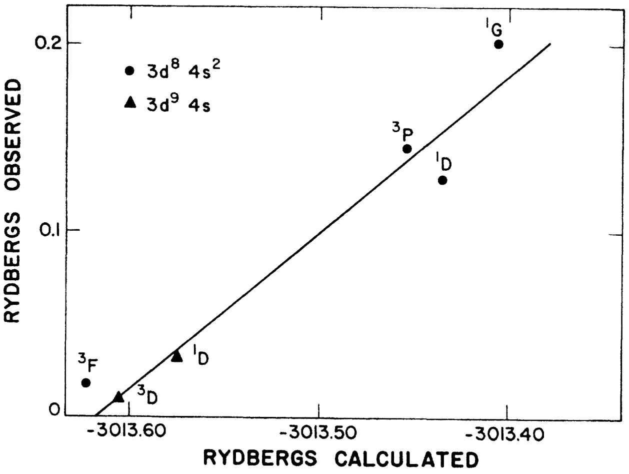

FIG. 6. Observed energies of multiplets $3d^84s^2$ and $3d^94s$ configurations of Ni, as ordinates, plotted against calculated energies of same multiplets, computed from HHF integrals appropriate to $n=8.63$, as in Fig. 9.

It is now interesting to see what the comparison would have shown if we had used some form of the statistical exchange approximation, as we would have done in an energy-band calculation, rather than carrying through the HHF calculation. We would have found $E_{3d}-E_{4s}$ as computed from eigenvalues, say, of the XKSG method, but we would not have had the HHF calculation of $E_{3d}'-E_{4s}'$. Suppose we had tentatively adopted the hypothesis that it would not be a bad approximation to substitute $(E_{3d}-E_{4s})_{\text{XKSG}}$ for $(E_{3d}'-E_{4s}')_{\text{HHF}}$; in our discussion of Fig. 2 in Sec. IV, we pointed out that there was a resemblance between these curves. We could then invert our procedure, and instead of getting $E_{3d}'-E_{4s}'$ by differentiating the HHF curve of E_{av} as a function of x, we could construct a curve of E_{av} as a function of x by integrating $E_{3d}-E_{4s}$ from the XKSG method. Now it is rather easy to calculate the values of this quantity for the XKSG method by a quadratic approximation. Thus, we find to a good approximation

$$\begin{aligned}(E_{3d}-E_{4s})_{\text{XKSG}}&=-0.1782+0.2850(q\text{-}7)\\&\quad-0.0600(q\text{-}7)^2 \quad \text{for Co},\\&=-0.2170+0.3090(q\text{-}8)\\&\quad-0.0640(q\text{-}8)^2 \quad \text{for Ni}. \qquad (20)\end{aligned}$$

If we integrate these expressions with respect to q to get an average energy, we find

$$\begin{aligned}E_{\text{av}}&=E_0-0.1782(q\text{-}7)+0.1425(q\text{-}7)^2-0.0200(q\text{-}7)^3\\&\qquad \text{for Co},\\&=E_0-0.2170(q\text{-}8)+0.1545(q\text{-}8)^2-0.0213(q\text{-}8)^3\\&\qquad \text{for Ni}. \qquad (21)\end{aligned}$$

In Eq. (21) E_0 stands for the average energy when q equals 7 or 8, respectively.

For the energies of the configurations $3d^84s$ or $3d^94s$‘ respectively, we can now substitute q-7 or q-8 = 1 in Eq. (21). We then find

$$\begin{aligned}E(3d^84s)-E(3d^74s^2)&=-0.0557\text{ Ry}, \quad \text{for Co}\\E(3d^94s)-E(3d^84s^2)&=-0.0838\text{ Ry} \quad \text{for Ni}. \qquad (22)\end{aligned}$$

The experimental values are -0.0534 Ry for Co, as was stated earlier, and -0.0803 Ry for Ni. The agreement between the values of Eq. (22) and experiment is surely fortuitously good. Nevertheless it shows that if we were to use one-electron eigenvalues determined by the XKSG method, in place of the energies E_i' found from the HHF method, we should have found energy separations between the configurations in the Co and Ni atoms in very close agreement with experiment. This suggests, in other words, that we may well have one of those approximate cancellations of errors which frequently seem to help in energy-band theory, and that it may well be empirically justified to use eigenvalues of the Schrödinger equation using an exchange not far from the XKSG value to determine energy values in an atom containing $3d$ and $4s$ electrons, or presumably also in a crystal containing the energy bands derived from these atomic levels.

In the discussion which we have just given concerning the agreement with experiment, we have assumed that we should use the integrals appropriate to the configuration $3d^74s^2$ of Co, for instance, for calculating the multiplets of that configuration, and those appropriate to $3d^84s$ for calculating the multiplets of that configuration. This is a desirable method of procedure, but it could well be too complicated in actual practice. In particular, in an energy-band calculation, we find a single set of wave functions, which must serve as well as possible for discussing both the $3d$ and the $4s$ parts of overlapping energy bands. Let us consider, from an atomic point of view, whether we could find such a set of wave functions and integrals. We shall ask the question, is it possible to find a single set of orbitals and integrals, computed for some fractional occupation number between $3d^74s^2$ and $3d^84s$, which will give a satisfactory description of the whole spectrum, including the multiplets arising from both configurations? We shall base our discussion on the HHF method, but remember that the discussion which we have just given shows that the results will have to be modified considerably to bring them into agreement with experiment.

To answer our question, we shall compute the energies of all multiplets in the configurations $3d^74s^2$ and $3d^84s$ of Co, or in the configurations $3d^84s^2$ and $3d^94s$ of Ni, using integrals calculated by the HHF method for different n values. We shall plot these energies as functions of n, and shall examine the resulting plots to see if there is some value of n for which the spectrum of excited states would agree with experiment. The energies of these multiplets depend on two quantities, E_{av} and the collection of F and G integrals which determine the multiplet separations from E_{av}. The quantities F and G do not vary much with n, so that these separations will not depend strongly on n. However, as we shall now show, the average energies E_{av} of the two configurations under consideration vary strikingly as n changes, one configuration moving rapidly upward, the other downward. Hence we cannot possibly match the calculated and the observed multiplets unless the difference between the average energies of the configurations is given approximately in agreement with experiment.

Let us then investigate these average energies. In Eq. (16), we have given the average energy $E_n(x)$ of the Co atom, determined by the HHF method, as a function of n, the number of $3d$ electrons in the HHF problem for which the integrals were computed, and of $x=q-n$, where q is the number of $3d$ electrons in the atom. In Fig. 3 we plotted the information from this equation, by giving parabolas showing the energy as a function of q, for several different values of the quantity n. We shall now show some of the same information in a different way, more appropriate to our present question. In Fig. 7 we show $E_n(x)$ from Eq. (16), as a function of n, for Co, for the configurations given by $q=7$, 8, and 9, or for $x=7\text{-}n$, $8\text{-}n$, $9\text{-}n$, respectively. The equations from which Fig. 7 was constructed were set up by substituting $x=7\text{-}n$, etc., in Eq. (16) giving in each case a function of n. Similar curves for Ni are much like those of Fig. 7. We can also find values of the various integrals, such as $F^2(3d,3d)$, etc., which come into the calculations of the multiplet energies, as functions of n, from our HHF calculations, and can use these integrals, together with the values of E_{av} shown in Fig. 7, to find the energies of each individual multiplet of each configuration $3d^74s^2$ or $3d^84s$, as functions of n. We show the resulting calculation for the multiplets of Co in Fig. 8, and a similar set of calculations for Ni in Fig. 9.

When we consider Fig. 7, we must remember the minimum principle of wave mechanics. If we used the

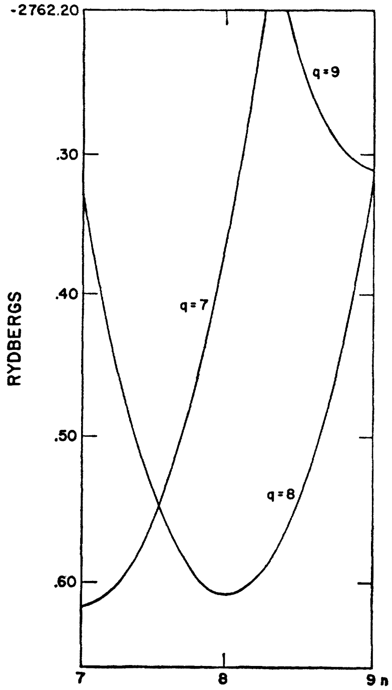

FIG. 7. E_{av} of $3d^74s^2$, $3d^84s$, and $3d^9$ configurations of Co, as function of n, the number of $3d$ electrons for which the HHF calculation was made. From Eq. (16), setting $q=n+x=7, 8$, and 9.

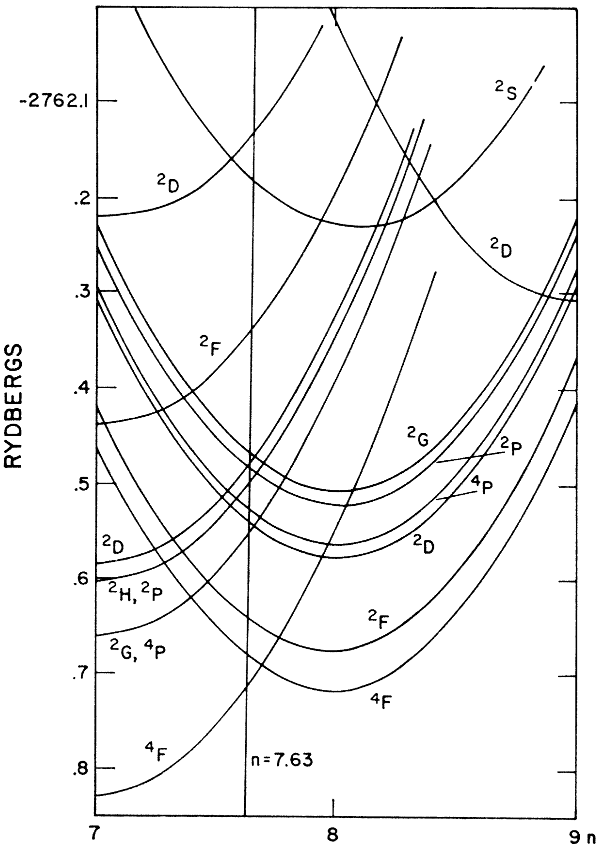

FIG. 8. Multiplets of $3d^7 4s^2$, $3d^8 4s$, and $3d^9$ configuations of Co, as function of n, the number of $3d$ electrons for which the HHF calculation was made. The line at $n=7.63$ intersects the various curves at the energies marked "calculated" in Fig. 5.

orbitals and integrals appropriate to Co $3d^7 4s^2$ to calculate the average energy of the multiplets of $3d^7 4s^2$, we should get the lowest possible value for this average energy; we should find a higher value for the same energy expression if we used the orbitals and integrals appropriate to $3d^8 4s$, and still higher values if we used those for $3d^9$. Similarly if we were finding the energy of $3d^8 4s$ we should get a lower energy if we used the orbitals and integrals appropriate to that configuration than if we used the integrals for either $3d^7 4s^2$ or for $3d^9$, etc. These facts are clearly illustrated in Fig. 7, where each curve has a minimum for $n=q$. This fact appears mathematically when we substitute $x=q-n$ in Eq. (16), and write $E_n(x)$ as a polynomial in $q-n$; the linear term automatically vanishes. From Figs. 8 and 9 we note that the curves for the various multiplets arising from one configuration shift upward or downward as we change n, very much in the same way as does the curve for E_{av}; this is a result of the fact that the F and G integrals responsible for the multiplet separations from E_{av} vary only slightly with n. Thus, the set of multiplets arising from one configuration shifts upward and downward very rapidly with respect to those from another configuration, as we change the orbitals, on account of the sensitivity of the average energy of the configuration to the value of n for which the integrals are computed.

We can now use Figs. 8 and 9 to answer our question: it is possible to find a single value of n, such that the multiplets computed from the orbitals and integrals found for this value of n will represent the experimental spectrum satisfactorily? What we must do is locate a vertical line in the figures, corresponding to a particular n, such that the points of intersection between this vertical line and the curves representing the multiplets of both configurations will agree well with experiment. Obviously the important thing is to locate the value of n so that the relative positions of the two sets of multiplets will be correct; the absolute value of the energy is less important, when our problem is to study the spectrum. In order to do this, from our previous discussion, we need merely have the energy differences between the E_{av} values for the configurations $3d^7 4s^2$ and $3d^8 4s$ for Co, or $3d^8 4s^2$ and $3d^9 4s$ for Ni, agree with the experimental values. We can read off this value of n for Co from Fig. 7, or compute it from the equations of Eq. (16), and can use Eq. (17) for Ni. When we do this, we find that the required values of n are 7.63 for Co, and 8.63 for Ni. We have drawn vertical lines in Figs. 8 and 9 corresponding to these values of n, and we see by comparison with Figs. 5 and 6 that the

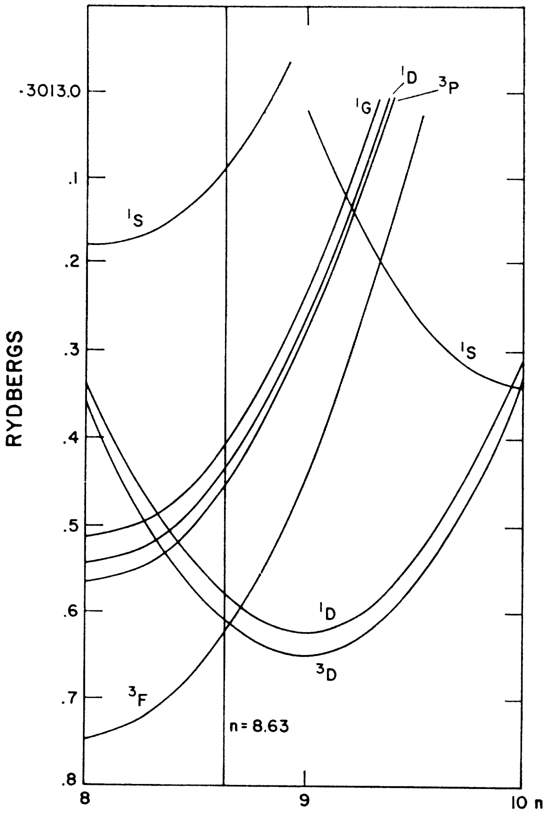

FIG. 9. Multiplets of $3d^8 4s^2$, $3d^9 4s$, and $3d^{10}$ configurations of Ni, as function of n, the number of $3d$ electrons for which the HHF calculation was made. The line at $n=8.63$ intersects the various curves at the energies marked "calculated" in Fig. 6.

multiplet levels come in the right relation to each other along these lines. As a matter of fact, the calculated multiplet energies plotted in Figs. 5 and 6 were actually found by the procedure just mentioned from Figs. 8 and 9. In this way, then, we see that we can give a physical meaning to nonintegral occupation numbers for an individual atom, in a way not considered earlier in this paper: these numbers yield a charge distribution, a set of eigenfunctions, and a set of integrals, which can be used satisfactorily for calculation of the multiplets of more than one of the lower configurations of the atom, without having to use separate values of the integrals for each configuration. We note that the nonintegral configurations $3d^{7.63}4s^{1.37}$ for Co, $3d^{8.63}4s^{1.37}$ for Ni, which seem to give the best agreement with the optical spectrum, are not far from the values $3d^{7.46}4s^{1.54}$ and $3d^{8.52}4s^{1.48}$ quoted in Sec. IV giving the minimum energy of the HHF method, though they are not exactly equal to these values. We have no explanation for this discrepancy, beyond the obvious fact that the use of nonintegral configurations is not a very quantiative concept, though it is useful qualitatively. In the next section, on spin-polarized calculations, we shall find still further nonintegral configurations for Co and Ni, which do not agree exactly with either of the values which we have just quoted.

VII. THE SPIN-POLARIZED CALCULATION FOR ATOMS

The calculation that we have been making so far in the present paper is really only a poor approximation to the true state of affairs, because we are averaging over the multiplet structure. We know in fact that as we increase the number of $3d$ electrons, from 1 to 5, we get multiplets of larger and larger multiplicity, which according to Hund's rule are the lowest multiplets of the system. It is much more realistic, if we are interested in the true ground state of the atoms, to take account of this multiplet structure. To do this in detail, we should make separate calculations for each multiplet, but we may make a good approximation by using spin-polarized spin orbitals, which have been discussed by the senior author in several papers.[15] In these references, it was shown how one can set up formulas for the average energy of multiplets of each multiplicity, in an atom. For the present purpose, we consider the multiplets of the highest possible multiplicity. We now set up the required formulas for the average energy of the multiplets of this highest multiplicity, and then we treat the resulting formula according to the methods which we have been describing for the nonmagnetic case in Secs. II–VI.

We refer the reader to Ref. 15 for the method used in deriving the average energy. The case taken up in those references was a restricted one, in that only one partially filled shell of electrons was considered. In the present case we need more than one partially filled shell, and in fact it is just as simple to set up the energy formula for the general case where all shells are partially occupied.[16] Let us proceed as in Sec. III but let us now refer to a shell as consisting of those spin-orbitals with given n, l, different m_l, but a given m_s, either $\frac{1}{2}$ or $-\frac{1}{2}$. If we need to describe it, we can do so by using such symbols as $3d\uparrow$, $3d\downarrow$, where $\uparrow$ and $\downarrow$ refer to the spin orientations. We assume different orbitals for different spins; that is, the radial wave function will depend on n, l, and m_s, though not on m_l.

We then find that we can still use Eq. (1) for the average energy, provided we use different definitions for Eq. (2) for the two-electron integrals. In place of Eq. (2), we must assume

$$\begin{aligned}(i,i)&=F^0(n_il_im_{\mathrm{si}};n_il_im_{\mathrm{si}})\\&\quad-\sum_{k\neq0}\frac{c^k(l_i0;l_i0)}{2l_i}F^k(n_il_im_{\mathrm{si}};n_il_im_{\mathrm{si}}),\\(i,j)&=F^0(n_il_im_{\mathrm{si}};n_jl_jm_{\mathrm{sj}})\\&\quad-\delta(m_{\mathrm{si}}m_{\mathrm{sj}})\sum_k\frac{c^k(l_i0;l_j0)}{[(2l_i+1)(2l_j+1)]^{1/2}}\\&\quad\times G^k(n_il_im_{\mathrm{si}};n_jl_jm_{\mathrm{sj}}).\end{aligned}\qquad(23)$$

The reader can verify Eq. (23) in two cases. First, if we let there be equal numbers of electrons with $m_s=\frac{1}{2}$ and $-\frac{1}{2}$ in each shell, so that there is no spin polarization and the orbitals are independent of m_s, we can show that Eq. (23) reduces to Eq. (2). Secondly, if all of the shells except one are filled with electrons of both spins, but only one is partially filled, Eq. (23) reduces to Eq. (8) of Ref. 15 (II).

We can now vary one of the spin orbitals in Eqs. (1) and (23), set the variation of average energy equal to zero, and hence find the analog of the Hartree–Fock equation for this orbital. The resulting equation is identical with Eq. (4), with the following exceptions. In each of the integrals, like $Y_k(n_il_i;n_jl_j/r_1)$, we must include also the quantum numbers m_{si}, m_{sj} among the quantum numbers on which the integrals depend. In the term involving $Y_k(n_il_im_{\mathrm{si}};n_il_im_{\mathrm{si}}/r_1)$, the denominator must be $2l_i$ rather than $4l_i+1$. The term involving $Y_k(n_il_im_{\mathrm{si}};n_jl_jm_{\mathrm{sj}}/r_1)$ is present only in case $m_{\mathrm{si}}=m_{\mathrm{sj}}$, and in that case it is twice as great as in Eq. (4).

Next we can find the one-electron energies, as E_i. This can be done, as before, either by multiplying the modified form of Eq. (4) by the complex conjugate of P_i and integrating, or by starting with the energy expression of Eq. (1) and subtracting from it an equivalent expression in which q_i is replaced by q_i-1. The result obtained by either method is the same as in Eq. (6), provided we use Eq. (23) for evaluating the integrals. Since we are assuming different orbitals and occupation numbers for different spins, the one-

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[15] J. C. Slater, Phys. Rev. **165**, 655 (1968); **165**, 658 (1968). These will be referred to as I, II respectively. J. C. Slater, J. Appl. Phys. **39**, 761 (1968).

[16] This fact was first pointed out to the senior author by G. F. Koster.

electron energies will depend on m_s. We can then proceed to vary the occupation numbers, as in Sec. III, and we again find that the condition for minimum energy is the equality of the modified one-electron energies E_i' for two states between which electrons can be interchanged, provided that in Eqs. (11) and (12) for the modified one-electron energies we use the integrals as in Eq. (23).

We can now apply these methods to the case of $3d$ atoms, which we have handled in the nonmagnetic approximation in the preceding sections. We can find the one-electron energies $E_{3d\uparrow}'$, $E_{3d\downarrow}'$, $E_{4s\uparrow}'$, $E_{4s\downarrow}'$, provided we know the occupation numbers of the various shells and the energy integrals. We start by assuming the results of Mann, from Ref. 6 and the present calculations. We assume, as in Ref. 15 (II), that the integrals depend only slightly on spin orientation. It was shown in that reference that if we use Mann's integrals, calculated from a nonmagnetic postulate, energy calculations for the spin-polarized case can be made with fair accuracy, and therefore we make that assumption. As for the occupation numbers, since we wish the multiplets of lowest energy and consequently highest multiplicity, we assume that spin orbitals with spin up are occupied in preference to spin down, as far as possible consistent with the exclusion principle.

When we make these assumptions, we find values of the one-electron energies $E_{3d\uparrow}'$, etc., given in Table V. The formulas from which these energies are calculated are given in the Appendix. In this table we give the assumed configuration, in terms of the occupation numbers of the four possible $3d$ and $4s$ states. We can now examine the resulting energies E_i', and we see that in several cases the one-electron energies are arranged in such an order that the assumed occupation number would in fact correspond to the lowest energy. Thus, in Sc, the one-electron energies, in order of increasing energy, are $4s\uparrow$, $4s\downarrow$, $3d\uparrow$, and $3d\downarrow$. This is in agreement with the assumed configurations, in which the $4s\uparrow$ and $4s\downarrow$ states are occupied with the maximum of one electron each, and the $3d\uparrow$ has one electron. In Cr, we find similarly that the $3d\uparrow$ and $4s\uparrow$ orbitals, which are assumed to be occupied, have energies below the $4s\downarrow$ and $3d\downarrow$, which are assumed to be empty. In Mn, which has the same occupation as Cr except for the electron in the $4s\downarrow$ state, the one-electron energies are again in the proper order, as they also are in Fe $(3d\uparrow)^5 3d\downarrow 4s\uparrow 4s\downarrow$. Finally, in Zn where all states are occupied, we again have agreement with the one-electron picture.

In the remaining cases, there are discrepancies for the cases of integral occupation numbers, which are removed by assuming nonintegral occupation numbers. Thus in Ti, the lowest one-electron energy is the $3d\uparrow$, which contains only two electrons in the assumed configuration. The $4s\uparrow$ and $4s\downarrow$ states both have higher one-electron energies. Let us then assume that we increase the occupation number of the $3d\uparrow$ and see what happens. We would naturally do this at the expense of the $4s\downarrow$, the highest state which might be occupied. We know from our previous work that as we shift electrons from a $4s$ state to a $3d$, the energy of the $3d$ state rapidly rises, much more rapidly than does that of the $4s$. Thus as the occupation number of the $3d\uparrow$

TABLE V. One-electron energies as defined in Eqs. (6), (11), and (23), for $3d$ and $4s$ orbitals of both spins, in spin-polarized energy levels for the atoms from Sc to Zn, determined from calculations of Mann in Ref. 6 and the present work. The integrals were determined from the nonspin-polarized case. Assumed configurations for the spin-polarized calculations are tabulated. Energies in Ry.

		$E_{3d\uparrow}'$	$E_{4s\uparrow}'$	$E_{4s\downarrow}'$	$E_{3d\downarrow}'$
Sc	$3d\uparrow 4s\uparrow 4s\downarrow$	−0.1617	−0.2006	−0.1830	−0.1034
Ti	$(3d\uparrow)^2 4s\uparrow 4s\downarrow$	−0.2563	−0.2198	−0.1873	−0.1242
V	$(3d\uparrow)^3 4s\uparrow 4s\downarrow$	−0.3515	−0.2369	−0.1908	−0.1330
Cr	$(3d\uparrow)^5 4s\uparrow$	−0.1663	−0.2178	−0.1407	+0.1950
Mn	$(3d\uparrow)^5 4s\uparrow 4s\downarrow$	−0.5503	−0.2682	−0.1962	−0.1241
Fe	$(3d\uparrow)^5 3d\downarrow 4s\uparrow 4s\downarrow$	−0.5641	−0.2689	−0.2125	−0.1998
Co	$(3d\uparrow)^5 (3d\downarrow)^2 4s\uparrow 4s\downarrow$	−0.5708	−0.2696	−0.2280	−0.2806
	$(3d\uparrow)^5 (3d\downarrow)^{2.2} 4s\uparrow (4s\downarrow)^{0.8}$	−0.4762	−0.2571	−0.2185	−0.2075
	$(3d\uparrow)^5 (3d\downarrow)^{2.4} 4s\uparrow (4s\downarrow)^{0.6}$	−0.3852	−0.2446	−0.2090	−0.1374
	$(3d\uparrow)^5 (3d\downarrow)^{2.5} 4s\uparrow (4s\downarrow)^{0.5}$	−0.3410	−0.2385	−0.2043	−0.1035
	$(3d\uparrow)^5 (3d\downarrow)^{2.6} 4s\uparrow (4s\downarrow)^{0.4}$	−0.2978	−0.2323	−0.1996	−0.0704
	$(3d\uparrow)^5 (3d\downarrow)^{2.8} 4s\uparrow (4s\downarrow)^{0.2}$	−0.2143	−0.2202	−0.1905	−0.0066
	$(3d\uparrow)^5 (3d\downarrow)^{3.0} 4s\uparrow$	−0.1348	−0.2083	−0.1814	0.0538
Ni	$(3d\uparrow)^5 (3d\downarrow)^3 4s\uparrow 4s\downarrow$	−0.5709	−0.2704	−0.2430	−0.3663
	$(3d\uparrow)^5 (3d\downarrow)^{3.2} 4s\uparrow (4s\downarrow)^{0.8}$	−0.4720	−0.2573	−0.2329	−0.2883
	$(3d\uparrow)^5 (3d\downarrow)^{3.4} 4s\uparrow (4s\downarrow)^{0.6}$	−0.3765	−0.2444	−0.2228	−0.2130
	$(3d\uparrow)^5 (3d\downarrow)^{3.5} 4s\uparrow (4s\downarrow)^{0.5}$	−0.3300	−0.2379	−0.2178	−0.1765
	$(3d\uparrow)^5 (3d\downarrow)^{3.6} 4s\uparrow (4s\downarrow)^{0.4}$	−0.2845	−0.2315	−0.2129	−0.1407
	$(3d\uparrow)^5 (3d\downarrow)^{3.8} 4s\uparrow (4s\downarrow)^{0.2}$	−0.1963	−0.2188	−0.2030	−0.0715
	$(3d\uparrow)^5 (3d\downarrow)^{4.0} 4s\uparrow$	−0.1119	−0.2062	−0.1932	−0.0006
Cu	$(3d\uparrow)^5 (3d\downarrow)^4 4s\uparrow 4s\downarrow$	−0.5649	−0.2711	−0.2576	−0.4572
	$(3d\uparrow)^5 (3d\downarrow)^5 4s\uparrow$	−0.0835	−0.2044	−0.2044	−0.0708
Zn	$(3d\uparrow)^5 (3d\downarrow)^5 4s\uparrow 4s\downarrow$	−0.5531	−0.2718	−0.2718	−0.5531

is increased, with compensating decrease of that of the $4s\downarrow$, the energy $E_{3d\uparrow}'$ will rapidly rise, not only up to the value of the $4s\uparrow$, but above it, to achieve equality with the energy of the $4s\downarrow$. When we have achieved this equality, we shall get the minimum energy for the system. This will come for an occupation number of something over 2 in the $3d\uparrow$, with a correspondingly decreased occupation number in the $4s\downarrow$. We may anticipate that this tendency will be carried even further in V, the number of electrons in $4s\downarrow$ being a good deal smaller than unity, approaching the situation of Cr, with no electrons at all in the $4s\downarrow$.

In the elements from Co to Cu, we have calculations in Table V assuming nonintegral occupation numbers, from which we can understand the situation in detail. In Co $(3d\uparrow)^5$ $(3d\downarrow)^2$ $4s\uparrow 4s\downarrow$, the energy of $3d\downarrow$ lies below that of $4s\uparrow$ and $4s\downarrow$. Hence we must assume that electrons will be transferred from $4s\downarrow$ to $3d\downarrow$. As this is done, the values given in Table V show that the energy of $3d\downarrow$ will rapidly rise, achieving equality with $4s\downarrow$ at approximately the configuration $(3d\uparrow)^5$ $(3d\downarrow)^{2.16}$ $4s\uparrow$-$(4s\downarrow)^{0.84}$. This situation is shown in Fig. 10, in which the values of E' for all four states are plotted as a function of x, where the configuration is $(3d\uparrow)^5$ $(3d\downarrow)^{2+x}$ $4s\uparrow$-$(4s\downarrow)^{1-x}$. Similar curves are given in Fig. 11 for Ni and Cu, which lead to configurations of approximately $(3d\uparrow)^5$ $(3d\downarrow)^{3.39}$ $4s\uparrow(4s\downarrow)^{0.61}$ for Ni, and $(3d\uparrow)^5$ $(3d\downarrow)^{4.59}$ $4s\uparrow(4s\downarrow)^{0.41}$ for Cu. We note that the numbers of d electrons given in Co, Ni, and Cu by this spin-polarized calculation are 7.16, 8.39, and 9.59, to be compared with values for Co and Ni of 7.46 and 8.52 as given by the energy minimum of the nonspin-polarized HHF calculations, and 7.63 and 8.63 given by the comparison with the observed optical spectrum. In other words, these different methods of calculations are not in exact agreement with each other, but they indicate similar trends from element to element.

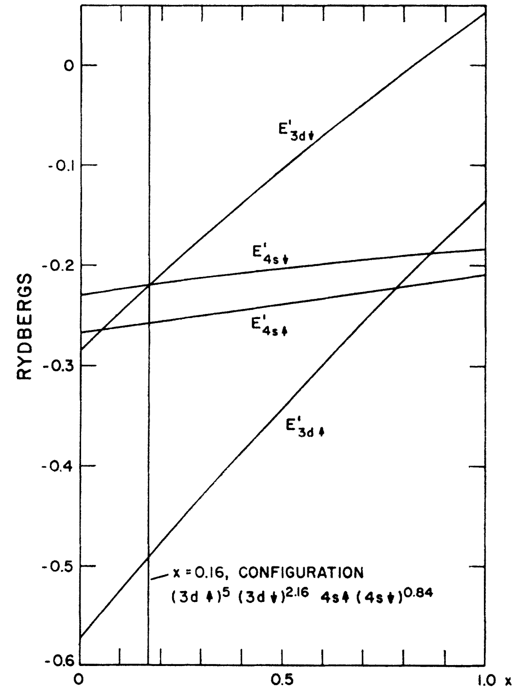

FIG. 10. Energies $E_{3d\uparrow}'$, $E_{3d\downarrow}'$, $E_{4s\uparrow}'$, $E_{4s\downarrow}'$ for spin-polarized case of Co, as a function of x.

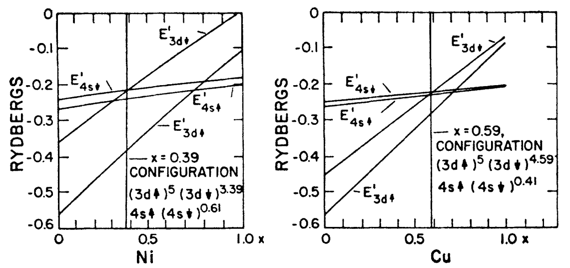

FIG. 11. Energies $E_{3d\uparrow}'$, $E_{3d\downarrow}'$, $E_{4s\uparrow}'$, $E_{4s\downarrow}'$ for spin-polarized cases of Ni and Cu, as a function of x.

Another interesting way to indicate the results of the spin-polarized calculations graphically is given in Fig. 12. Here in (a) we give the values of E' for the four states $3d\uparrow$, $3d\downarrow$, $4s\uparrow$, and $4s\downarrow$, for all the elements from Ca to Zn, for the configurations $3d^n4s^2$, in which both $4s$ levels are filled and the $3d$ electrons are distributed by putting as many as possible into the $3d$ state. (We interpolate for Cr, for which we have no calculations.) The way in which the separation between $3d\uparrow$ and $3d\downarrow$ increases from Ca to Mn, and then decreases as the $3d$ shell is filled, is very striking. To indicate the trend as the number of $3d$ electrons builds up beyond n, and the number of $4s$ electrons decreases, we show in Fig. 12(b) the corresponding curves, as far as we have the necessary information, for the configurations $3d^{n+1}4s$. (Here we must interpolate for Mn and Fe.) This shows the rapid increase in the energy of the $3d$ states, far greater than of the $4s$ states, when electrons are transferred to the $3d$ orbital, a tendency which is shown in more detail in Figs. 10 and 11. The greatest separation between $E_{3d\uparrow}'$ and $E_{3d\downarrow}'$ in this case comes for Cr, with its half-filled d shell.

We cannot of course be sure that the details of these spin-polarized calculations will be retained when integrals calculated for the spin-polarized problem are used. However, the general trends must certainly be similar to what we have indicated. We hope to return to this spin-polarized problem in a later paper. We will certainly expect that the situation described here will be found in a more accurate calculation, namely a

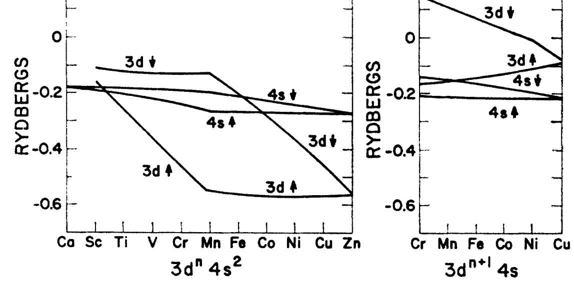

FIG. 12. (a). Energies $E_{3d\uparrow}'$, $E_{3d\downarrow}'$, $E_{4s\uparrow}'$, $E_{4s\downarrow}'$, for elements Ca to Zn, for spin-polarized configurations $3d^n4s^2$. (b). Same as Fig. 12(a) for elements Cr to Cu, for configuration $3d^{n+1}4s$.

break in properties halfway through the $3d$ group, at Cr, with the occupation number of $4s_\downarrow$ gradually decreasing from unity to zero as we go through the sequence from Sc to Cr, and varying in the same general way as we go through the sequence from Mn to Cu (though the number does not seem to be quite zero at Cu).

VIII. GENERAL SIGNIFICANCE OF THE MODIFIED ONE-ELECTRON ENERGIES

We have seen in the preceding sections that the modified one-electron energies $\partial E_{\text{av}}/\partial q_i = E_i'$ of Eq. (9) have an important property: if we have two partially filled shells in an atom, the condition for equilibrium between them is that they have equal modified one-electron energies. Since these quantities E_i' are rapidly changing functions of the occupation numbers q_j, this equilibrium condition can be satisfied only for specified q_j's so that it determines the occupation numbers in the state of lowest energy. Thus equalizing the E'_i's of the two shells which can interchange electrons is mathematically equivalent to minimizing the energy with respect to the occupation numbers, and presumably it will be easier to accomplish with numerical computing methods.

Are there other useful properties of these energies? They have interesting mathematical properties, which follow at once from their definitions. Thus, let us ask what is the energy required to remove an electron from the ith shell. This is the energy of an ion with $q_i - 1$ electrons in this shell, minus the energy of the atom with q_i electrons in the shell. Thus it is

$$E_{\text{av}}(q_i - 1) - E_{\text{av}}(q_i) = -\int_{q_i-1}^{q_i} \frac{\partial E_{\text{av}}}{\partial q_i} dq_i = -\int_{q_i-1}^{q_i} E'_i(q_i) dq_i. \quad (24)$$

This is simply the negative of the average value of E_i' averaged over the range of q_i's from $q_i - 1$ to q_i.

In a similar way, we may find the excitation energy, the energy of an atom with $q_i - 1$ electrons in the ith shell, $q_j + 1$ in the jth shell, minus the energy of the atom with q_j, q_j electrons in the two shells. This is the energy required to excite an electron from the ith shell to the jth. It is

$$E_{\text{av}}(q_i - 1,\ q_j + 1) - E_{\text{av}}(q_i, q_j) = \int_{q_i, q_j}^{q_i - 1, q_j + 1} \left(\frac{\partial E_{\text{av}}}{\partial q_i} dq_i + \frac{\partial E_{\text{av}}}{\partial q_j} dq_j \right), \quad (25)$$

which is a line integral in a two-dimensional space in which q_i and q_j are variables. We can rewrite this in the form

$$E_{\text{av}}(q_i - 1,\ q_j + 1) - E_{\text{av}}(q_i, q_j) = \int_{q_i, q_j}^{q_i - 1, q_j + 1} \left(E_i' \frac{dq_i}{ds} + E_j' \frac{dq_j}{ds} \right) ds, \quad (26)$$

where ds is an element of distance in the two-dimensional space. The integral will be independent of the path. It we choose a path such that $dq_i + dq_j = 0$, we can then reduce it to an integral with respect to dq_i alone. Then we have

$$E_{\text{av}}(q_i - 1,\ q_j + 1) - E_{\text{av}}(q_i, q_j) = \int_{q_i - 1}^{q_i} (E_j' - E_i') dq_i. \quad (27)$$

This is essentially the case which we took up in Secs. III and IV. Here, however, we are carrying out an average of $E_j' - E_i'$ over a finite range of occupation numbers, rather than using the vanishing of $E_j' - E_i'$ as a condition of equilibrium, or of vanishing excitation energy from the ith to the jth state.

In the very similar cases of Eqs. (24) and (27), we note that there are two ways in which the modified one-electron energies E_i' and E_j' can depend on the occupation numbers. First, they depend explicitly on the q's, as we see from Eq. (11). But secondly, they also depend indirectly on the q's because it is assumed that at each set of q's, the orbitals have been varied to minimize the energy for the appropriate q's. When we take account of these two sorts of dependence on the q's, we make a correct calculation of ionization or excitation energy between a ground state and an ionized or excited state, in which the energy of each has been determined by the HHF method.

However, we may simplify by considering only the dependence of the E_i''s explictly on the q's, disregarding the change of orbitals or integrals as the q's are changed. In the latter case, the ionization energies which we compute are those found by Koopmans' theorem. That is, we find the E_i's of Eq. (6). It is well known that in this case the energy $E_{\text{av}}(q_i - 1)$ will be too high, since we have not minimized the energy by varying the orbitals for the ion. Thus the calculated energy $E_{\text{av}}(q_i - 1) - E_{\text{av}}(q_i)$ will be too large. This error in Koopmans' theorem is shown in Table III in which the Hartree–Fock energies E_i are numerically larger than the experimental values.

If, however, we calculate the E_i's properly, varying the orbitals as well as the q's, we should find that the average of E_i' would be slightly smaller numerically than E_i, and in fact would be very slightly smaller numerically than the experimental ionization energy. The reason is that the error in this case would be the difference between the correlation energies of atom and ion (where we now define the correlation energy as the difference between the true energy and the average energy of the HHF problem). The correlation energy, which is known to be roughly proportional to the number of electrons, will be numerically greater for the atom than for the ion, but by a small amount, of the order of magnitude of 0.08 Ry.[17] This means that E_i' will have an average value numerically too small by about this amount, rather than numerically too

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[17] J. C. Slater, Intern. J. Quant. Chem. **1S**, 783 (1967).

large by several percent, as follows from the results such as those in Table III. This gives us some feeling for the magnitude of the differences between the E_i', as calculated properly and as calculated with disregard of the modification of the orbitals on ionization.

For the case of excitation, we have an example of the corresponding difference between $E_i'-E_j'$, as calculated properly and as calculated disregarding the change of the integrals, from our calculations as shown in Fig. 3. In that figure, we are showing total energy as a function of occupation number, so that the slope of the curves is what gives the difference between modified one-electron energies, $E_i'-E_j'$. The envelope curve is calculated taking proper account of the modification of the orbitals when an electron is shifted from one state to the other, in this case from the *3d* to the *4s* or vice versa. The parabolas tangent to the envelope are calculated for fixed values of the integrals. Suppose for instance that we were to start with the configuration corresponding to the minimum of the envelope curve and were to ask what energy would be required to excite the atom to a configuration with one additional *3d* electron, which had been excited from the *4s* shell. Properly, this would be given by the difference between the ordinates of the envelope curve for the two values of occupation number in question. If, however, we were to disregard the change of integrals on excitation, we should use the difference between ordinates of one of the parabolas tangent to the envelope, between the same two values of occupation number. Clearly, we would get a result several times too large. Putting it otherwise, this case of shifting of electrons between *3d* and *4s* shells is one in which the errors involved in Koopmans' theorem are greatly exaggerated in relative importance, though not in absolute value, as compared to the ordinary problem of x-ray ionization.

The cases which we are taking up in the present section are those in which an atom loses or gains a whole electron. In the energy-band problem, however, where an electron is often shared between many atoms, an excitation may well be a case in which there is only a small fraction of an electron changing in each atom. Thus we are nearer the case of an infinitesimal change of the q_i's than of a change by a whole unit. In such a case the integration or averaging over a range of q_i's, which we are taking up in the present section, will not be necessary. In these cases, we may use the change in modified one-electron energy $E_j'-E_i'$ as an excitation energy, without having to carry out an averaging. This is essentially the case postulated in the use of Fermi statistics. The problem of excitation is really more complicated than would appear from this elementary discussion, since we often are concerned with an exciton, in which an atom has a large change in the value of the q_i's on excitation. We shall not take up these matters further in the present paper, except for a mention in the next section, but merely warn the reader that these complications exist. However, they are much less severe when we understand that the excitation energy can better be described in terms of differences of modified one-electron energies E_i', rather than in terms of differences of the energies E_i concerned in Koopmans' theorem.

IX. DISCUSSION

In the preceding sections, we feel that we have justified the hope expressed earlier in this paper, that our study of the nonintegral occupation numbers in the transition atoms may throw light on the general problem of the one-electron approximation in the problem of an atom, or more particularly of a crystal. Let us now ask just how these general considerations can be applied in actual energy-band calculations.

We must first ask what we hope to accomplish by an energy-band calculation. To judge by the practical uses made of the theory of energy bands, we wish to have a set of one-electron eigenvalues and eigenfunctions, such that we can assign a Fermi energy separating the occupied from the empty energy levels at the absolute zero of temperature. We then wish the energy difference between an empty and an occupied energy level to correspond as closely as possible to the energy involved in the excitation, optical or thermal or otherwise, from the lower to the upper energy level, in the actual physical system. Similarly if the excitation arises from electromagnetic fields of low frequency, we wish the excitation calculated from the one-electron eigenfunctions and eigenvalues to agree as well as possible with that actually observed. We wish the one-electron eigenfunctions to be such that we can calculate transition probabilities in the form of one-electron integrals of suitable operators between the initial and final state. In other words, we want to be able to use the conventional one-electron theory of the electrical and magnetic properties of the system as straightforwardly as possible.

There has been a good deal of skepticism as to whether such a program could actually be carried through, and as to where its limits will come. Surely we have these limits. The corresponding theory for a single atom can go no further than to give the sort of one-electron energies given by a central field model of an atom, with perhaps the spin-polarized feature built into it. The multiplet structure is necessarily a many-electron phenomenon, which must come as an additional calculation superposed on a one-electron treatment. Such problems will arise in solids, when we have partially filled inner shells of such ions as *3d* transition ions, and must consider the multiplet structure associated with the partially filled inner shells, as modified by the ligand field in the crystal.

Up to this point where many-electron theory is surely required, however, the more refined the energy-band calculations have been made, the further it appears that we can go with the one-electron picture. Even the former skeptics are beginning to realize that many types of problems which were formerly throught to be impossible can be treated by energy-band theory. Consequently, it is highly desirable to refine the theory as far as possible, before the point of applying typically many-electron corrections is reached.

In the history of atomic calculations, this general situation was met very early. During the 1920's, central fields were set up with the aim of leading to eigenvalues and eigenfunctions which could be used in just the way we have described. The well-known potential of Prokofjew,[18] for the sodium atom, is an example of this sort of work. Prokofjew was interested in studying the transition probabilities for optical transitions in the sodium atom, and he set up an empirical potential which led to eigenvalues and eigenfunctions of the desired sort. It is to be noted that such potentials, pure functions of position, had excited energy levels which represented the excited states of the sodium atom with good accuracy.

This promising line of development was interrupted by the introduction of the Hartree–Fock method. That method not only leads to an effective potential which is not a simple function of position, but is a more complicated exchange operator; even more, it leads to eigenfunctions and eigenvalues for the excited states which are completely inappropriate for describing the actual excited levels of an atomic system. The reason for this is well known.[19] The potential in which an excited electron (unoccupied orbital) moves, in the Hartree–Fock method, is that of the nucleus and all electrons, including the electron which is being considered, rather than having a correction, which we call exchange, for the fact that the electron does not act on itself. The resulting one-electron energies, in the language for instance of Eq. (6) of the present paper, instead of containing the term (q_i-1) (i,i), in which the term -1 corrects for the self-interaction, rather contain terms like $q_i(i,i)$. Since the integrals (i,i) are large quantities, we see that this results in a large energy gap between the one-electron energies of occupied and of excited states, a gap which seems to have no counterpart in the actual physical problem. In other words, the Hartree–Fock method has led us into a very unsuitable starting point for a many-electron system.

Some workers have realized this difficulty for many years. Thus, Wigner and Seitz,[20] in their pioneering study of the energy bands of the sodium crystal, based their potential on the empirical potential of Prokofjew, not on a Hartree–Fock method. This difficulty again was in the mind of the senior author, when he proposed an exchange potential which was a function of position only, in 1951.[3] But the more abstract thinkers about many-electron theory seem more often than not to be unaware of these great difficulties with the Hartree–Fock method.

From the discussion of the present paper, one sees that these difficulties are largely removed by the HHF method. The modified one-electron energies E_i' which we have been discussing are half way between those for the occupied states in the Hartree–Fock method, involving a term (q_i-1) (i,i), and those of the excited states, involving $q_i(i,i)$. They indicate no sharp break in one-electron energies between occupied and empty states. Thus, for instance, in the problem of the configuration $3d^{n+x}4s^{2-x}$ which we have been considering, the $4s$ level goes from being filled when $x=0$ to being empty when $x=2$; but the energy E_i' for this level varies perfectly smoothly from the one limit to the other, as is shown in the calculations for fractional occupation number in Table IV.

In spite of this good feature of the HHF method, it is too complicated to use for actual energy-band calculations; even the present calculations, on individual atoms, have been rather a computational *tour de force*. We must as a practical matter look for some scheme, not appreciably more complicated than those now in use, to approximate the exchange for routine energy-band calculations.

Suggestions as to how to proceed come from energy-band calculations which have actually been carried out by one of the authors (TMW), on the antiferromagnetic crystal MnO, and which are underway on NiO.[21] These crystals have been discussed by the senior author in several papers,[15] giving references to earlier work. For many years they have been regarded as a test of the possibility of using energy-band theory for such complicated magnetic problems. In order to be able to explain the fact that they are insulators, though they contain partially filled $3d$ bands, it is necessary to have the splitting of the $3d$ band into $3d\uparrow$ and $3d\downarrow$ produced by the use of spin-polarized orbitals, and also it is necessary to have the $3d\uparrow$ and $3d\downarrow$ in turn split by a crystal field, into the e_g and t_{2g} types of orbitals. Furthermore, there are other energy bands in the neighborhood of these arising from the $3d$, coming from the O^{-2} ion, and these must come in the correct relative position with respect to the Fermi level to result in the observed optical spectrum.

Wilson has found that a potential can be set up, leading to energy bands fulfilling all of these requirements (including an *a priori* calculation of the ligand field splitting in excellent agreement with experiment), by what seems at first sight a rather arbitrary assumption: within the APW (augmented-plane-wave) sphere describing the Mn or Ni ion, he uses the Xα method. Within the sphere describing the O^{-2} ion, he uses the XS method. And in the regions between the spheres, he uses the XKSG method. We may mention that Cho[22] in his studies of EuO, EuS, and EuSe, still largely unpublished, has been led independently to a rather similar set of assumptions, and he also is obtaining energy bands describing successfully the behavior of those interesting compounds. It was largely as a result

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[18] W. Prokofjew, Z. Physik **58**, 255 (1929).

[19] Reference 8, Vol. 2, Sec. 17-2. J. C. Slater, *Quantum Theory of Molecules and Solids*, (McGraw-Hill Book Co., New York, 1963), Vol. 1, Secs. 5-2, 6-2; Vol. 3, (1967), Secs. 11-3, 11-4.

[20] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934).

[21] T. M. Wilson, Intern. J. Quant. Chem. **IIS**, 269 (1968); J. Appl. Phys. (to be published).

[22] S. J. Cho, Phys. Rev. **157**, 632 (1965), and unpublished work. The authors are much indebted to Dr. Cho for information regarding this unpublished work.

of discussions between Wilson, Cho, and the other authors of this paper, that the ideas presented here grew up.

Let us now ask how the rather arbitrary assumption described in the preceding paragraph can be rationalized. The first requirement of the energy bands for MnO and NiO is that gaps appear in the right places and have the right magnitudes. Earlier study of the NiO problem by Switendick[23] has shown that the energy bands are extremely sensitive to the occupation numbers of the *3d* states, and he had made one of the early suggestions that it would be desirable to examine the problem for variable occupancy. Wilson was led to his assumptions in order to move the bands around to the relative positions which seem to agree with our knowledge regarding the optical, electrical and magnetic properties of these crystals. But as a first step, we see from our present discussion that it must be very important to use one-electron energies similar to the E_i''s of the HHF method for discussing the relative positions of the *3d* and *4s*-like bands, and that of all the simple approximations to exchange the XKSG method has one-electron energies most closely approximating to the E_i''s. Since the wave functions associated with the energy bands close to the Fermi energy have large amplitudes in the regions outside the spheres, we can attain approximately the situation we desire by using the XKSG exchange in this region between the spheres.

The next difficulty noted, however, was that if one used the XKSG exchange throughout the spheres, the energy band arising from the *2p* atomic level of the O^{-2} came too high. By using the XS exchange for this ion, the energy levels arising from the O^{-2} electrons are depressed, and they then fall into a reasonable location with respect to the Mn^{+2} or Ni^{+2} levels. Cho had found a similar situation for the O^{-2}, S^{-2}, and Se^{-2} levels in his crystals. We note from Table III that the eigenvalues arising from the XS method not only lie lower than those from the XKSG method. but in most cases they lie closer to the experimental x-ray values than any other set of eigenvalues. Similarly we may assume that the $X\alpha$ eigenvalues for the lower-energy levels of the Mn^{+2} or Ni^{+2} are closer to the experimental values than those that would be found from the XKSG exchange. Thus it seems reasonable to use these larger exchanges for these regions inside the spheres representing the ions.

We should look at this problem more closely, however. Speaking very roughly, the XS or $X\alpha$ eigenvalues agree better with x-ray energy levels, while the XKSG method is better for the energy levels met in the valence and conduction bands. Why is there this distinction, and does it make sense to use different exchanges in the different regions for this reason? We must remember that there are two quite different sorts of optical excitations of a crystal. When an electron is excited from a valence band of a semiconductor into the condutcion band, for instance, it is in an itinerant state, and almost immediately travels away from the atom which it has left to distant parts of the crystal. Similarly the hole left behind travels away, and very shortly both electrons and hole are spread throughout the crystal. Hence in such an excitation, the change in electron occupancy of any individual atom is infinitesimal. In such a case, it is reasonable to use an energy like the E_i' or $\partial E_{\mathrm{av}}/\partial q_i$ of the present paper to find the energy difference. On the other hand, when an electron is ejected from an inner, x-ray level of an atom, the hole is very strongly localized, corresponding to a very high effective mass. The electron may remain trapped by the hole, as an exciton, or may go into an itinerant state, but in any case the atom remains with a vacancy of a whole electron in an inner shell. This leads to an energy indistinguishable from that observed with an isolated atom, and the energy of excitation is well approximated by the Hartree–Fock eigenvalues E_i, or in fact somewhat better (on account of cancellation of errors) by the eigenvalues of the XS approximate method.

We wish a set of energy bands which will describe the most prominent type of optical excitation both for the inner and the outer electrons. Hence it seems reasonable to try to get eigenvalues which will describe those of the x-ray levels for the inner electrons, and those of the conventional energy-band theory for the outer ones. It is this which, in a crude way, we are achieving with the assumptions which Wilson has made in his case.

Further than this we cannot go at the moment in suggesting potentials to use in individual cases. We believe that energy-band theory at last, 40 years after Hartree's first proposal of the method of the self-consistent field, and 35 years after the work of Wigner and Seitz, has reached a point where by small and reasonable modifications of the assumptions regarding exchange, one can get energy bands fulfilling the requirements which we stated in an earlier paragraph. It will still be a long and difficult task to try such small modifications for many different types of crystals, and so gradually to build up an adequate knoweldge of how to predict *a priori* the exact potential that should be used in actual cases. But we believe that such considerations as have been brought out in the present paper can throw enough light on the physical aspects of the problem so that the workers in the field can make reasonable guesses as to the direction in which to proceed.

APPENDIX

We wish to state the formulas for the modified energies E_i' of the $3d\uparrow$, $3d\downarrow$, $4s\uparrow$, and $4s\downarrow$ orbitals in a spin-polarized calculation for the *3d* transition elements, in the case in which we are disregarding the effect of spin-polarization on the orbitals and the integrals between them. We shall consider two cases: ***Case I*, for the *d* shell less than half full, in which we**

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[23] A. C. Switendick, Ph.D. thesis, Massachusetts Institute of Technology, 1963 (unpublished); Bull. Am. Phys. Soc. 8, 211 (1963).

assume a configuration $(3d\uparrow)^{n+x}4s\uparrow(4s\downarrow)^{1-x}$, and *Case II*, for the d shell more than half full, with the configuration $(3d\uparrow)^5(3d\downarrow)^{n-5+x}4s\uparrow(4s\downarrow)^{1-x}$, where in each case x can be between 0 and 1. It is convenient to give formulas for the difference between the spin-polarized and non-spin-polarized one-electron energies. First therefore we give the formulas for the non-spin-polarized case, the HHF calculation for the configuration $3d^{n+x}4s^{2-x}$. These formulas follow from Eqs. (2), (7), and (11), and are

$$E_{3d}'(\mathrm{HHF})=I(3d)+(n-\tfrac{1}{2}+x)\{F^0(3d,3d)-2/63[F^2(3d,3d)+F^4(3d,3d)]\}$$
$$+(2-x)[F^0(3d,4s)-\tfrac{1}{10}G^2(3d,4s)]+\sum_{\text{filled shells } j} q_j(3d,j)\,,$$
$$E_{4s}'(\mathrm{HHF})=I(4s)+(\tfrac{3}{2}-x)F^0(4s,4s)+(n+x)[F^0(3d,4s)-\tfrac{1}{10}G^2(3d,4s)]+\sum_{\text{filled shells } j} q_j(4s,j)\,. \tag{28}$$

Equation (28) is used in computing the entries of Table IV.

For the spin-polarized case, we must use the interaction integrals of Eq. (23) rather than Eq. (2). However, the interaction between a spin-polarized $3d$ or $4s$ orbital and an inner filled shell j is the same for the spin-polarized as for the non-spin-polarized case, provided we disregard the effect of spin polarization on the integrals. Hence, the summations over filled shells j cancel when we take the energy difference between the spin-polarized and non-spin-polarized cases. Also the one-electron integrals $I(3d)$ or $I(4s)$ cancel, and likewise the contributions of the F^0 integrals. We are left with the following formulas:

Case I

$$E_{3d\uparrow}'(\mathrm{SPHHF})-E_{3d}'(\mathrm{HHF})=(n-\tfrac{1}{2}+x)(-5/126)[F^2(3d,3d)+F^4(3d,3d)]-(x/10)G^2(3d,4s)\,,$$

$$E_{3d\downarrow}'(\mathrm{SPHHF})-E_{3d}'(\mathrm{HHF})=[(2/63)(n+x)+(5/252)][F^2(3d,3d)+F^4(3d,3d)]+(x/10)G^2(3d,4s)\,,$$

$$E_{4s\uparrow}'(\mathrm{SPHHF})-E_{4s}'(\mathrm{HHF})=-[(n+x/10)]G^2(3d,4s)\,,$$

$$E_{4s\downarrow}'(\mathrm{SPHHF})-E_{4s}'(\mathrm{HHF})=[(n+x/10)]G^2(3d,4s)\,.$$

Case II

$$E_{3d\uparrow}'(\mathrm{SPHHF})-E_{3d}'(\mathrm{HHF})=[(2/63)(n+x)-(85/252)][F^2(3d,3d)+F^4(3d,3d)]-(x/10)G^2(3d,4s)\,,$$

$$E_{3d\downarrow}'(\mathrm{SPHHF})-E_{3d}'(\mathrm{HHF})=[-(5/126)(n+x)+(95/252)][F^2(3d,3d)+F^4(3d,3d)]+(x/10)G^2(3d,4s)\,,$$

$$E_{4s\uparrow}'(\mathrm{SPHHF})-E_{4s}'(\mathrm{HHF})=[(n+x)/10-1]G^2(3d,4s)\,,$$

$$E_{4s\downarrow}'(\mathrm{SPHHF})-E_{4s}'(\mathrm{HHF})=-[(n+x)/10-1]G^2(3d,4s)\,. \tag{29}$$

We have used Eq. (29) in constructing Table V.

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Thermal Diffuse X-Ray Scattering Measurements of the Fermi Surface of Chromium*†

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Thermal diffuse x-ray scattering measurements have been made on the [100] L-dispersion curve of chromium in the vicinity of the zone boundary at 329°K in the paramagnetic state and at 277°K in the antiferromagnetic state. Anomalies in the differential scattering intensity $[I(329°\mathrm{K})-I(277°\mathrm{K})]$ were observed in reciprocal space at (0.87,0,0), (1.11,0,0), and (2.90,0,0) (in units of $2\pi/a$). These anomalies are interpreted as arising from the intersection of the x-ray resolution function with a Kohn surface about H. This surface is due to transitions between the Γ and H octahedra of the paramagnetic Fermi surface. In the antiferromagnetic state, this surface vanishes. Correcting for a shift due to the resolution function, an average value for the Γ-H transitions along [100] is obtained which is given by $q/q_{\max}=0.90\pm0.01$. By comparing the angular dependence of the scattered intensity with that calculated from known dispersion curves, an estimate of the one-phonon contributions is obtained. This yields an estimate of $\Delta\omega/\omega=3\%$ at the anomaly.

I. INTRODUCTION

In this paper, we present results of a Kohn[1] anomaly measurement of the Fermi surface of chromium by means of thermal diffuse scattering (TDS) of x rays. These results demonstrate the disappearance of portions of the Fermi surface when Cr passes from the paramagnetic to the antiferromagnetic state. In addi-

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[1] W. Kohn, Phys. Rev. Letters 2, 393 (1959).