JOURNAL OF SOLID STATE CHEMISTRY **12**, 397–401 (1975)

# A Localized-Orbital Theory of Mott Insulators

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Received July 11, 1974

An elementary but formally satisfactory localized-orbital theory is presented and shown to explain the basic characteristics of Mott insulators. Problems concerning the $3d$ orbital degeneracy, the optical bandwidth, and the electrical bandwidth are discussed and resolved.

We wish to present a simple conceptual model for the electronic structure of Mott insulators. This model explains the most prominent experimental characteristics of these materials in a direct and intuitive manner. As specific examples, we shall use NiO and CoO. The main questions which we consider are: (1) Why does the ground state insulate? (2) Why do the insulating band gap and the local moment features persist above $T_N$? (3) Where does the antiferromagnetic coupling come from? (4) Why are the observed optical and electrical bandwidths so very narrow for the $3d$ electrons? Questions (2) and (3) can be answered in a very straightforward manner, but we shall see that complete answers for (1) and (4) must unfortunately be more complicated and subtle.

Mott pointed out long ago (*1*) that the electrons of NiO and similar materials seem to be localized, at least in some vague phenomenological sense. He was mainly concerned with the insulation feature (No. 1 above), although the other three characteristic features also provide strong support for the notion of localized electrons. If one could somehow provide a concrete realization of Mott's intuitive picture, this should go a long way towards answering the above questions. We shall present localized orbitals with the desired properties by employing Hartree–Fock (HF) theory in a novel manner (*2*, *3*).

In the past, the main objection to localized orbitals has been that they seemed to conflict with Bloch's theorem. In the case of a filled band, however, the equivalent localized description is known to take on a very simple form: A single determinant of Bloch orbitals is replaced by a single determinant of Wannier orbitals. The essence of our approach is to extend this filled-band relation to other electronic configurations, including the disordered-local-moment configurations encountered above $T_N$.

Consider an array of hydrogen atoms whose lattice structure allows a simple two-sublattice antiferromagnetic spin configuration. For sufficiently large lattice spacings in two or three dimensional systems, and for all lattice spacings in one dimension, the HF ground state of this system will be Slater's antiferromagnetic band state (*4*, *5*). This provides an insulating band gap $\Delta \approx (U-W)$, where $U$ is the one-site Coulomb repulsion integral and $W$ is the width of the occupied Slater band. Thanks to the doubling in size of the magnetic unit cell, one now has a filled-band configuration, so this state permits a simple Wannier orbital description. (The Bloch → Wannier transformation must be applied separately to each sublattice.) Furthermore, one can set up (and actually solve) the HF equations of Slater's theory directly in terms of the self-consistent Wannier orbitals,

$$\mathscr{F}\varphi_n = \sum_j \lambda_{jn}\varphi_j, \tag{1}$$

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Printed in Great Britain

$$\lambda_{jn} = \langle \varphi_j | \mathscr{F} | \varphi_n \rangle, \qquad (2)$$

where $\mathscr{F}$ is the usual Fock operator consisting of kinetic, ionic, direct, and exchange terms. A calculation done in this nondiagonal (non-canonical) representation is completely equivalent to one carried out in the usual Slater–Bloch representation where the $\lambda$ matrix becomes diagonal ($\equiv$ canonical representation).

The thermal HF version (*6*) of this theory is closely analogous to the Stoner theory of band ferromagnetism. It predicts that the band gap and the strength of the individual moments should both vanish at a $T_N$ of order $\frac{1}{4}\Delta$; above this $T_N$ the result is a paramagnetic metal, contrary to experiment. We conclude that although the Slater theory is satisfactory at $T = 0$, it gives a very wrong picture of the thermal excitations. This theory must be modified to demonstrate the existence of low-energy ($\sim t^2/U$) excitations corresponding to *disordering* of the local moments. (The RPA approach has demonstrated the existence of spin wave excitations (*5*), but this approach does not describe the highly disordered configurations for $T \gtrsim T_N$.)

We now consider Ising-like electronic configurations, where the net spin polarization at each site is either "up" or "down". There are $2^N$ such Ising configurations, and we assume that *each one* should correspond to a *different* self-consistent solution of the HF equations. There should be $2^N$ different HF solutions of this Ising character, at least when the lattice spacing (or the $U/t$ ratio) is sufficiently large. Most of these Ising configurations have such low symmetry that the magnetic unit cell becomes very large, usually as large as the entire crystal. Bloch periodicity is still maintained, but in a far weaker sense than usual, since there is now a different magnetic sublattice for each Ising configuration. This picture was proposed some years ago (*7*), but it had never gained acceptance. This is probably because the existence of these $2^N$ different solutions had never been demonstrated, and because it was observed (*7*) that this approach did not suffice to explain why the ground state of CoO is not metallic.

To put the existence problem in perspective we take the basic question to be "Can HF theory support local moments for magnetic sublattice configurations with unusually large unit cells, and with unusually low symmetry within these unit cells?" To settle this question, we constructed a one-dimensional model in which the nonlocality of the exchange potential could be treated exactly by standard numerical methods (*2*). The system consists of an infinite row of "one dimensional hydrogen atoms," with a Coulomb-like interaction which is rounded off near the origin and cut off smoothly at large distances,

$$V(r) = V_0(r^2 + \Delta^2)^{-1/2} \exp[-(r/L)^4], \qquad (3)$$
$$\Delta \ll \text{lattice spacing} \ll L.$$

Figure 1 shows the Wannier orbitals of a self-consistent solution, for a seven-site unit cell with the assigned spin configuration $\downarrow\downarrow\uparrow\uparrow\uparrow\downarrow\uparrow$. This unit cell is unusually large (for 1-D), it has no internal symmetry, and it presents a variety of different "local spin environments." The calculation was carried out directly within the Wannier basis appropriate for the assigned magnetic sublattices; Eqs. (1) and (2) were solved iteratively by an extension of techniques described in Ref. (*2*).

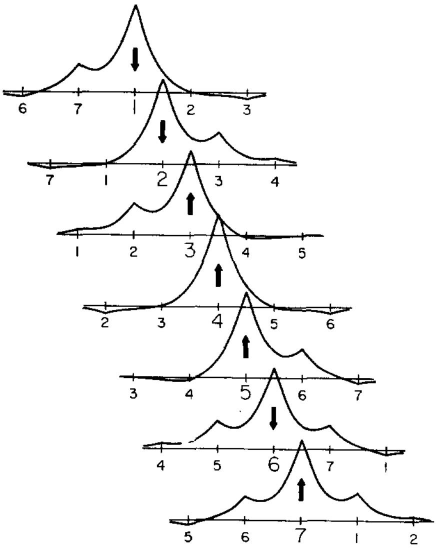

FIG. 1. Self-consistent Wannier orbitals for a periodic spin configuration of low symmetry.

The following features of the solution should be noted.

(a) The orbitals shown are not canonical; the corresponding canonical orbitals are Bloch functions with seven-site periodicity. If desired, the final self-consistent $\lambda$ matrix (2) could be diagonalized numerically in order to generate the corresponding eigenvalues and eigenfunctions.

(b) The present orbitals are obviously localized, thus providing a specific realization of Mott's intuitive picture (*1*).

(c) The detailed shapes of the orbitals are dependent on their local spin environments, due to the fact that parallel-spin orbitals must be space orthogonal, whereas opposite spin orbitals need not be, and thus the total HF energy depends on the spin arrangement. This gives rise to an antiferromagnetic Heisenberg spin interaction, in full agreement with the standard kinetic exchange theory. In fact, these orbitals may be said to provide the natural extension of Anderson's two-cation cluster model (*8*) to the more realistic case of a bulk periodic many-electron system.

(d) This configuration has exactly as many spin-up electrons as there are spin-up sites, so the canonical Bloch band for the present spin-up sublattice is exactly full. The same is true for the spin-down band, so the Fermi level falls within a band gap, and the insulation feature of Slater's theory is preserved.

(e) Consider orbital No. 6 in Fig. 1, a down spin sandwiched between two up spins. The amplitude of this orbital is strongly reduced on both of the neighboring up sites by the Coulomb repulsion from these sites. (This is much more true for actual Mott insulators; Fig. 1 involves a rather weak interaction $V_0$ for the sake of illustration.) This means that the "net hopping integral" $\lambda_{86}$, from $\varphi_6$ to the closest available same-spin neighbor, $\varphi_8$ (which looks the same as $\varphi_1$), is very strongly reduced, as compared to $\lambda_{12}$ for example. In the simple antiferromagnetic configuration this hopping suppression applies to *all* of the nonvanishing off-diagonal $\lambda$ elements, thus for this case it is obvious that the canonical eigenvalue bandwidth will be narrower by a factor of $t/U$ than for the corresponding ferromagnetic configuration.

It is important to note that this scheme involves *strong orbital rearrangement*, since each Ising configuration involves a *different* set of canonical Bloch eigenfunctions. This orbital rearrangement feature is what distinguishes the present theory from Slater's, and which enables the so-called strong correlations of Mott insulators to be treated within a single-determinant framework. It must also be recognized that we have focused on the Ising configurations purely for the sake of convenience, in order to justify the existence of a Heisenberg spin Hamiltonian. Our philosophy is to justify this Hamiltonian in the manner outlined, and then use this to describe other aspects of the spin dynamics. This is consistent with the fact that the ground state of CoO is known to have *four* different magnetic sublattices (*9*). This philosophy is identical to that of the usual superexchange theory; we have simply embedded the latter theory in a more general framework.

We have now provided answers to questions (2) and (3) of the opening paragraph, and partial answers to questions (1) and (4).

The subtlety in the ground-state insulation problem is due to 3*d* orbital degeneracy. In actual Mott insulators, this tenfold degeneracy is partially lifted by the crystal field (*CF*) and exchange splittings. We first consider NiO, whose $Ni^{2+}$ ions carry eight 3*d* electrons. Using the $U$, $U'$, $J$ parametrization (*10*) for the intraatomic Coulomb and exchange interactions, we find a 3*d* band structure with the schematic form shown in Fig 2. This pattern of splittings should apply to all $2^N$ of our Ising–HF configurations. Since $\varepsilon_F$ falls within a band gap, the physical picture described above is also valid for NiO, with the under-

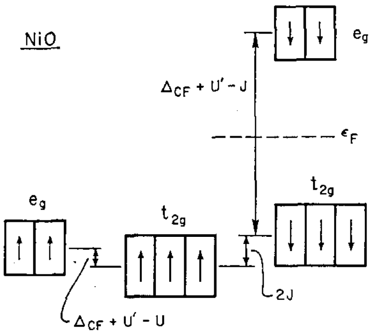

FIG. 2. Schematic band structure for NiO.

standing that the insulating gap $\Delta$ is now somewhat less than $(U - W_{3d})$. (The actual optical gap of 3.8 eV is believed to arise from $3d \rightarrow 4s$ transitions (*11*).) Note that $\Delta_{CF}$ does not prevent the $e_g\uparrow$ and $t_{2g}\uparrow$ subbands from overlapping (*12*); the gap at $\varepsilon_F$ is due primarily to the large value of the Slater $F^0$ integral. It is essential to distinguish between the five different 3*d* orbital symmetries, as done by the *UU'J* parametrization for example, since the local $\rho^{1/3}$ exchange approximation is too crude to explain the large insulating gap of NiO.

In contrast to NiO, the Fermi level for CoO (seven 3*d* electrons) falls within a subband (the $t_{2g}\downarrow$ band; see Fig. 2), so all of our Ising–HF configurations should be metallic. Our way out of this embarrassment is suggested by crystal field theory (*13*, *14*) where one considers only a *single* $Co^{2+}$ ion and its surrounding cage of six $O^{2-}$ ions. The crystal-field ground state involves *three* Slater determinants which are mixed by spin-orbit coupling (*14*). To describe the Ising configurations of the bulk solid, we propose wavefunctions which are essentially direct products of such crystal field wavefunctions; each of these total wavefunctions now involves $3^N$ determinants. Such wavefunctions are not difficult to visualize in terms of a Wannier basis. The connection with ordinary HF theory is sacrificed, but this can be partially restored by using the many-determinant generalization of HF theory (*15*). That formalism is unfortunately quite complicated, but it does maintain the connection with Mott's elementary argument for insulation, based on minimizing the total energy. There should still be a gap of order $F^0$ between the empty and occupied 3*d* orbitals in each determinant. A previous attempt to resolve this CoO problem has tried to preserve a single-determinant description (*16*). We believe, however, that the large orbital magnetic moment (*9*, *14*) and the detailed form of the excitation spectrum (*13*) constitute strong evidence in favor of the present type of wavefunction.

Finally, we consider the problem of extremely narrow 3*d* bandwidths deduced from optical and electrical data (*11*), which seem to be in striking disagreement with the widths of order 2 eV obtained in conventional band calculations (*12*). We saw above that the simple antiferromagnetic configuration should have its bandwidth reduced by a factor of $t/U$; taking $W_0 \approx 2$ eV $\approx 12\ t$, $U \approx 10$ eV gives $t/U \approx 1/60$. However, NiO and CoO do not possess such simple antiferromagnetic configurations. Above $T_N$ about half of the neighboring bonds must be ferromagnetic anyway, with $\lambda_{ij} = -t$, so this mechanism can only reduce the $T > T_N$ hopping by a factor of 2. The 3*d* peak widths from photoelectron spectroscopy (*17*) are consistent with this. The very narrow ($\lesssim 0.1$ eV) optical bandwidth was obtained (*11*) from the sharpness of the crystal field exciton peaks (*11*, *13*). Their widths are determined (*13*) by the exciton hopping matrix elements; these are known (*18*) to be of order $t^2/U$ instead of $t$, regardless of the local spin order.

The 3*d* electrical bandwidth is deduced from the hopping of holes ($Ni^{3+}$ ions in NiO) bound to trapping centers ($Li^+$ impurities or Ni vacancies); small polaron theory is used to infer the hypothetical transfer of these holes in the absence of lattice deformation. The magnitude of the resulting effective nearest-neighbor electron hopping element "*J*" has been controversial (*11*, *19*), but the more recent studies (*19*) conclude merely that this is somewhat less than 0.1 eV. Mattheiss's calculation (*12*) gives 0.17 eV. We suggest that the discrepancy can be explained by rearrangements of the "passive" electrons: polarization of the neighboring oxygen orbitals, and changes in their covalent mixing with the 3*d*'s on the $Ni^{3+}$ sites. We estimate that these effects should reduce "*J*" by roughly a factor of 3.

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