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Antiferromagnetism in Narrow-Band Solids*

J. B. Sokoloff
Brookhaven National Laboratory, Upton, New York 11973†

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The single-band Hubbard Hamiltonian is examined in the limit of bandwidth much less than intra-atomic Coulomb interaction of electrons. We make use of the canonical transformation and "spectral decomposition" of the electron creation operators proposed by Harris and Lange to write down a Green's function which describes electrons in the lower of the split bands of Hubbard's solution. The equation of motion is solved using the moment-conserving decoupling approximation of Tahir-Kheli and Jarrett. We find within our approximation that it is impossible to have an antiferromagnetic state for other than one electron per site. To remedy this defect of the single-band model, we investigate a simplified two-band model in the limit of intra-atomic Coulomb and exchange interaction much greater than the bandwidth, and find that antiferromagnetism is possible for the two nearly half-filled bands. We also discuss effects of the antiferromagnetic ordering on the conductivity in our simplified model and discuss applicability of the theory to real transition metals and transition-metal oxides.

I. INTRODUCTION

It is well known that the Hubbard Hamiltonian[1]

$$\mathcal{H}=\sum_{ij\sigma} h_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}+U\sum_{j} n_{j\uparrow}n_{j\downarrow}\,, \tag{1}$$

(where $n_{i\sigma}=c_{i\sigma}^{\dagger}c_{i\sigma}$, and $c_{i\sigma}$ is the annihilation operator for a spin-σ electron in a Wannier function on site i) with intra-atomic screened Coulomb interaction $U\gg$ hopping term h_{ij}, with one electron per lattice site, has an antiferromagnetic ground site.[2] In this paper we consider Eq. (1) in the limit $U\gg h_{ij}$ with fewer than one electron per site (the case of more than one per site is obtained by electron-hole equivalence). In this limit, since the single narrow s band breaks up into two bands separated by a gap,[1,2] the model should be applicable to semiconducting and insulating transition-metal oxides.[3] We look for the possibility of antiferromagnetic ordering of the electrons of the system (necessarily in the lower band), using the canonical transformation used by Harris and Lange,[2] and by Kohn,[4] and the moment-conserving decoupling procedure suggested by Tahir-Kheli and Jarrett.[5] We restrict h_{ij} to near neighbors. If we only keep those terms in our decoupling corresponding to the decoupling used in Hubbard I, it is found that Hubbard's approximation predicts that antiferromagnetism does not occur for any number of electrons less than one per atom in agreement with the results of Penn[6] in the infinite U limit. Within our complete approximation, it is shown that antiferromagnetic ordering does not occur in the limit as the number of electrons *approaches* one per atom. This is in agreement with the work of Nagaoka,[7] which predicts ferromagnetism in this limit. We give a physical picture for why there should be no antiferromagnetism for fewer than one electron per site. We also discuss antiferromagnetism in a two-band generalization of Eq. (1) introduced by Roth.[8] In the limit of intra-atomic Coulomb and exchange interactions much larger than the hopping term, the system should be antiferromagnetic for two electrons per lattice site. We show by applying the methods used on Eq. (1) to the Hamiltonian that for between one and two electrons per site an antiferromagnetic ordering is also possible. We also estimate the number density of electrons in the system at which the antiferromagnetic state energy becomes equal to the ferromagnetic-state energy and thus the ferromagnetic state becomes the ground state.

The picture of motion of electrons in narrow bands presented by the two-band model is much like that presented in Hubbard II and IV, but the method of approximation in this paper is different, and the model is simpler. The simplicity of the model should permit calculation of transport and other measurable phenomena in narrow-band systems.

II. ANTIFERROMAGNETISM IN NARROW *S* BANDS

To treat the $U\gg h_{ij}$ limit of Eq. (1) we apply the canonical transformation of Eq. (4.42) in Harris and Lange's paper[2] to Eq. (1) to obtain their Eq. (4.43). Keeping only zeroth-order terms in h_{ij}/U (Δ/I in their notation), the transformed Hamiltonian of their Eq.

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† Present address: Northeastern University, Boston, Mass. 02115.

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[3] D. Adler, in *Advances in Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York, 1968), Vol. 21, p. 1; D. Adler and J. Feinleib, J. Appl. Phys. **40**, 1586 (1969).

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[6] D. Penn, Phys. Letters **26A**, 509 (1968); and (private communication).

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[8] L. Roth, Phys. Rev. **149**, 306 (1966).

(4.43) can be written in our notation as

$$\mathcal{H}_{\text{eff}}\approx\sum_{ij\sigma} h_{ij}(a_{i\sigma}{}^{\dagger}a_{j\sigma}+b^{\dagger}{}_{i\sigma}b_{j\sigma})+U\sum_{j} n_{j\uparrow}n_{j\downarrow}\,, \qquad (2)$$

where

$$a_{i\sigma}=(1-n_{i,-\sigma})c_{i\sigma}\,,\quad b_{i\sigma}=n_{i,-\sigma}c_{i\sigma}\,.$$

Here $c_{i\sigma}$ is understood to denote $\bar{c}_{i\sigma}$ in Harris and Lange.[2] The higher-order terms in h_{ij}/U give rise to an effective antiferromagnetic exchange interaction between electrons, which is important for the case of one electron per atom. For less than one electron per atom, the hopping energy should dominate in the infinite-U limit.

To discuss antiferromagnetism for less than one electron per atom, we consider the one-electron Zhubarev Green's function[9]

$$\langle\langle a_{i\sigma};\,a_{j\sigma'}{}^{\dagger}\rangle\rangle=i\theta(t)\langle\{a_{i\sigma}(t),\,a_{j\sigma'}{}^{\dagger}(0)\}\rangle\,, \qquad (3)$$

where $\theta(t)$ is a step function of time, $\{\cdots\}$ denotes an anticommutator, and $\langle\cdots\rangle$ denotes a thermal average. Thus, we are only looking at the lower band.[2] Using Eq. (2), we find that the equation of motion for this Green's function is

$$\begin{aligned} i\frac{\partial}{\partial t}&\langle\langle a_{i\sigma};\,a_{j\sigma'}{}^{\dagger}\rangle\rangle\\ &=\textstyle\sum_l h_{il}\langle\langle[(1-n_{i,-\sigma})a_{l\sigma}+a_{l,-\sigma}c_{i,-\sigma}{}^{\dagger}c_{i\sigma}];\,a_{j\sigma'}{}^{\dagger}\rangle\rangle\\ &\qquad+\delta(t)\delta_{ij}\langle[\delta_{\sigma\sigma'}(1-n_{i,-\sigma})+\delta_{\sigma',-\sigma}c_{i\sigma}{}^{\dagger}c_{i,-\sigma}]\rangle\,. \end{aligned} \qquad (4)$$

We now use the moment-conserving decoupling procedure of Tahir-Kheli and Jarrett[5] to decouple the Green's function on the right-hand side. To accomplish this, we approximate Eq. (4) by

$$\begin{aligned} i\frac{\partial}{\partial t}\langle\langle a_{i\sigma};\,a_{j\sigma'}{}^{\dagger}\rangle\rangle&=\textstyle\sum_l M_{il}\langle\langle a_{l\sigma};\,a_{j\sigma'}{}^{\dagger}\rangle\rangle\\ &\qquad+\delta(t)\delta_{ij}\langle[\delta_{\sigma\sigma'}(1-n_{i,-\sigma})+\delta_{\sigma',-\sigma}c_{i,-\sigma}c_{i\sigma}{}^{\dagger}]\rangle\,. \end{aligned} \qquad (5)$$

We choose M_{il} such that the zeroth and first moments of the spectral function of Eq. (3) are given correctly. Moment-conserving decoupling makes sense in this problem because the Green's function in Eq. (3) only describes the lower band. Hence, there should be only one peak in the spectral function, and therefore the first moment of the spectral function (i.e., the average energy of the peak) can be taken to be the one-electron energy. For simplicity we take $\sigma=\sigma'$. Then we obtain by setting the zeroth moment of the right-hand side of Eq. (4) equal to that of the right-hand side of Eq. (5):

$$\begin{aligned} (1-n_{l,-\sigma})&M_{il}\\ &=h_{il}\langle(1-n_{i,-\sigma})(1-n_{l,-\sigma})\rangle-h_{il}\langle c_{l\sigma}{}^{\dagger}c_{l,-\sigma}c_{j,-\sigma}{}^{\dagger}c_{j\sigma}\rangle\\ &\qquad+\delta_{ij}\sum_{l'}h_{il'}\langle(1-n_{l',\sigma})c_{l',-\sigma}c_{i,-\sigma}{}^{\dagger}\rangle\,. \end{aligned} \qquad (6)$$

With this approximation, our resulting spectral function gives the same zeroth and first moments as obtained by Harris and Lange to zeroth order in the ratio of bandwidth to U.

We neglect the spin-spin correlation function [second term on right-hand side of Eq. (6)]. This should be a good approximation away from a magnetic phase transition for close to one electron per site.[10] We also replace the correlation function in the last term on the right-hand side of Eq. (6) by

$$\langle c_{l',-\sigma}c_{i,-\sigma}{}^{\dagger}\rangle\,.$$

This is justified because the probability of having two electrons on a site is of higher order in h_{ij}/U. We also make the approximation

$$\langle(1-n_{i,-\sigma})(1-n_{l,-\sigma})\rangle\simeq\langle(1-n_{i,-\sigma})\rangle\langle(1-n_{l,-\sigma})\rangle\,, \qquad (7)$$

which should be a good approximation away from the region of a magnetic phase transition, for close to one electron per site.[10]

We assume a two-sublattice antiferromagnetic ordering, which restricts us to simple-cubic- and body-centered lattices. We also restrict h_{ij} to near neighbors. We assume that on the up-spin sublattice, $\langle n_{i\uparrow}\rangle$ is n_1 and $\langle n_{i\downarrow}\rangle$ is n_2, where $n_1>n_2$. On the down-spin sublattice, the reverse is true. Applying the approximations of the previous paragraph to Eq. (6), substituting in Eq. (5), and Fourier transforming, we obtain

$$\begin{aligned} [\omega-\bar{\epsilon}(\mathbf{k})]\langle\langle a_{\mathbf{k}\sigma};\,a_{\mathbf{k}'\sigma}{}^{\dagger}\rangle\rangle&-J(\mathbf{k}+\mathbf{Q})\langle\langle a_{\mathbf{k}+\mathbf{Q},\sigma};\,a_{\mathbf{k}'\sigma}{}^{\dagger}\rangle\rangle\\ &=(2\pi)^{-1}(1-n)\delta_{\mathbf{k},\mathbf{k}'}+(2\pi)^{-1}\sigma\tfrac{1}{2}m\delta_{\mathbf{k},\mathbf{k}'-\mathbf{Q}}\,, \end{aligned} \qquad (8)$$

where

$$\begin{aligned} \bar{\epsilon}(\mathbf{k})=(1-n)\epsilon(\mathbf{k})&+\frac{1}{N}\sum_{\mathbf{k}'}\epsilon(\mathbf{k}')[(1-n)\langle c_{\mathbf{k}',-\sigma}c_{\mathbf{k}',-\sigma}{}^{\dagger}\rangle\\ &+\sigma m\langle c_{\mathbf{k}',-\sigma}c_{\mathbf{k}'+,\mathbf{Q}-\sigma}{}^{\dagger}\rangle]\frac{1}{(1-n_1)(1-n_2)}\,, \end{aligned} \qquad (9a)$$

$$\begin{aligned} J(\mathbf{k})=\sigma m\epsilon(\mathbf{k})&+\frac{1}{N}\sum_{\mathbf{k}'}\epsilon(\mathbf{k}')[(1-n)\langle c_{\mathbf{k}',-\sigma}c_{\mathbf{k}'+\mathbf{Q},-\sigma}{}^{\dagger}\rangle\\ &+\sigma m\langle c_{\mathbf{k}',-\sigma}c_{\mathbf{k}',-\sigma}{}^{\dagger}\rangle]\frac{1}{(1-n_1)(1-n_2)}\,, \end{aligned} \qquad (9b)$$

where $\epsilon(\mathbf{k})$ is the Fourier transform of h_{ij}, $\mathbf{Q}$ is a wave vector such that $e_i{}^{i\mathbf{Q}\cdot\mathbf{R}i}=+1$ on an up-spin sublattice site and -1 on a down-spin sublattice site, and

$$n=\tfrac{1}{2}(n_1+n_2)\,,\quad m=\tfrac{1}{2}(n_1-n_2)\,.$$

Solving Eq. (8) and using the methods of Ref. 9, we

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[9] D. N. Zhubarev, Usp. Fiz. Nauk. **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

[10] D. M. Esterling and R. V. Lange, Rev. Mod. Phys. **40**, 796 (1968); Phys. Rev. (to be published); and (private communication).

obtain for the infinite-U limit

$$n\approx\frac{1}{N}\sum\nolimits_{\mathbf{k}}\langle a_{\mathbf{k}\sigma}{}^{\dagger}a_{\mathbf{k}\sigma}\rangle=\frac{1}{N}\sum\nolimits_{\mathbf{k}}\int d\omega[A_{-}(\mathbf{k})\delta(\omega-\omega_{-}(\mathbf{k})) +A_{+}(\mathbf{k})\delta(\omega-\omega_{+}(\mathbf{k}))]\frac{1}{e^{\beta(\omega-\mu)}+1}, \tag{10a}$$

$$m\approx\sigma\frac{1}{N}\sum\nolimits_{\mathbf{k}}\langle a_{\mathbf{k}\sigma}{}^{\dagger}a_{\mathbf{k}+\mathbf{Q},\sigma}\rangle=\frac{1}{N}\sum\nolimits_{\mathbf{k}}\int d\omega[B_{-}(\mathbf{k})\delta(\omega-\omega_{-}(\mathbf{k})) +B_{+}(\mathbf{k})\delta(\omega-\omega_{+}(\mathbf{k}))]\frac{1}{e^{\beta(\omega-\mu)}+1}, \tag{10b}$$

where

$$\omega_{\pm}(\mathbf{k})=\tfrac{1}{2}[\bar{\epsilon}(\mathbf{k})+\bar{\epsilon}(\mathbf{k}+\mathbf{Q})]\pm[(\tfrac{1}{2}(\bar{\epsilon}(\mathbf{k})-\bar{\epsilon}(\mathbf{k}+\mathbf{Q})^2) +J(\mathbf{k}+\mathbf{Q})J(\mathbf{k})]^{1/2}, \tag{11a}$$

$$A_{\pm}(\mathbf{k})=\pm\frac{(1-n)[\bar{\epsilon}(\mathbf{k}+\mathbf{Q})-\omega_{\pm}(\mathbf{k})]-mJ(\mathbf{k}+\mathbf{Q})}{\omega_{-}(\mathbf{k})-\omega_{+}(\mathbf{k})}, \tag{11b}$$

$$B_{\pm}(\mathbf{k})=\pm\frac{m[\bar{\epsilon}(\mathbf{k})-\omega_{\pm}(\mathbf{k})]-(1-n)J(\mathbf{k})}{\omega_{-}(\mathbf{k})-\omega_{+}(\mathbf{k})}. \tag{11c}$$

If we neglect all except the first term on the right-hand side of Eq. (6) and make the approximation of Eq. (7) [which leaves us with the first terms in Eqs. (9a) and (9b)], we obtain the approximation of Hubbard I to lowest order in h_{ij}/U. [This is equivalent to decoupling Eq. (4) in the way suggested by Hubbard[1]]. Making this approximation we obtain from Eq. (10), using Eqs. (9) and (11),

$$n/(1-n)=\tfrac{1}{2}(C^{+}+C^{-}), \tag{12a}$$

$$m=[\tfrac{1}{2}(C^{+}+C^{-})]m, \tag{12b}$$

where

$$C^{\pm}=\frac{1}{N}\sum\nolimits_{\mathbf{k}}\frac{1}{1+\exp\{\pm|\epsilon(\mathbf{k})|[(1-n_1)(1-n_2)]-\mu^{1/2}\}}.$$

Since $C^{\pm}\leq 1$, we find from Eq. (12) that we can only find an antiferromagnetic solution for one electron per atom [i.e., when $C^{\pm}=1$, as is seen from Eq. (12a)]. In fact, Hubbard's approximation does not even give a magnetic band splitting, as is seen from Eq. (11a).

Let us now include the last term in Eq. (6), which results in the rest of the terms in Eq. (9). These terms result in the band shift discussed by Harris and Lange[2] for the paramagnetic and ferromagnetic states. The problem now reduces to a self-consistency problem in that the correlation functions as well as n and m appearing in Eq. (9) can be calculated from Green's function of Eq. (3), which is a solution to Eq. (8), using the methods of Ref. 9. The problem is fairly difficult but it simplifies in two cases, for $m\ll 1$ and for close to one electron per site. If the sublattice magnetization m is assumed to be $\ll 1$, we find from Eqs. (9)–(11) that the splitting of the bands due to the antiferromagnetic ordering (i.e., due to the reduced translational symmetry) occurs in the middle of the lower band and is much smaller than the bandwidth. Then Eq. (10) reduces to

$$m\approx m[1-2(1-2n)+(1-2n)^2]+(0)m^2, \tag{13a}$$

$$n=(1-n)\frac{1}{N}\sum\nolimits_{\mathbf{k}}\frac{1}{1+\exp\beta[\bar{\epsilon}(\mathbf{k})-\mu]}+(0)m^2, \tag{13b}$$

for $\frac{1}{2}-n\ll 2$. Thus, again we see that, unless there is close to one electron per site (i.e., $n=\frac{1}{2}$) or unless n is ≈ 0, there is no weak antiferromagnetism in the approximation of this paper. This agrees with the results of Penn.[6]

We now look for an antiferromagnetic solution for close to one electron per site for arbitrary m. For close to one electron per site, the correlation functions in Eq. (9b) are expected to be small since very little hopping is possible in this limit. Therefore, the second term in Eq. (9b) contributes significantly in this limit only if the sublattice magnetism is close to saturation since in that limit $n_2\approx 1-n_1\approx 0$. In this limit from Eq. (9b), we may write

$$J(\mathbf{k})\approx m\epsilon(\mathbf{k})+\sum_{\mathbf{k}'}\epsilon(\mathbf{k}) \times\frac{1}{1+\exp\{\beta[\omega_{-}(\mathbf{k})-\mu]\}}\frac{1-n_2}{1-n_1}. \tag{14}$$

This equation is obtained by taking $|J(\mathbf{k})|\gg$ the bandwidth, which from Eq. (10b) is a necessary condition for saturation magnetization since m is an increasing function of $|J(\mathbf{k})|$. For nearly one electron per site at temperature much less than U, the second term in Eq. (14) gives a value $\approx\epsilon_{\max}$, the maximum value of $\epsilon(\mathbf{k})$, using the fact that $(1-n_1)\sim 1/N$. Thus, since $J(\mathbf{k})$ is not much greater than the bandwidth, an antiferromagnetic self-consistent solution is not possible.

We conclude that there probably is no antiferromagnetism in the strong interaction limit as the number of electrons approaches one per site, unless there is exactly one electron per site. The physical reason for this is illustrated in Fig. 1. If we annihilate one electron in a previously antiferromagnetic system with one electron per site, that hole can move among sites having electrons of either spin, causing the spins to become disordered. It is reasonable to expect that this physical picture persists for any number of electrons in the system. We have left out of our calculation the width of the one-electron states caused by electron-electron scattering, which can be a sizeable fraction of the bandwidth.[1,2] We do not expect, however, that electron-electron scattering tends to make the system more likely to be antiferromagnetic. We cannot conclude from the calculations in this paper that the antiferromagnetic state is the ground state for precisely one

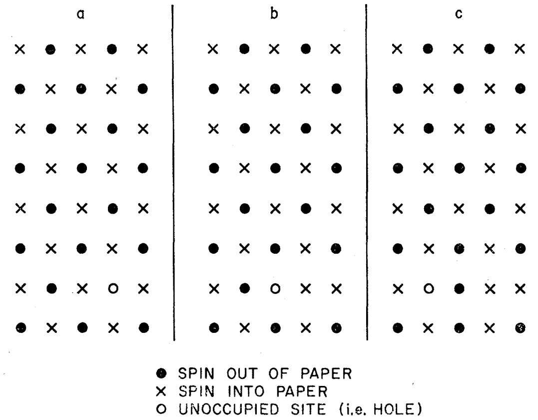

FIG. 1. Motion of a hole in an otherwise perfect two-dimensional antiferromagnetic lattice is shown. Time progresses from *a* to *c*.

electron per atom because, as is well known, we must include terms of order h^2/U in the transformed Hamiltonian in Eq. (2) to make the antiferromagnetic state have lower energy than the paramagnetic and ferromagnetic states for one electron per atom. We can only say that it is a possible eigenstate. Our result appears to agree with Penn's result to zeroth order in b_{ij}/U, but to higher order there probably will be differences.[6] If we include first-order terms in h_{ij}/U, we conclude that since they give a small effective electron-electron interaction, when we have fewer than one electron per atom, an effective field or Hartree-Fock approximation should be good. Then, these terms have the effect of renormalizing the one-electron energies in Eqs. (10) and (11) slightly and of adding a term of order mh/U to the right-hand side of Eq. (13a). This term could make antiferromagnetism possible only if $h/U>1-2n$. The main point that we illustrate in this section is that there is an essential difference between one electron per atom and slightly less than one electron per atom. Once the electrons are able to hop, the effects due to hopping dominate over the effective-exchange interaction. Since there is no reason to expect the omitted terms in Eq. (6) to favor antiferromagnetism, we expect our conclusion about the nonexistence of antiferromagnetism to be valid over a large range of electron densities away from one electron per atom.

III. ANTIFERROMAGNETISM IN A SIMPLE TWO-BAND MODEL

Since most transition-metal oxides are antiferromagnetic,[3] in this section we propose to show that although there probably cannot be antiferromagnetism in a single less-than-half-filled band, antiferromagnetism is possible in a simplified two-band model of a transition metal considered by Roth[8] to discuss ferromagnetism for less-than-half-filled bands. The Hamiltonian for this model can be written as

$$\mathcal{H}=\sum_{ij\alpha} h_{ij}c_{i\alpha\sigma}{}^{\dagger}c_{j\alpha\sigma}+U\sum_{i\alpha}\Big[n_{i\alpha\uparrow}n_{i\alpha\downarrow}+\sum_{\sigma\sigma'}n_{i1\sigma}n_{i2\sigma'}\Big]-J\sum_{\sigma\sigma'}c_{i1\sigma}{}^{\dagger}c_{i1\sigma'}c_{i2\sigma'}{}^{\dagger}c_{i2\sigma}. \quad (15)$$

Following Roth, there are assumed to be two orbitals of each spin per atom, and there is hopping only from one orbital into the same orbital on a different site, i.e., we neglect hopping between orbitals 1 and 2. Only intra-atomic Coulomb and exchange interaction U and J are included in Eq. (15). Roth argued that for one electron per atom or less, the system should be ferromagnetic, whereas for two electrons per site it should be antiferromagnetic, at least for U and J large compared to h_{ij}. We look for antiferromagnetism in the case of between 1 and 2 electrons per atom in the limit of $U\gg J\gg|h_{ij}|$, which should apply to transition-metal oxides.[3]

The ground state will be a linear combination of Slater determinants of atomic orbitals containing one or two electrons as these wave functions will minimize the Coulomb and exchange energy. Following Sec. II we introduce a canonical transformation that removes those hopping terms in Eq. (15) which increase the Coulomb energy of the system. These are terms which result in the formation of atoms containing three electrons. If $|\alpha\rangle$, $|\beta\rangle$ denote Slater determinants of atomic orbitals on all sites and if we make the proposed canonical transformation

$$e^{-S}\mathcal{H}e^{S}\approx\mathcal{H}_0+\mathcal{H}_1'+[\mathcal{H}_0,S]+\mathcal{H}_1+\cdots \quad (16)$$

(where $\mathcal{H}_1'$ is the part of the hopping term not removed by the transformation and $\mathcal{H}_1$ is the part that is removed), then by demanding that the last two terms in Eq. (16) vanish, we obtain to lowest order, for example,

$$\langle\alpha|S|\beta\rangle=-h_{ij}/(U+J),$$

if $|\alpha\rangle$ has site i triply occupied and site j singly occupied and $|\beta\rangle$ has i and j doubly occupied with parallel spin electrons on each site. If $|\alpha\rangle$ has site i triply occupied and site j unoccupied and $|\beta\rangle$ has site i doubly occupied and j singly occupied,

$$\langle\alpha|S|\beta\rangle=-\tfrac{1}{2}h_{ij}/U$$

to lowest order. After performing this transformation, Eq. (15) still has hopping terms which can increase the energy of system by J. For $J\gg|h_{ij}|$, we may perform another transformation $e^{-S'}\mathcal{H}e^{S'}$ which eliminates these terms to lowest order in h_{ij}/J. If $|\beta\rangle$ has site i occupied by two electrons of the same spin, site j contains one electron of spin opposite the spin of site i, and in $|\alpha\rangle$ there are two opposite-spin electrons on site j and one electron site i:

$$\langle\alpha|S'|\beta\rangle=-h_{ij}/J.$$

After performing these canonical transformations, the remaining hopping terms do not increase the intra-atomic Coulomb or exchange energy of the system.

If we consider only zeroth-order terms in h_{ij}/J and h_{ij}/U in the transformed Hamiltonian, we are left with

$$\tilde{H}=e^{-s'}e^{-s}\mathcal{H}e^{s}e^{s'}=U\sum_{i\alpha\beta\sigma\sigma'}n_{i\alpha\sigma}n_{i\beta\sigma'}-J\sum_{\sigma\sigma'}c_{i1\sigma}{}^{\dagger}c_{i1\sigma'}$$
$$\times c_{i2\sigma'}{}^{\dagger}c_{i2\sigma}+\sum_{ij\alpha\sigma}h_{ij}a_{i\alpha\sigma}{}^{\dagger}a_{j\alpha\sigma} \qquad (17)$$

plus terms that act only on excited states of excitation energy $\sim J$ or U, where

$$a_{i\alpha\sigma}=c_{i\alpha\sigma}P_{i\alpha\sigma} \qquad (18)$$

and where

$$P_{i\alpha\sigma}=(1-\delta_{\alpha\beta})n_{i\beta\sigma}\prod_{\gamma}(1-n_{i\gamma,-\sigma}).$$

The operators $c_{i\alpha\sigma}$ denote the transformed operators. The operator $a_{i\alpha\sigma}$ only annihilates an electron in state i, α, σ if the other orbital of spin σ on site i is occupied and the two orbitals of spin $-\sigma$ are empty. We consider the Green's function

$$\langle\langle a_{i\alpha\sigma};\, a_{j\beta\sigma'}{}^{\dagger}\rangle\rangle. \qquad (19)$$

Differentiating Eq. (19) with respect to time, using Eq. (17), we obtain

$$i\frac{\partial}{\partial t}\langle\langle a_{i\alpha\sigma};\, a_{j\beta\sigma'}{}^{\dagger}\rangle\rangle$$
$$=\sum_l h_{il}\langle\langle[P_{i\alpha\sigma}a_{l\alpha\sigma}+(1-\delta_{\alpha\gamma})c_{i\alpha\sigma}a_{i\gamma\sigma}{}^{\dagger}a_{l\gamma\sigma}];\, a_{j\beta\sigma'}{}^{\dagger}\rangle\rangle$$
$$+(U-J)\langle\langle a_{i\alpha\sigma};\, a_{j\beta\sigma'}{}^{\dagger}\rangle\rangle+\delta(t)\delta_{ij}\delta_{\sigma\sigma'}$$
$$\times\langle[\delta_{\alpha\beta}P_{i\alpha\sigma}+(1-\delta_{\alpha\beta})c_{i\alpha\sigma}a_{i\beta\sigma}{}^{\dagger}]\rangle. \qquad (20)$$

Applying moment-conserving decoupling and assuming close to two electrons per atom, we find

$$\left[i\frac{\partial}{\partial t}-(U-J)\right]\langle\langle a_{i\alpha\sigma};\, a_{j\beta\sigma'}{}^{\dagger}\rangle\rangle$$
$$=\sum_{l\gamma'}M_{il\sigma}{}^{\alpha\gamma'}\langle\langle a_{l\gamma'\sigma};\, a_{j\beta\sigma'}{}^{\dagger}\rangle\rangle+\delta(t)\delta_{ij}\delta_{\sigma\sigma'}$$
$$\times\langle[\delta_{\alpha\beta}P_{i\alpha\sigma}+(1-\delta_{\alpha\beta})c_{i\alpha\sigma}a_{i\beta\sigma}{}^{\dagger}]\rangle, \qquad (21a)$$

where

$$M_{il\sigma}{}^{\alpha\gamma'}\approx\delta_{\alpha\gamma'}h_{il}\langle P_{i\alpha\sigma}P_{l\gamma'\sigma}\rangle/\langle P_{l\gamma'\sigma}\rangle. \qquad (21b)$$

In obtaining Eq. (21b) we have neglected in $M_{il\sigma}{}^{\alpha\gamma'}$ complicated correlation functions which involve transfer of electrons between orbitals, as those should be small for close to two electron per atom. Following Sec. II, we make the approximation

$$\langle P_{i\alpha\sigma}P_{l\gamma'\sigma}\rangle\approx\langle P_{i\alpha\sigma}\rangle\langle P_{l\gamma'\sigma}\rangle,$$

as $P_{i\alpha\sigma}$ is analogous to the operator $1-n_{i,-\sigma}$. Operator $P_{i\alpha\sigma}$ has eigenvalue 1 if the orbital of spin σ other than α is occupied and all spin $-\sigma$ states are unoccupied. Carrying through the above approximations Eq. (21) becomes

$$\left[i\frac{\partial}{\partial t}-(U-J)\right]\langle\langle a_{i\alpha\sigma};\, a_{j\beta\sigma'}{}^{\dagger}\rangle\rangle$$
$$=\sum_l h_{il}\langle P_{i\alpha\sigma}\rangle\langle\langle a_{l\alpha\sigma};\, a_{j\beta\sigma'}{}^{\dagger}\rangle\rangle$$
$$+\delta_{\alpha\beta}\delta_{ij}\delta(t)\langle P_{i\alpha\sigma}\rangle. \qquad (22)$$

As in the one-band model, we assume a simple-cubic or body lattice and a two-sublattice antiferromagnetic ordering, which is the ground state in the case of two electrons per atom. We also assume h_{ij} to extend to near neighbors only. Then we take $\langle P_{i\alpha\uparrow}\rangle=P_1$ and $\langle P_{i\alpha\downarrow}\rangle=P_2$ on the spin ↑ sublattice and the reverse on the spin ↓ sublattice, independent of α, where $P_1\gg P_2$. We now Fourier transform Eq. (22) in space and time and solve using the above assumptions to obtain

$$\langle\langle a_{\mathbf{k}\alpha\sigma};\, a_{\mathbf{k}\alpha\sigma}{}^{\dagger}\rangle\rangle=\frac{1}{2\pi}\frac{P\omega-(P^2-\bar{P}^2)\epsilon(\mathbf{k}+\mathbf{Q})}{[\omega-\omega_+(\mathbf{k})][\omega-\omega_-(\mathbf{k})]}, \qquad (23a)$$

$$\langle\langle a_{\mathbf{k}+\mathbf{Q},\alpha\sigma};\, a_{\mathbf{k}\alpha\sigma}{}^{\dagger}\rangle\rangle=\frac{1}{2\pi}\frac{\bar{P}\omega}{[\omega-\omega_+(\mathbf{k})][\omega-\omega_-(\mathbf{k})]}, \qquad (23b)$$

where

$$P=\tfrac{1}{2}(P_1+P_2),\quad \bar{P}=\tfrac{1}{2}(P_1-P_2),$$

$$\epsilon(\mathbf{k})=\frac{1}{N}\sum_i e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)}h_{ij},$$

$$\omega_{\pm}(\mathbf{k})=\pm|\epsilon(\mathbf{k})|[P^2-\bar{P}^2]^{1/2}=\pm|\epsilon(\mathbf{k})|(P_2P_1)^{1/2}.$$

By the definitions of $a_{i\alpha\sigma}$ and $P_{i\alpha\sigma}$, we find at zero temperature

$$m=\frac{1}{N}\sum_{i\alpha}[\langle P_{i\alpha\uparrow}\rangle-\langle P_{i\alpha\downarrow}\rangle]=2(P_1-P_2)=4\bar{P}, \qquad (24a)$$

$$\Delta m=\frac{1}{N}\sum_{i\alpha}[\langle a_{i\alpha\uparrow}a_{i\alpha\uparrow}{}^{\dagger}\rangle-\langle a_{i\alpha\downarrow}a_{i\alpha\downarrow}{}^{\dagger}\rangle], \qquad (24b)$$

$$n=\frac{1}{N}\sum_{i\alpha\sigma}\langle P_{i\alpha\sigma}\rangle=4P, \qquad (24c)$$

$$\Delta n=\frac{1}{N}\sum_{i\alpha\sigma}\langle a_{i\alpha\sigma}a_{i\alpha\sigma}{}^{\dagger}\rangle=4P, \qquad (24d)$$

where m is the sublattice magnetization per site, $\Delta m=2-m$, n is the number of electrons per site, and $\Delta n=2-n$.

Applying the methods of Ref. 9 to Eq. (23) and using Eq. (24), we obtain

$$m=n=2/(1+C), \qquad (25a)$$

where

$$C=\frac{1}{N}\sum_{\mathbf{k}}\frac{1}{\exp\beta[-\epsilon(\mathbf{k})(P_1P_2)^{1/2}-\mu]+1} \qquad (25b)$$

for close to saturated sublattice magnetization. Hence, we see that an antiferromagnetic solution can be found in the two-band model for the bands nearly half-filled. Since $C \leq 1$, we find from Eq. (25a) the expected trivial result that the sublattice magnetization is equal to the number of electrons in the system, which is between 1 and 2 per atom. The one-electron energy is $\epsilon(\mathbf{k})(P_1P_2)^{1/2}$, which for a totally antiferromagnetic state (i.e., $P_2 \approx 0$) is zero as Harris and Lange showed would be true for the one-band model in the totally antiferromagnetic state. For close to two electrons per atom, we expect the lifetime of the one-electron states to be long for the following reason: For close to two electrons per site a missing electron (i.e., a hole) in orbital α of spin σ on site i will be able to hop into orbital α of the same spin on any near-neighbor site if there is some probability of the spin of that site being parallel to that of site i. Since the probability of it colliding with another hole is small, the major damping mechanism should be spin-disorder scattering, which is negligible away from a magnetic phase transition. A calculation of the second moment indicates that the second moment is zero for nearly two electrons per site (since correlation functions involving transfer of electrons are negligible). As the bands empty we get the same scattering as in the single-band model; i.e., a hole in orbital α on site i does not hop onto neighboring sites that do not contain an electron in orbital β, which leads to disorder scattering. In fact, if we consider the completely ferromagnetic state for one electron per site, we find, as Roth did,[8] a spatial ordering with all near-neighbor sites of an electron in orbital 1 having an electron in orbital 2, because for one electron per site Eq. (15) becomes the same as Eq. (1) with orbital index replacing spin index. For fewer than one electron per site the results of the Sec. II show that such ordering does not occur.

We now estimate the critical electron density at which the antiferromagnetic state is no longer the ground state of this model. For close to two electrons per atom, we may use the approximations discussed in this section. Then the mean hole hopping or kinetic energy is obtained by calculating the density of states $\rho(\omega)$ by taking the imaginary part of Eq. (23a) and summing over $\mathbf{k}$ and α. From $\rho(\omega)$ the zero-temperature average kinetic energy of holes is found to be

$$E_{\text{kin}} = -N\int_{\mu}^{\epsilon_{\text{max}}} \omega\rho(\omega)d\omega$$
$$= -\textstyle\sum_{\mathbf{k}} 2\epsilon(\mathbf{k})(P_1P_2)^{1/2}\theta(\epsilon(\mathbf{k})(P_1P_2)^{1/2}-\mu),$$

where θ is a step function. In the completely antiferromagnetic state the factor $(P_1P_2)^{1/2}$ is zero; in the completely ferromagnetic state it is seen to be replaced by the magnetization, by solving Eq. (22) for the uniform ferromagnetic state. Then for the ferromagnetic state,

$$E_{\text{kin}} \approx -N\Delta n\epsilon_{\text{max}}. \tag{26}$$

For close to two electrons per site the effective exchange interaction energy by which the Néel state is below the ferromagnetic state is

$$E_{\text{ex}} \approx -2(h_{ij}^2/U)zNn, \tag{27}$$

where z is the number of near-neighbor sites. It follows that for large U the critical density is found by equating (26) and (27) to be

$$n_{\text{crit}} = \frac{2}{1+4\epsilon_{\text{max}}/zU}. \tag{28}$$

The critical density becomes closer to two electrons per site as U becomes larger compared with the bandwidth, and as U becomes smaller, the critical density becomes smaller. Such behavior should be seen in real transition metals and oxides (as impurities are added). As we move away from the large-U limit, the critical density becomes closer to one per atom, at which point complicated many-body effects characteristic of the single-band model set in and Eq. (28) is no longer valid. The above tendency to ferromagnetism for lower electron densities is in line with the ideas of Zener.[11]

IV. APPLICATION TO TRANSITION METALS AND TRANSITION-METAL OXIDES

For real transition metals, the number of "polar states" (i.e., negatively charged atoms) occupied in the ground state compared with that given by the Hartree-Fock approximation has been estimated by Herring to be about $\frac{1}{3}$ or $\frac{1}{4}$.[12] In our theory, this would imply that the ratio bandwidth/U is of the order of 0.7.[12] Our perturbation expansion in h_{ij}/U, however, may still give reasonable results for some transition metals. Electrical conduction is predicted to occur in transition metals in our model because of the *s-d* band overlap. The *d* bands conduct because they do not contain an integral number of electrons per lattice site, not because of polar-state admixture into the ground state. Since this paper applies in a limit opposite that of band theory (i.e., opposite the small-U limit), and since real transition metals lie in the middle, the large-U results should complement the results of band theory. We will, in future publications, using our model, look for possible experimentally observable effects of electron correlations in transition metals.

We expect the method presented in this paper to be most applicable to the theory of electrical conduction in narrow-band transition-metal oxides. Many of these compounds are either semiconductors or insulators; ordinary band theory, however, predicts that they are conductors.[3] It was suggested by Adler[3] that something

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[11] C. Zener, Phys. Rev. **82**, 403 (1951).

[12] C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IV, p. 201.

analogous to the Hubbard theory[1] of narrow bands might be appropriate to these materials.

Our one- and two-band models give such a split-band picture. When there is exactly an integral number of electrons, the electrons cannot hop, and consequently, might behave like localized electrons (at least as far as their magnetic properties are concerned). If we consider the lower bands in our models to be nearly filled for a doped sample, since there are few sites for an electron to hop to, we expect to see both electrical conduction and localized properties, indicating that the multiband models considered should predict nearly the same optical spectrum as if we had localized atomic *d* states. We plan to examine this point further in future publications.

One drawback of applying the approximation of this paper to electrical conduction in transition-metal oxides is that near the Néel temperature it probably would predict spin-disorder scattering of electrons which would show up in the electrical conductivity, as found by deGennes and Friedel for a model of electrons interacting with localized spins.[13] Such an effect is observed for nickel oxide but not for cobalt oxide.[3] This tends to favor for cobalt oxide the method of conduction in oxygen *p* bands proposed by Adler, over conduction in the *d* bands themselves.[3] Another drawback is that for nonmetallic systems, the Coulomb interaction should be long range. If, however, the valence band is nearly full, we do not expect the results to be quantitatively different from those predicted by this paper, since the effect of a long-range interaction in the narrow-band system is simply to keep electrons apart. If we have nearly an integral number of electrons per site, the electrons in the ground-state manifold are always spread apart as much as possible.

For the completely saturated antiferromagnetic state of the two-band model, we saw that electrons cannot hop onto neighboring sites because the large Coulomb interaction of the opposite-spin electrons on those sites makes such hopping highly improbable. Thus, our two-band model predicts that a hole created in the *d* states of a half-filled narrow multiband system by doping is trapped in a two sublattice antiferromagnetic state, but it is free to hop in the paramagnetic state. This would be a type of conductor-to-insulator transition. Most transition-metal oxides, however, are antiferromagnets for which not all near-neighbor sites of a given site have spin opposite the spin of that site, and thus this effect would not be a complete conducting–to–nonconducting–state transition at the Néel temperature, but rather simply a possible change in the conductivity in the antiferromagnetic state. In future publications we will investigate conductivity and other transport properties in the two-band model of this paper to see how they might be affected by magnetic ordering. Another problem that we will consider is antiferromagnetism in the single-band model taking into account the nonzero width of the one-electron states.

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[13] P. G. de Gennes and J. Friedel, Phys. Chem. Solids **9**, 71 (1958).