

Band theory and Mott insulators: Hubbard U instead of Stoner I

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We propose a form for the exchange-correlation potential in local-density band theory, appropriate for Mott insulators. The idea is to use the “constrained-local-density-approximation” Hubbard parameter U as the quantity relating the single-particle potentials to the magnetic- (and orbital-) order parameters. Our energy functional is that of the local-density approximation plus the mean-field approximation to the remaining part of the U term. We argue that such a method should make sense, if one accepts the Hubbard model and the success of constrained-local-density-approximation parameter calculations. Using this *ab initio* scheme, we find that all late-3d-transition-metal monoxides, as well as the parent compounds of the high- T_c compounds, are large-gap magnetic insulators of the charge-transfer type. Further, the method predicts that LiNiO_2 is a low-spin ferromagnet and NiS a local-moment p -type metal. The present version of the scheme fails for the early-3d-transition-metal monoxides and for the late 3d transition metals.

I. IS THE LSDA REPAIRABLE?

Despite the many successes of local- (spin-) density-approximation [L(S)DA] band theory, it is often claimed that this method is useless for strongly correlated materials. This criticism relates in the first place to the failure of LSDA to give a proper description of Mott insulators like the 3d-transition-metal oxides. Although the method reproduces the ground-state magnetic structure in the series NiO-MnO , it predicts CoO and FeO to be metals, while in reality they are insulators with well-developed correlation gaps, and the LSDA gives gaps in NiO and MnO which are too small by an order of magnitude.^{1,2} One could then defend the LSDA by claiming that the method is not meant for excited-state properties. However, the ground state also is not properly described. The local moments tend to be too small and, moreover, in relatively covalent materials like the high- T_c cuprates (among others) the magnetism vanishes altogether in LSDA, while in reality they are still rather strong antiferromagnets.³

It is generally accepted that strongly correlated systems are quite well described by the multiband Hubbard or Anderson-lattice type of models.⁴⁻⁷ The essential assumption in these models is that the strongly correlated d or f electrons (describable in a tight-binding single-particle basis) are subject to on-site quasiatomic interactions. The most important of these is the Hubbard parameter U , defined as

$$U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n), \quad (1)$$

i.e., the Coulomb-energy cost to place two electrons at the same site. In these strong-correlation models, one accounts only for a limited subset of all electronic degrees of freedom. This is rationalized by arguing that the other degrees of freedom (like metal d -s, ligand p -s transitions, etc.) are fast compared to the fluctuations involving the d or f electrons. The former can therefore be integrated

out, leading to a renormalization (“screening”) of the model parameters, compared to their atomic counterparts.⁸ One can use the LDA to calculate these model parameters. As a first step, one represents the d electrons in an orthonormal atomiclike basis to enable the identification with the single-particle basis of the model, which can be done using, e.g., the basis of orthonormal linear muffin-tin orbitals [LMTO’s].⁹ By applying a variety of constraints, one can find the model parameters. For instance,¹⁰ in order to calculate the screened U , one removes the transfer integrals between the d orbitals and the rest of the system and the occupancy of the d orbitals is varied (δn_d), while the other electrons are allowed to relax self-consistently, and it follows that $U = \delta^2 E_{\text{tot}} / \delta n_d^2$, where E_{tot} is the LDA total energy. It turns out, that for a variety of strongly correlated systems (rare-earth compounds,¹¹ 3d-transition-metal Mott insulators¹² and impurity systems,¹⁰ high- T_c superconductors¹³⁻¹⁵), this LDA-parameters-Hubbard-model approach is surprisingly accurate.

One thus faces a paradox. On the one hand, the standard LSDA is unfit for the description of magnetic insulators. On the other hand, all the “correct” information is apparently there. The purpose of this paper is to point out that the results of constrained-LDA calculations can be implemented in the standard LDA framework, resulting in a parameter-free, approximate “band” theory for Mott insulators. For this purpose, we have to abandon the conventional homogeneous-electron-gas framework. To engineer another energy functional, we find inspiration in the success of the “band approach” to Hubbard-type models.

LSDA is structured like a weak-coupling mean-field (MF) theory. It is implicitly assumed that the interactions (like the Hubbard parameter U) are small compared to the bandwidth (W), although in Mott insulators this is obviously not the case. However, due to the work of Brandow¹⁶ and others, it is nowadays common

knowledge¹⁷ that MF theory can also make sense for large couplings, in particular at half-filling. Consider the simple case of a system, characterized by a single band of correlated (“*d*”) electrons, subjected to a Hubbard-type interaction:

$$H_1 = \sum_i U n_{di\uparrow} n_{di\downarrow}, \quad (2)$$

where $n_{di\sigma}$ is the number operator of the *d* electron at site *i* with spin σ . In MF theory, the fluctuations around the average occupancies ($\langle n_{i\sigma} \rangle$) are neglected and Eq. (2) is approximated as

$$H_1^{\text{MF}} = \frac{1}{2} \sum_i U [n_i(n_{i\uparrow} + n_{i\downarrow}) - m_i(n_{i\uparrow} - n_{i\downarrow})] - \frac{1}{4} U (n_i^2 - m_i^2), \quad (3)$$

defining the average occupancy and moment as $n_i = \langle n_{i\uparrow} \rangle + \langle n_{i\downarrow} \rangle$ and $m_i = \langle n_{i\uparrow} \rangle - \langle n_{i\downarrow} \rangle$, respectively. Let us now consider the case that $U \gg W$ and $n_i \rightarrow 1$ (integral valency). The paramagnetic MF ground state would be at much too high energy ($\approx U/4$). However, upon the complete spin polarization ($m_i \rightarrow 1$), the ground-state energy drops to ~ 0 . The *d* band is split into an occupied and unoccupied part located at $-U/2$ and $U/2$, respectively, and the system is characterized by a gap $\sim U$. The lowest-order hybridization correction yields the correct expression for Anderson’s superexchange,¹⁸ i.e., for the single-band Hubbard model on a square lattice the energy difference between the antiferromagnetic and ferromagnetic MF solutions is $z(2t^2/U)$. The only remaining problem is that MF maps on a classical (instead of a quantum) Heisenberg spin system. As Schrieffer *et al.* showed recently,¹⁹ this is easily cured by including random-phase-approximation (RPA) fluctuations.

We have thus made the observation that MF theory works quite well, not only for $U \ll W$, but also in the extremely localized limit ($U/W \gg 1$, $n_i \rightarrow 1$), at least at half-filling. This has a good reason: In the spin-polarized solution the probability that a “wrong-spin” electron enters a “right-spin” site approaches zero if $m_i \rightarrow 1$, so that double occupancy is projected out automatically. Because the extreme limits are well treated, one expects that MF theory should also work reasonably well in intermediate cases, although this does not mean that it is “exact” in any sense. Here the problems become more significant, because one can no longer profit from the complete spin polarization. This is particularly clear in multiband situations, where the electrons can redistribute themselves over the unit cell. In, e.g., transition-metal oxides (TMO), the electrons can delocalize onto the oxygens, and this covalency is controlled by the charge-transfer energy (or *p-d* splitting) Δ versus the *p-d* hopping t_{pd} .^{20,21} Comparison with Gutzwiller-approximation results (which are excellent for local properties²²) shows that the polarized MF solutions tend to overestimate the degree of localization.²³ On the other hand, on a somewhat cruder level, the MF solutions are sound. If $U < \Delta$, one finds charge-transfer insulators²⁰ (instead of the classical Mott-Hubbard insulators for

$U > \Delta$), one finds mean-field analogs^{24,25} of the Zhang-Rice singlets,^{26,27} etc. Away from half-filling, things are less well settled. The least one can say is that MF solutions can be quite suggestive as exemplified by the recent discovery of charged-domain-wall solutions in the context of doped Mott-Hubbard insulators.^{24,28} Alternatively, for truly hard cases like the itinerant-electron magnets, MF results are a necessary input.²⁹

If the MF character of the LSDA is not the problem, what then has gone wrong? The problem is that in the LSDA the localization is not controlled by *U* but, rather, by a quantity which represents the Hund’s rule exchange, the “Stoner parameter *I*”. The LSDA total energy can be written in the form

$$E^{\text{LSDA}} = E^{\text{LDA}}\{n(\mathbf{r})\} + E_{\text{xc}}\{n\uparrow(\mathbf{r}), n\downarrow(\mathbf{r})\} - E_{\text{xc}}^{\text{LDA}}\{n(\mathbf{r})\}, \quad (4)$$

where E^{LDA} is the energy of the nonmagnetic state, which is a functional of the charge distribution $\{n(\mathbf{r})\}$, and E_{xc} is the exchange-correlation energy which depends on the spin distribution. The exchange splitting is in general a function of the magnetization $m(\mathbf{r})$,

$$V_{\uparrow} - V_{\downarrow} = \frac{\delta E^{\text{LSDA}}}{\delta n\uparrow(\mathbf{r})} - \frac{\delta E^{\text{LSDA}}}{\delta n\downarrow(\mathbf{r})} = f(\mathbf{r})m(\mathbf{r}). \quad (5)$$

For small magnetization the exchange splitting is independent of \mathbf{k} , and we can write

$$\langle \psi_j^k | f(\mathbf{r})m(\mathbf{r}) | \psi_j^k \rangle \sim -mI. \quad (6)$$

It turns out that in 3*d*-transition-metal systems the Stoner parameter *I* is rather independent of crystal structure, magnetization, etc., and it is therefore characteristic for the 3*d*-transition-metal atom itself, reflecting the tight-binding character of the 3*d* electrons.³⁰ In the isolated atom, the same quantity controls the spin splittings. Under the assumption that the LSDA reproduces the energies of single-determinant states,³¹ one obtains an accurate description of the atomic term splittings.³² In other words, the LSDA Stoner parameter *I* has to be identified with the Hund’s-rule exchange. The Hund’s-rule exchange parameter (*J*) is typically of order 1 eV and the Hubbard parameter *U* is of order 10 eV. We have thus identified the main LSDA problem.^{16,33–35} In the homogeneous electron gas, the spin dependence has its physical origin in the Hund’s-rule exchange, while in Mott insulators the Hubbard parameter *U* is responsible, and the latter is an order of magnitude larger than the former.

In the model MF approach it is easy to account for the orbital degeneracy of the *d* or *f* bands.^{16,17,34,36,37–39} In a spin- and orbital-degenerate system, the Hubbard term is written as (neglecting, for the moment, Hund’s-rule exchange)

$$H_1 = \frac{1}{2} U \sum_{\nu, \nu'} n_{i\nu} n_{i\nu'}, \quad (7)$$

($\nu \neq \nu'$)

where $\nu = (m, \sigma)$ labels collectively both the orbital (*m*) and the spin (σ). Focusing again on the atomic limit $U \gg W$, the paramagnetic MF ground state would as usual be energetically quite unfavorable

$\{ \simeq U[2N(2N-1)/2](n/2N)^2 = \frac{1}{2}U(1-1/2N)n^2$, where N is the orbital degeneracy and n the number of electrons per atom}. If one only allows for spin polarization, the MF ground state is not so good either if the shell is not half-filled. Neglecting single-particle (ligand-field) splittings, the occupancy of every orbital in a given spin channel is the same (n/N if $n < N$ and 1 for the majority channel, and $(n-N)/N$ for the minority channel if $N \leq n \leq 2N$). The MF energy is therefore $\simeq \frac{1}{2}U(1-1/N)n^2$ if $n \leq N$ and $\simeq \frac{1}{2}U(1-1/N)n^2 + U(n-N)$ if $n \geq N$. Because the Slater gap is now only between states of different spin, one finds metals (or single-particle gap insulators), except for the half-filled shell. This is the reason why conventional LSDA calculations predict FeO or CoO to be metallic.¹ Usually, one spheridizes the atomic charge densities in practical calculations [atomic-spheres approximation (ASA)]. In this case, the Hartree and exchange-correlation (xc) potentials see the average charge density, and only spin polarization can enter. However, if one accounts for the non-spherical nature of the atom, the Hartree and xc potentials will become orbital dependent, and this can cure the metallicity problem to some extent. These correction terms⁴⁰ are rather small ($\Delta J \sim 0.1$ eV), and as Norman recently showed, they hardly change the outcomes for FeO and CoO. The problem is again that Hund's-rule couplings are made responsible. In our Hubbard- U interpretation, however, spins and orbitals appear essentially on the same footing in the Hamiltonian, insofar as the interactions are concerned [Eq. (7)]. The best MF solution of Eq. (7) in the localized limit is obtained by occupying n specific orbitals on every atom,³⁶ and the ground-state energy is then of order $\simeq U^{n(n-1)}/2$. These occupied orbitals are separated by a gap $\simeq U$ from the unoccupied ones, and all stoichiometric systems are therefore large-gap insulators.¹⁶ The somewhat unusual aspect is that, besides the spins, the atomic-orbital degrees of freedom also get polarized due to the interactions. The lowest-order hybridization corrections will not only give rise to spin-spin superexchange but the same mechanism will also couple the orbitals, which can give rise to distinct orbital-ordering patterns.⁴¹ Of course, spin and orbital ordering are physically distinct in the sense that the continuous atomic-orbital symmetry is explicitly broken in the solid, giving rise to, e.g., crystal- and ligand-field splittings. For a MF treatment this is, in fact, an advantage, because the anisotropies in orbital space will lead to a reduction of the fluctuations. Furthermore, the electron-phonon ("Jahn-Teller") interactions have the tendency to stabilize the same orbital ordering as the electronic interactions,⁴¹ and often the right ordering pattern follows directly from the crystal structure.

We have now arrived at a stage where we can write down our energy functional. We postulate the following expression for the total energy functional:

$$E = E^{\text{LDA}} + \frac{1}{2} \sum_{m, m', \sigma} U(n_{im\sigma} - n^0)(n_{im'\sigma} - n^0) + \frac{1}{2} \sum_{\substack{m, m', \sigma \\ (m \neq m')}} (U - J)(n_{im\sigma} - n^0)(n_{im'\sigma} - n^0). \quad (8)$$

E^{LDA} is the usual (spin-independent) LDA total energy. Equation (8) is only defined with respect to an orthonormal single-particle basis with localized orbitals, representing the strongly correlated electrons, and n^0 is the average occupancy of one d orbital ($n^0 = n_d/10$). The quantities $n_{im\sigma}$ are the spin- and orbital-dependent occupancies of these local orbitals. Finally, the parameters U and J are identified with the LDA U and Stoner parameter I , respectively. In analogy with the formulation of usual LDA, the total energy Eq. (8) can be represented by single-particle equations, and the single-particle potentials are then given by

$$V_{m\sigma} = U \sum_{m'} (n_{m'\sigma} - n^0) + (U - J) \sum_{m' (\neq m)} (n_{m'\sigma} - n^0) + V^{\text{LDA}}, \quad (9)$$

where V^{LDA} are the usual LDA potentials, corresponding to the charge density with the number of d electrons given by $n_d = \sum_{m, \sigma} n_{im\sigma}$.

In Eqs. (8) and (9) only the differences between the polarized spin and/or orbital occupancies and the unpolarized LDA occupancies show up. This is the essence of our construction; we conjecture that the charge-charge term in Eq. (3) is properly included in standard LDA. We note that this is consistent with the constrained LDA, as the mean-field technique introduced by Hybertsen *et al.* shows.¹⁵ If this is the case, then Eqs. (8) and (9) follow for the orbital and spin dependence on the mean-field level. Therefore, our correction is only nonzero if spin and/or orbital order develops. Otherwise, it reduces to standard LDA.

In Eqs. (8) and (9) we use the average d occupancy (n^0) as a reference point. Although the occupancies in the different m channels will in general be different from one another due to single-particle (crystal-field, ligand-field) effects, the LDA Hartree and xc potentials are orbital independent in the LMTO-ASA calculations, because the charge density is averaged. The normal LDA calculation has thus to be identified with a model MF solution which is independent of the orbital occupancies and then Eqs. (8) and (9) follow for the energy and potentials of the unrestricted solutions. In Eq. (8) only the first Hund's rule is obeyed. This is not a fundamental restriction. It is not difficult to generalize the expression to account for the orbital dependence of the Hund's-rule interaction.⁴⁰ However, in this case we need explicit values for the ΔJ 's which we cannot obtain from our spheridized LDA calculation, and we decided to ignore these small corrections for the time being.

There are cases known where the interactions lead to a rehybridization of the orbitals [e.g., K_2CuF_4 (Refs. 41 and 42)]. Equations (8) and (9) are not sufficiently general to account for these cases; not only are the orbital occupancies needed, but the phase relations between the on-site orbitals are also required. It is again obvious what has to be done: From a variational point of view, one can improve Eqs. (8) and (9) by also allowing the "orbital flip" amplitudes $\sim \langle d_{m\sigma}^\dagger d_{m'\sigma} \rangle$ with $m \neq m'$ to develop. These will carry the needed phase information. These

rehybridization effects are unimportant in the cases we considered and we neglected these off-diagonal amplitudes altogether.

Finally, our scheme has one serious disadvantage: The exchange-correlation energy is necessarily dependent on the choice of single-particle representation, the reason being that the “orbital-order parameter” in the interacting system can only be defined with respect to a particular representation of the noninteracting system. We choose, inspired by the model approach, orthogonal short-ranged orbitals. Of course, the practical restriction of the scheme is set by the range of validity of the Hubbard-model approach: It only makes sense for rather localized systems.

Before going into details let us quickly indicate the kind of results we obtain for the 3d-transition-metal oxides (Figs. 1–3). Because of the large U 's, the occupied and unoccupied parts of the d bands are split by ~ 8 eV, and we find that the late-3d-transition-metal oxides are charge-transfer insulators.^{20,43} The occupied part of the d band is located below the oxygen band and these two bands are strongly mixed. On the other hand, the lowest-lying unoccupied bands are mainly of d character.

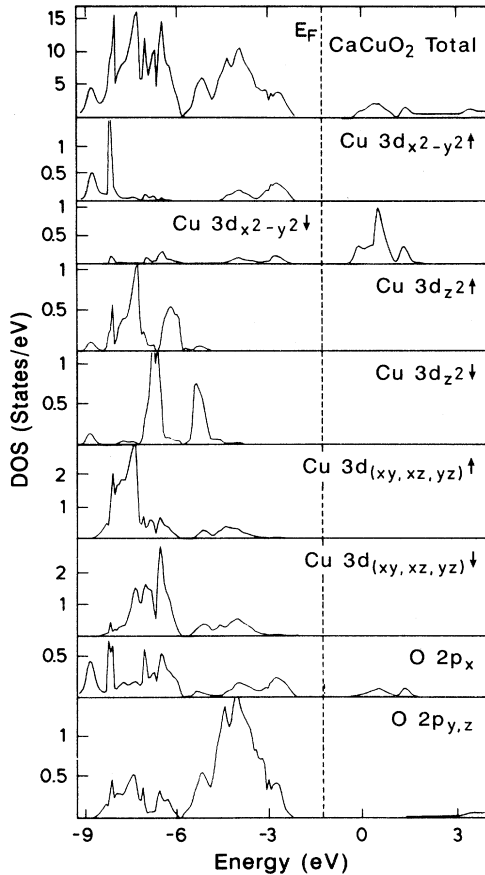


FIG. 1. The total and partial densities of states of O and Cu in CaCuO_2 , according to our new functional. $\text{O } 2p_x$ and $\text{O } 2p_{y,z}$ refer to the oxygen p orbitals pointing towards and perpendicular to the $\text{Cu } 3d_{x^2-y^2}$ orbitals, respectively.

II. RESULTS AND DISCUSSION

We have tested our method for the 3d-transition-metal monoxides, generally considered the archetypal Mott insulators. We further considered a couple of special cases: NiS because of its unusual metal-insulator transition, CaCuO_2 as a representative of the insulating parent materials of the high- T_c superconductors, and LiNiO_2 as an example of a trivalent charge-transfer-like material.

The standard LDA calculations were done using the linear muffin-tin-orbital method in the atomic-sphere approximation (LMTO-ASA) in the orthogonal representation.⁹ We used the low-temperature experimental lattice constants for all materials,^{44,45} which differ by only a few percent from the LSDA lattice constant. We note that the (magneto)volume effects induced by the form Eq. (8) are negligible.

For the calculation of the parameters U and J we used the method introduced by Gunnarsson *et al.*,¹⁰ as discussed in the Introduction. Instead of performing an impurity calculation, we used an 8-unit supercell, and set the hopping integrals to the d shell of the central transition-metal ion equal to zero. The d occupancies of the other 3d ions were kept fixed at integral values by removing the hopping. We note that the values of U barely depend on how one constrains the other 3d shells as long as the systems are rather localized. We then fixed the occupancies of the d shell of the central atom at two values ($n_{d\uparrow} = n^0/2 + \frac{1}{2}$, $n_{d\downarrow} = n^0/2$, and $n_{d\uparrow} = n^0/2 + \frac{1}{2}$, $n_{d\downarrow} = n^0/2 - 1$) and for these configurations the fully self-

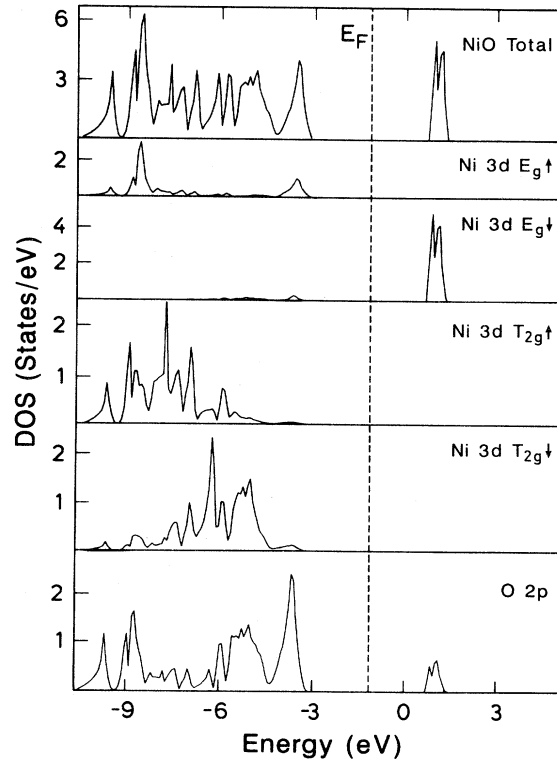


FIG. 2. The total and partial densities of states of NiO .

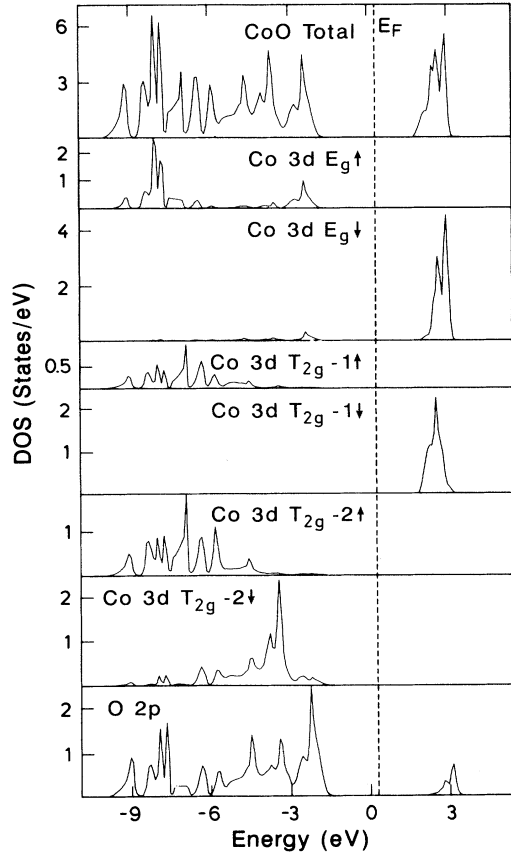


FIG. 3. The total and partial densities of states of CoO. Notice the inequivalence of the t_{2g} orbitals, due to the orbital dependence of the potentials.

consistent potentials were determined, allowing all electrons (except the 3d-electrons) to contribute to the screening. According to Slater's transition-state rule,⁴⁶ one obtains

$$U = \epsilon_{3d\uparrow} \left[n_{d\uparrow} = \frac{n^0}{2} + \frac{1}{2}, n_{d\downarrow} = \frac{n^0}{2} \right] - \epsilon_{3d\downarrow} \left[n_{d\uparrow} = \frac{n^0}{2} + \frac{1}{2}, n_{d\downarrow} = \frac{n^0}{2} - 1 \right] \quad (10)$$

and

$$J = \epsilon_{3d\uparrow} \left[n_{d\uparrow} = \frac{n^0}{2} + \frac{1}{2}, n_{d\downarrow} = \frac{n^0}{2} - \frac{1}{2} \right] - \epsilon_{3d\downarrow} \left[n_{d\uparrow} = \frac{n^0}{2} + \frac{1}{2}, n_{d\downarrow} = \frac{n^0}{2} - \frac{1}{2} \right], \quad (11)$$

where $\epsilon_{3d\sigma}$ are the 3d eigenvalues at the central atom, calculated at the fixed occupancies.

In Table I we summarize our results for parameters U and J for the 3d-transition-metal monoxides, as found from Eqs. (10) and (11). For nonzero J , the d bands split up further and it is then convenient to define a U^{eff} , which is derived from Eq. (1) using the lowest-energy (high-spin) $d^{n\pm 1}$ and d^n configurations. These values are also indicated in the table, as well as empirical estimates⁴³ for these quantities ($U_{\text{emp}}, U_{\text{emp}}^{\text{eff}}$), which we will discuss later in more detail. Using the calculated values for U and J , we determined the self-consistent solutions of Eqs. (8) and (9). In all cases we found the experimental spin structure (e.g., AF-II for the rocksalt oxides) to be the most stable one. The orbital ordering is a more delicate affair; in the cuprates as well as in MnO and NiO the degeneracy of the ground state is already lifted at the single-particle level. In CoO, the small tetragonal distortion pushes the $t_{2g} 3d_{xy}$ orbital to higher energy. On the other hand, the $t_{2g} 3d_{xz,yz}$ orbitals are still degenerate and this opens up the possibility of an electronically driven orbital ordering. However, the "orbital superexchange" energy scale is tiny, and the energy differences between ferro- and staggered orbital configurations turned out to be inside the noise of our calculation. We arrived at the same conclusion in the case of FeO.

The actual level splitting (before the hybridization with the d orbitals is switched on) in the self-consistent solutions of Eqs. (8) and (9) will be in general smaller than the "bare" U or J , because of the deviation from integral valency. If the actual d occupancy is d^{n+2x} (instead of d^n , e.g., $x=0.2$ in NiO), the splitting between the occupied spin-up and the unoccupied spin-down e_g levels is $(U+J)(1-x)$, and the splitting between the occupied t_{2g} and unoccupied e_g level with the same spin is $(U-J)(1-x)$ in the case of NiO. Because of our

TABLE I. Coulomb (U) and exchange parameters (J) and the splitting between the d^{n-1} and d^{n+1} high-spin states (U^{eff}), calculated using the constrained-density-functional method, compared to empirical estimates (Ref. 42) ($U_{\text{emp}}, U_{\text{emp}}^{\text{eff}}$). Further, the (diagonal) splittings between the highest occupied and lowest unoccupied d state, as well as the splitting between the O 2p level and the lowest unoccupied d state in the converged mean-field solution, are shown (U_{SCF} and Δ_{SCF} , respectively). For comparison, we also show the empirical p - d splitting (Ref. 42) (Δ_{emp}). All energies are in eV.

	U	J	U^{eff}	U_{emp}	$U_{\text{emp}}^{\text{eff}}$	Δ_{emp}	U_{SCF}	Δ_{SCF}
CaCuO ₂	7.5	0.98	6.5				4.3	2.5
NiO	8.0	0.95	7.1	6.7	6.1	6.0	5.7	4.0
CoO	7.8	0.92	6.9	5.3	4.9	5.4	5.8	5.1
FeO	6.8	0.89	5.9	5.1	3.5	6.1	5.2	4.9
MnO	6.9	0.86	10.3	7.8	8.8	8.9	9.2	5.5
VO	6.7	0.81	5.9	4.0	4.8	9.9		
TiO	6.6	0.78	5.8	3.5	2.9	8.3		

(mean-field) account of the Hund's-rule coupling, the occupied (or unoccupied) levels are also split. For instance, the splitting between the up- and down-spin t_{2g} states in NiO equals $J(2-2x)$. In Table I we indicate the energy difference between the highest-lying occupied and the lowest-lying unoccupied d orbitals (U_{SCF}) in the self-consistent-field solution. Finally, we also include in Table I the splitting between the oxygen p level and the lowest unoccupied d level (Δ_{SCF}), to be compared with the empirical charge-transfer energy (Δ_{emp}).

In Figs. 1–3 we show the partial densities of states (DOS) of CaCuO_2 , NiO, and CoO. The DOS of FeO and MnO are similar to that of CoO, except for the growing number of unoccupied t_{2g} bands. First, focusing on the unoccupied density of states of NiO (Fig. 2), we see that all the weight is concentrated in the narrow $E_g \downarrow$ peak, in agreement with the experimentally observed $d^8 \rightarrow d^9$ peak.² In CoO (Fig. 3) the $3d_{xy} \downarrow$ orbital is emptied too, and this band is located at ~ 0.5 eV lower energy. This crystal-field splitting of the unoccupied d band is also found experimentally.⁴⁷ The calculated splitting seems to be somewhat too small, which is probably due to our neglect of nonspherical corrections. Comparing now the unoccupied DOS of CoO or NiO with that of CaCuO_2 , we find that the width of the $3d_{x^2-y^2} \downarrow$ band of the cuprate is larger by a factor of 4–5 compared to that of the rocksalt oxides. As a result, a sharp $d^9 \rightarrow d^{10}$ peak is missing, which is in striking agreement with experiment.⁷ This is obviously related to the formation of a broad Cu $3d_{x^2-y^2}$ –O $2p$ band caused by the relatively small in-plane Cu–O bond length and a Cu–O–Cu bond angle of 180° . In CuO, on the other hand, the bond angles are much smaller (between 96° and 146°) so that two neighboring Cu $3d_{x^2-y^2}$ orbitals hardly couple via the same ($2p_x$ or $2p_y$) O orbital. One expects thus a strong decrease of the bandwidth in going from CaCuO_2 to CuO,⁴⁸ despite the similarity of both systems on a local level.⁴⁹ In Fig. 4 we show our result for the DOS of CuO. The CuO structure has four equivalent Cu atoms per cell. Experimentally, the unoccupied DOS of CuO is characterized by a relatively sharp peak corresponding with the unoccupied d band, which is strongly contrasting with the “blurred” unoccupied DOS of the high- T_c cuprates.⁵⁰ Our results suggest that this difference comes from the smaller bandwidth in the former. [Our calculation for CuO incorrectly splits the narrow band into four subbands due to slight inaccuracies in the directions of the local x and y axes. The proper bandwidth must lie between the calculated widths of the subbands (~ 0.1 eV) and the entire band (~ 1 eV).]

It is dangerous to compare our calculated DOS directly with photoemission (PES) line shapes. In general, one expects that satellites will have too much weight, features in the MF DOS will be too narrow, main-line satellite splittings will be underestimated, etc. Nevertheless, the differences between the calculated occupied DOS of CaCuO_2 , on the one hand, and CoO and NiO, on the other hand, are striking. In the former, a rather broad “main band” (between ~ -2 and -6 eV in Fig. 1) is found, while in the latter the low binding energy (BE) part of the

DOS is indicative of a two- (narrow-) peak structure (~ -4 and -5 eV in Fig. 2), as in experiment.^{7,51} The character of the low-lying ionization states of the cuprate is in rather good agreement with the expectations from many-body theory. These states are of $3d_{x^2-y^2}$ and $2p_{x,y}$ character, and the added hole has its spin antiparallel to the ground-state Cu spin (this is evident from the $3d_{x^2-y^2} \uparrow$ DOS). This is the mean-field analog²⁵ of the Zhang-Rice singlet.²⁶ We note that the “local singlet” binding energy is underestimated in MF. In the limit $\Delta, U - \Delta \gg t_{pd}$, one finds for this binding energy $\sim t_{pd}^2 / (U - \Delta)$ and the Kondo fluctuations add another $\sim t_{pd}^2 [1/\Delta + 1/(U - \Delta)]$.⁵² It is interesting to note that the “local singlet” bandwidth is, according to our calculation, rather large (~ 3 eV; see the $3d_{x^2-y^2} \uparrow$ DOS), in agreement with recent many-body calculations.⁵³ It is again instructive to compare CaCuO_2 with CuO. It can be seen that the local singlet bands and the unoccupied d bands are quite similar in shape, as if they are mirrored around E_F (suggestive with respect to the single-band ideas of, e.g., Zhang and Rice,²⁶). According to the calculation, the broad local singlet band is partially hidden under the main band in CaCuO_2 . On the other hand, in CuO this band is well separated and has a small dispersive width, although in the calculations the total width is only reduced by a factor $\frac{2}{3}$ compared with CaCuO_2 , due to the large splittings between the subbands. Gunnarsson *et al.*,⁴⁹ pointed out very recently that the photoemission spectrum of CuO is characterized by a peaklike

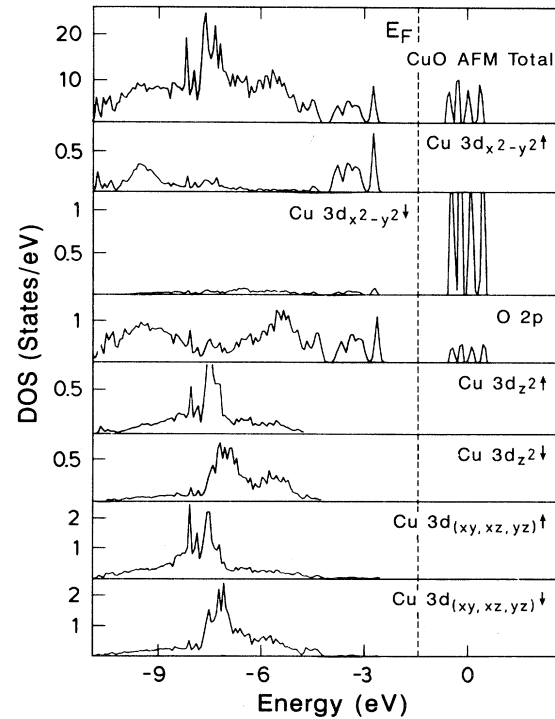


FIG. 4. The total and partial densities of states of CuO. Compared to CaCuO_2 , the unoccupied d , as well as the occupied local singlet, bandwidth is decreased.

structure at the valence-band top, which is missing in the spectra of high- T_c compounds.

In the case of NiO and CoO our results are less conventional. In the past, the lowest BE peak in the occupied DOS has been ascribed to the high-spin d^{n-1} state (e.g., ${}^4T_1 = e_g \uparrow e_g \uparrow t_{2g} \uparrow$ in NiO) and the higher BE shoulder to the low-spin state (in NiO ${}^2E = e_g \uparrow e_g \uparrow e_g \downarrow$),⁵¹ and this is also the outcome of several many-body-model calculations.^{5,6} According to our calculations, this high-spin-low-spin identification has to be reversed. The lowest peak in NiO is clearly of $\sim {}^2E$ character and of the same sort as the local singlet band in the cuprates. Due to our account of the Hund's-rule coupling, the $T_{2g} \downarrow$ DOS is shifted to lower BE compared to $T_{2g} \uparrow$, and the first maximum in the former coincides with the shoulder in the PES spectra. This low-spin nature of the lowest ionization state of NiO is in agreement with experiment. This follows unambiguously from doping experiments. NiO can be doped with large concentrations of Li, and the Ni(III) compound LiNiO_2 is especially well characterized.⁴⁵ In this compound, every second (111) plane of Ni is replaced by Li and the local environment of the Ni ions barely changes. LiNiO_2 is thus from a local perspective representative for NiO. According to x-ray absorption spectroscopy (XAS) data, the additional holes (introduced by Li doping) have O 2p character.⁵⁴ Further, LiNiO_2 is a low-spin ($S = \frac{1}{2}$) material.⁵⁵ The many-body interpretation is as follows: the added hole goes predominantly in the oxygen band and it gets bound to the Ni spin, forming a local doublet,

$$\sim (\sqrt{2} {}^3A_2(M=1)p_{e\downarrow} - {}^3A_2(M=0)p_{e\uparrow})/\sqrt{3},$$

in analogy with the Zhang-Rice singlet. In LiNiO_2 , a local doublet can be ascribed to each Ni site and the system is half-filled and therefore magnetically ordered.

Let us now consider what the electronic structure of LiNiO_2 looks like according to our mean-field theory. To simplify matters, we performed calculations for the rock-salt structure with every second (111) Ni plane substituted by Li, neglecting the small ($\sim 0.6\%$) contraction perpendicular to the (111) layers, which does not affect the states at E_F . In Fig. 5 we show the DOS for the most stable (ferromagnetic, ferro-orbital-ordered) ground-state configuration. Compared to NiO, there are some similarities. We find still a rather narrow $d^8 \rightarrow d^9$ unoccupied 3d band at roughly the same position as in NiO, relative to the first occupied state. The new aspect is that a new unoccupied band of predominantly O 2p character is found inside the "NiO gap," which is centered just above E_F . This is the same pattern as found by Kuiper *et al.*⁵⁴ in their XAS data.

How to interpret these findings? The important (180°) binding occurs along the cubic axis of the rock-salt structure. In Fig. 6 we show a simplified level diagram along one of these directions. As in NiO, the Ni ion is rather strongly polarized, and the 3d up- and down-spin levels are separated by $\sim U$. Because of the p - d hybridization the up- and down-spin O 2p levels next to an up-spin Ni will be pushed upwards and downwards, respectively. Adding one hole per Ni implies that the former gets

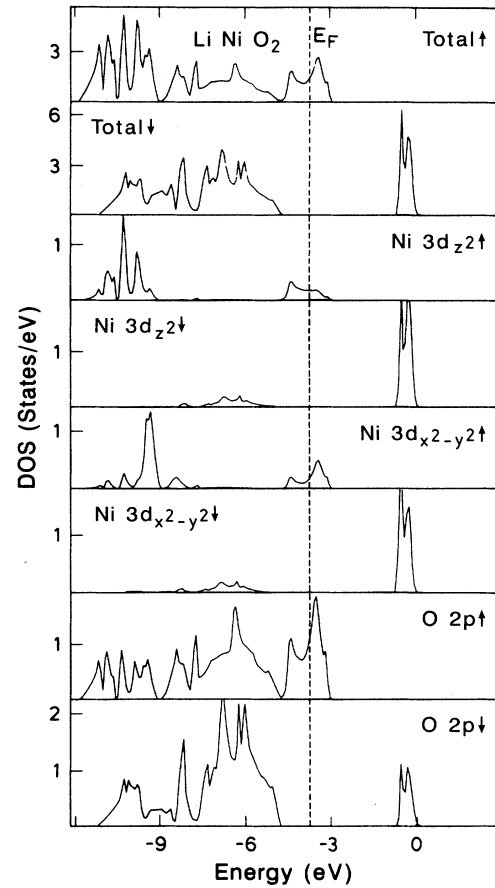


FIG. 5. The total and partial densities of states of LiNiO_2 , for a ferromagnetic arrangement of the local doublets perpendicular to the (111) planes.

unoccupied and we observe that the oxygen hole has its spin reversed relative to the 3d spin, and this one can call the MF version of the local doublet. In our calculation we find a moment of $1.30\mu_B$ and $-0.15\mu_B$ at the Ni and the O site, respectively, and the net moment per NiO_2 unit is therefore exactly $1\mu_B$ ($S = \frac{1}{2}$). Strictly speaking,

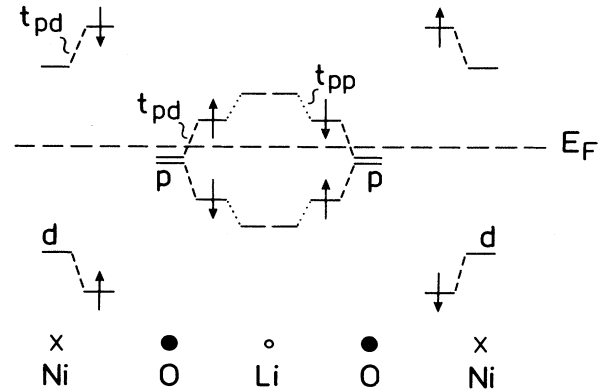


FIG. 6. Simplified level scheme for the binding along the cubic axis in LiNiO_2 for antiferromagnetic local doublet ordering. Dashed and dotted lines indicate shifts due to NiO and O-Li-O hybridization, respectively.

one should call this MF result a ferrimagnet, while in reality LiNiO_2 is better characterized by calling it a low-spin d^7 system. However, this difference is more of a quantitative than of a qualitative nature. The ferrimagnet will be characterized by an optical branch in the magnon spectrum, related to the out-of-phase rotation of the Ni and O spins. On the other hand, the low-spin system will have a doublet to quartet $d-d$ excitation, and the latter will be bigger than the magnon mass gap. Amusingly, the quantum fluctuations responsible for the increase of optical magnon gap are the O-hole Ni-spin Kondo spin-flip processes.

Turning to the overall magnetic structure, the issue is if the NiO_2 unit $S = \frac{1}{2}$ spins will order ferromagnetically (FM) or antiferromagnetically (AFM) and it is beforehand not obvious what will happen. In Fig. 6 we consider the AFM case. The “left” O $2p$ down-spin level will be occupied and to the right it will be unoccupied. These levels will hybridize via the Li site, pushing down the occupied state further, leading to an energy gain. In the FM this effect is not present and this (basically superexchange) mechanism will thus tend to favor antiparallel alignment. However, according to our calculations, the moments in the FM state are larger, and the resulting energy gain wins from the superexchange and we predict that LiNiO_2 is ferromagnetic. This is not a subtle balance. We find that the FM state is more stable than the AFM state by an amount ~ 0.15 eV/ LiNiO_2 , indicating that the NiO_2 units are not at all isolated from each other by the Li layers. The experimental situation is unclear. Some support for our prediction follows from the finding that at intermediate Li concentrations the Ni spins in next-nearest-neighbor layers have indeed a FM orientation.⁵⁵

According to (inverse) photoemission, LiNiO_2 is an insulator with a gap ~ 0.4 eV.⁵⁶ According to our calculation, it is still a metal (Fig. 5), although a metal-insulator transition is in the close neighborhood. The splitting between the up- and down local doublet bands is larger than their width and the problem is that there are two of these bands per spin direction. These have the symmetry of Ni-centered $3d_{x^2-y^2}$ and $3d_{3z^2-1}$ states, which are equivalent in the LiNiO_2 structure. We allowed for orbital polarization in the calculation and we found a ferromagnetic-type orbital polarization on the Ni site $n(3d_{x^2-y^2}) - n(3d_{3z^2-1}) = 0.15$. As can be seen from the figure, this tends to split the doublet band in an empty $3d_{x^2-y^2}$ and a filled $3d_{3z^2-1}$ part. However, Ni-centered orbital polarization is less effective in this respect than the spin polarization, and we find that the two bands still overlap. However, our result is very close to the metal-insulator transition and it is not hard to imagine that, e.g., a U on the oxygens (neglected by us) could drive the system insulating. Also, Jahn-Teller-type lattice distortions could be responsible. These distortions should be of the $O_h \rightarrow D_{4h}$ sort, and in Fig. 7 we show the result obtained if we elongate the NiO_6 octahedra by 4% in the z direction and contract the bonds with 2% in the x and y directions, stacking the distorted octahedra uniformly. It is seen that this relatively small distortion suffices to give

a gap of the right order of magnitude. This brings us to the remaining puzzle concerning LiNiO_2 . If Ni(III) low-spin counting makes sense, as we believe to be the case on rather general grounds, what is the reason that this system does not show a collective Jahn-Teller instability?

NiS has attracted much attention in the past because of its unconventional metal-insulator transition. Below the transition, NiS is a large-moment, small-gap antiferromagnetic insulator with an extrapolated Néel temperature of ~ 1000 K. At 260 K the volume contracts with $\sim 2\%$, and the material becomes a (semi)metal with a relatively low Pauli susceptibility.⁵⁷ In Fig. 8 we show our results for the DOS of NiS. Clearly, “ $U > W$ ” is well satisfied, and according to our calculation, NiS is a typical local-moment material. We also find that antiferromagnetic NiS is metallic and that the states at E_F are of nearly pure S $3p$ character. NiS is therefore a p -type material, as in the many-body picture.²⁰ Regarding the $M-I$ transition, the simplest assertion one can make is to ascribe this to a Stoner transition, where the volume effect leads to a change of bandwidth, quenching the exchange splitting.⁵⁸ We checked this possibility and, obviously, we found that the relatively small volume effects cannot fight the large U . This observation is supported by pho-

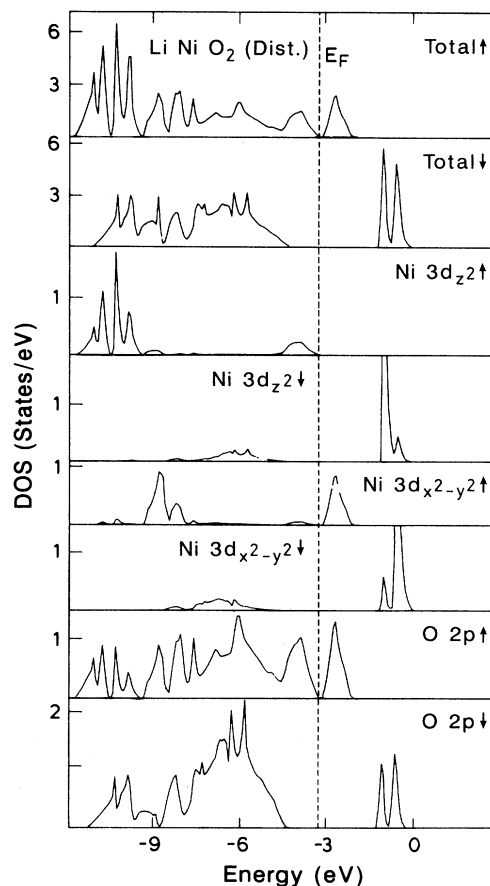


FIG. 7. The total and partial densities of states of NiLiO_2 as in Fig. 5, but now including a 2% (x,y) + 4% (z) tetragonal distortion of the Ni-O octahedra.

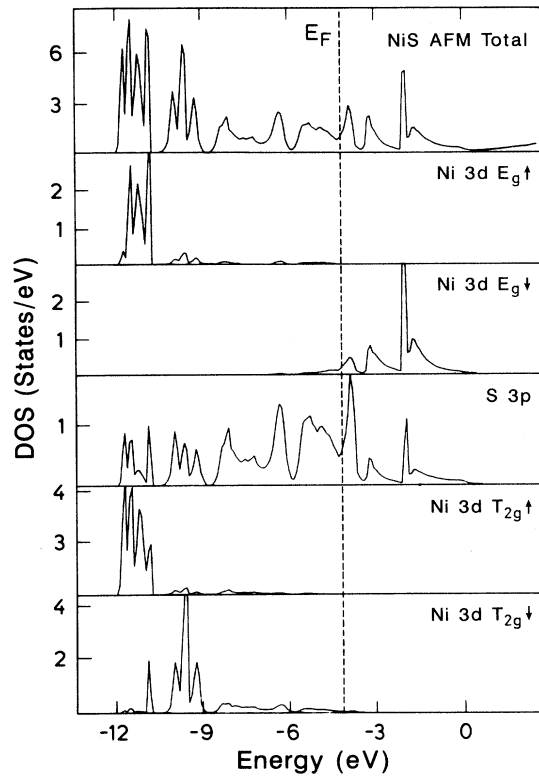


FIG. 8. Total and partial densities of states of NiS. This is a p -type local-moment metal.

toemission data of Fujimori's group.⁵⁸ We thus arrive at the interesting conclusion that the insulating state and the M - I transition of NiS are beyond mean-field theory.

So far, our method has been quite informative in qualitative respects. Let us now consider how well it works quantitatively. In Table II we summarize our findings for the band gaps and moments of the late-3d-transition-metal oxides. Especially at the end of the series, our moments are considerably larger than the LSDA moments, and these results are now within the experimental error bars. Notice that the values in brackets indicate the total moment, including the orbital contribution.

The calculated band gaps are more problematic. Experimentally, one finds the following pattern: the gaps in NiO and MnO are large and of equal magnitude, the gaps of FeO and CoO compounds are substantially smaller, and the cuprates have the smallest gaps. Except for the small cuprate gap, this trend is not reproduced by our method. We find instead that the gap is of the same order of magnitude in going from NiO to MnO, with a tendency to increase towards the middle of the series. Comparison of MF results for the gap with exact (diagonalization,⁵⁹ and quantum Monte Carlo²²) results in the case of the three-band Hubbard model indicates that MF theory always overestimates the gap magnitude, and from this point of view NiO and MnO seem to be more of the problem than the other compounds. In our results, the gap magnitude is limited by the charge-transfer energy, and this quantity is apparently underestimated in the calculations. We note that the standard LDA p - d splitting is

larger than ours; fixing $\langle n^0 \rangle$ in Eqs. (8) and (9) from the beginning (instead of adjusting it self-consistently) yields a NiO gap ~ 4 eV.

The underestimation of Δ cannot explain the small gaps of CoO and FeO, compared to the ones of NiO or MnO. Recently, Zaanen and Sawatzky conjectured that FeO and CoO are better characterized as classical ($U < \Delta$) Mott-Hubbard insulators, in contrast to the charge-transfer nature of, e.g., NiO or CuO.⁴³ The reason is that the U 's are relatively small in these two compounds. Zaanen and Sawatzky estimated the U 's from empirical atomic ionization potentials together with a constant screening contribution, determined by subtracting the empirical (PES) U from the atomic U of NiO. The smallest U is the one containing the exchange stabilization ($U_{\text{eff}}^{\text{emp}}$ in Table I) and this quantity is seen to be much smaller in CoO and (especially) FeO than in MnO or NiO, and it seems likely that $U_{\text{eff}} < \Delta$ in the former two. A relatively small gap is thus expected for FeO and CoO, and this "small U " interpretation is supported by the observation that the optical gap is rather blurred in these compounds, compared to the sharp (p - d excitonic) edges characteristic for nickelates and cuprates.⁴³ Looking at the LDA values for U and Δ , this crossover clearly cannot occur. The Δ 's tend to be smaller and the U 's larger than the empirical estimates (note that U_{eff} is $U - J$ for Fe, Co, and Ni and $U + 4J$ for Mn, neglecting orbital contributions) and FeO and CoO are, according to our method, also charge-transfer insulators. Further, a drop in U is also present in our results; however, it occurs between Co and Fe, instead of Ni and Co.

Although the Mott-Hubbard character of FeO and CoO remains to be proven, it seems quite probable that the LDA U 's and Δ 's are somewhat too large and too small, respectively. The same conclusion seems to follow from the comparison of impurity model results with experimental spectra.⁴⁹ We emphasize that this is not caused by our way of using these parameters: The mean-field treatment is merely a convenient test for the accuracy of the "constrained-LDA" parameters.

Although the problem is not acute for the localized materials considered up to now, it becomes quite serious in more delocalized systems. In Table I we have also included the LDA U 's for the early-3d-transition-metal monoxides. It can be seen that U stays about as large as in the late-3d-transition-metal monoxides, in disagreement with the generally accepted point of view. Accordingly, we find that also TiO and VO are relatively large gap insulators if we use these U 's in our functional. Alternatively, using Herring's⁶⁰ metallic screening (i.e., δn_d is exactly compensated by s, p charge), we find generally $U_{\text{met}} < 3$ eV. For such values of U , the MF treatment would predict VO and TiO to be nonmagnetic metals. This points to a rather serious problem with respect to the calculation of U : Even in strongly itinerant systems like the early-3d-transition-metal oxides, the metallic screening is not complete according to the LDA. This has a good reason; according to LDA, the d - sp Coulomb interaction is only a few eV, and this small interaction cannot compete with the large sp -band width. This problem deserves investigation.⁶¹

TABLE II. Experimental (expt) and calculated (LDA + U) spin moments (m , in μ_B) and energy gaps (E , in eV) of the late-3d-transition-metal monoxides. For comparison, we also show these quantities as calculated from LSDA (Ref. 1).

	E_{LSD}	$E_{\text{LSD}+U}$	E_{expt}	m_{LSD}	$m_{\text{LSD}+U}$	m_{expt}
CaCuO ₂	0.0	2.1	1.5 ^a	0.0	0.66	0.51 ^b
CuO	0.0	1.9	1.4 ^c	0.0	0.74	0.65 ^d
NiO	0.2	3.1	4.3, ^e 4.0 ^f	1.0	1.59	1.77, ^g 1.64, ^h 1.90 ⁱ
CoO	0.0	3.2	2.4 ^{j,k}	2.3	2.63 (3.60)	3.35, ^l 3.8 ^m
FeO	0.0	3.2	2.4 ⁿ	3.4	3.62 (4.59)	3.32 ⁿ
MnO	0.8	3.5	3.6–3.8 ^o	4.4	4.61	4.79, ^p 4.58 ⁱ

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III. CONCLUDING REMARKS

In this paper we have combined some common-sense notions (constrained LDA, the success of MF model theory, etc.) into a LDA-like parameter-free theory, which turns out to yield a sensible description of the electronic structure of Mott insulators. Admittedly, our construction is purely heuristic and it is, in this respect, different from the self-interaction correction (SIC) to LDA as recently applied by Svane and Gunnarsson to Mott insulators.³⁵ The SIC equations are derived within the framework of homogeneous-electron-gas theory,⁶² and this method is therefore a logical extension of LDA. This is obviously not the case for our construction. In the end, in SIC the localization is also driven by the on-site Coulomb interactions (now interpreted as a self-interaction effect), and the results of Svane and Gunnarsson for the 3d-transition-metal oxides seem similar to ours.³⁵ However, on closer inspection there are important differences. In our method, the orbital dependence of the potentials may quench the orbital moments further. In SIC, however, the nonspherical part of the xc energy tends to favor spherical orbitals, leading to an overestimation of the magnitude of the orbital moments.³⁵ On the other hand, the nonmagnetic character of the early-3d-transition-metal monoxides is reproduced in SIC, while our scheme has problems.

As emphasized before, our method should have the same deficiencies as the mean-field method in the context of the model Hamiltonian approach. However, as our examples make clear, it can be quite useful to have these mean-field solutions at hand, especially in complicated situations where band detail does matter. We foresee therefore that our method will have its major use in guiding the many-body approach in such situations. In some examples discussed in the present paper, it is not hard to imagine how the fluctuations will change the situation. In other cases this may not be so straightforward. For instance, in metallic Ni it is well established that the magnetism is well represented by the LSDA, which is an effective Stoner theory,³⁰ with $I \simeq 0.9$ eV.⁶³ In our MF approach, we would find a Stoner splitting $\sim U + J$, being too large by a factor of 5 ($U_{\text{LDA}} \sim 4$ eV). This large discrepancy is due to a rather severe breakdown of the MF approach in these metallic situations. However, in model theory it is well known that one has to go beyond a MF description in order to get a sensible description of itinerant magnets and also in this respect our method can be of use in the future. As shown by Stollhoff *et al.*,²⁹ these systems seem to be well described by the local-ansatz method of Stollhoff and Fulde.⁶⁴ However, up to now, these studies were for the 3d metals limited to model Hamiltonians, and our method makes it possible to perform *ab initio* local-ansatz calculations.

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