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IMPLICATIONS OF HUND'S SECOND RULE FOR THE INSULATING BEHAVIOR OF FeO and CoO*

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Implications of Hund's Second Rule for the Insulating Behavior of FeO and CoO

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A formal expression for Hund's second rule correlations is applied to energy band calculations for FeO, CoO, and NiO. In all three cases, insulating gaps are found, in contrast to standard band calculations, where an insulating gap is only found for NiO. The calculated orbital moments, though, are too large, due to the correction being based on the atomic limit.

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Standard unpolarized band calculations for the metal oxides MnO, FeO, CoO, and NiO give metallic behavior in sharp contrast to experiment. These results were anticipated long ago by Mott, which led to the development of the Mott insulator picture for these oxides (for reviews, see Refs. 1 and 2). The Mott gap is due to the fact that electrons in a d^n configuration (ground state) and a d^{n+1} configuration (excited state) see different effective potentials. The discontinuity of the effective potential between these two configurations then determines the size of the gap. If one wants to add a realistic version of this correction to an energy band calculation, one must have some distinction between occupied and unoccupied d states so as to apply the potential discontinuity properly. Therefore, on conceptual grounds, it would be desirable that some insulating gap (no matter how small) be present in the energy band calculation before such a self-energy correction was added.

About twenty years ago, Wilson [3] showed that a small insulating gap was obtainable for MnO and NiO if the correct type-II antiferromagnetic (AF) structure was taken into account. Later, Terakura et al [4] showed that gaps only existed for type-II AF (not type-I AF or ferromagnetic structures). This shows the important role that the correct symmetry plays in band theory as relates to ground state properties. For MnO, the t_{2g} down spin band is empty and for NiO it is completely filled. For FeO and CoO, one is therefore filling this band partially and no gap is possible. One suggestion was that CoO actually possesses a distorted bct AF structure, and that taking this into account might lead to a gap [1]. The author, though, performed a spin polarized band calculation in the bct structure and found no change in the density-of-states (DOS) at the Fermi energy as compared to the type-II AF case [5].

Another suggestion that has been made is that a partially filled t_{2g} band is unstable to orbital polarization, which may lead to a gap and an unquenched orbital moment. This has been suggested from a Mott picture by Brandow [2] and from a band picture

by Terakura et al [4]. Calculations from the Mott point of view using a simple model were performed early on by Wakoh [6], and recently sophisticated self-interaction-corrected (SIC) local density calculations have been performed by Svane and Gunnarsson [7]. The latter is one way of realistically including a Mott correction to the gap, and the results of Ref. 7 are quite promising in that reasonable sized gaps and magnetic moments were obtained for all the metal oxides. On the other hand, it is unclear how the differentiation between occupied and unoccupied d states was achieved in the calculation so as to properly include the SIC correction to the gap.

From the band point of view, the author recently showed that insulating gaps could in principle be obtained from band theory for FeO and CoO if Hund's second rule correlations were added [8]. Basically, the Hund's second rule correction splits the various m states apart, leading to an enhanced orbital moment. Once the orbital polarization is large enough, a gap is formed. The correction the author employed is a d electron version of a correction developed by Eriksson, Brooks, and Johansson for f electron systems [9]. One defect of Ref. 8, though, is that the prefactor of the correction has to be enhanced by 50% in CoO and 200% in FeO to obtain a gap. This implies that there is a need for an improved version of the correction.

The correction of Ref. 9 and 8 is obtained (for d electrons) by noting that the ground state energy of an atomic multiplet only involves two Racah parameters, A and B. The former primarily involves the F_0 Slater integral (i.e., U) and is multiplied by the number of pairs in the state, and thus is the same for all states with a particular d count. The latter involves the anisotropic part of the interaction and is composed of F_2 and F_4 Slater integrals. The A term is already included in an average sense in the band calculation (except for the Mott discontinuity effect). The value of the B term for various atomic configurations is given in Table 1. Also given is the average B term for that configuration, which is obtained by taking the B value of the closed shell, and multiplying this by the ratio of the number of pairs in the configuration to the number of

pairs in the closed shell. This "average" term is also assumed to be included in a local density calculation. The difference, ΔE , can be approximately represented by $-0.5 B L^2$ where L is the orbital moment, these values being listed in the column OP1. (Such a form is not exact for d^1 and d^4 , ΔE being zero since there is only self-interaction for these configurations.) This term, then, acts to enforce Hund's second rule (maximal L), which is not explicitly included in band theory since the exchange-correlation functional is based on that of an electron gas. This correction can then be applied at the eigenvalue level in a band code by functional differentiation, which leads to a term $-BL_m$ for a state with quantum number m .

It turns out, though, that for the d electron case, a formal expression can be derived which is exact for all atomic configurations. In the highest spin multiplet (assumed enforced by use of the local spin density approximation), the interaction between two d electrons is [10]

$$w_{12} = A - (8 + 3\mathbf{l}_1 \cdot \mathbf{l}_2) B \quad (1)$$

where $\mathbf{l}$ is the orbital moment of the electron. This results in a total energy

$$E = 0.5 n (n-1) (A-8B) + 1.5 [6n - L(L+1)] B \quad (2)$$

where n is the d count and L is the total orbital quantum number (this should be applied separately to each spin shell). If one then takes the difference between this and an "average" term as discussed above, one obtains the following for ΔE

$$\Delta E = \{ 2.25 n [5-n] - 1.5 L(L+1) \} B \quad (3)$$

These ΔE values agree with the exact results (by definition) as one can see from Table 1, column OP2. One notes that the L^2 term is larger by a factor of three than the correction used in Ref. 8.

The eigenvalue $L(L+1)$ is gotten from the operator $L_x^2 + L_y^2 + L_z^2$. If one assumes

in the solid case that the axis of quantization is along the direction of the orbital moment, then one can ignore the L_x and L_y terms (they can be included if needed). Functionally differentiating Eq. 3, one obtains the following correction for a basis function with eigenvalue m and spin quantum number s

$$\Delta\epsilon_s = \{ 2.25 [5-2n_s] - 3 L_s m \} B_s \quad (4)$$

where n_s and L_s are the d count and orbital moment constructed from states with quantum number s , and B_s is determined from the $l=2$ radial functions ϕ_s .

The details for the band structure calculations can be found in Ref. 8. The band structure program employed is an LMTO code with combined correction terms (two empty spheres are used per formula unit due to the open nature of the rock salt structure). A double-sized secular matrix is constructed using scalar relativistic basis functions, the upper (lower) block involving the spin up (down) potentials and $\sigma_z L_z$ part of the spin-orbit interaction, and the off-diagonal blocks involving the $\sigma_x L_x$ and $\sigma_y L_y$ parts of the spin-orbit interaction. The orbital polarization terms are added to the diagonal elements of the matrix (a more correct approach would be to put them in at the radial equation level; this would lead to m dependent radial functions and would involve significant modification of the LMTO codes). One then sums the resulting eigenvectors up to the Fermi energy to determine the spin occupations and orbital moments (each spin channel) to use in constructing the orbital polarization term for the next iteration (B_s is also determined at each iteration).

The results of the calculations can be found in Table 2. SO is spin-orbit only, OP1 is the old version of orbital polarization (Ref. 8) and OP2 the new version in this paper. The calculations assumed that the moments were aligned along the $\langle 001 \rangle$ axis for CoO and NiO, and along the $\langle 111 \rangle$ axis for FeO. The $\langle 001 \rangle$ results for SO and OP1 differ somewhat from the work of Ref. 8. In that work, trigonal symmetry was assumed.

If the moment is aligned along $\langle 001 \rangle$, though, only 4 of the 12 group operations survive due to breaking of trigonal symmetry. This was taken into account properly in the current calculation. One notes that for OP1, the DOS at the Fermi energy is little altered from the standard band case, although one obtains reasonable orbital moments. (The OP1 value for the CoO moment is consistent with experiment [11,12], whereas the experimental FeO moment [12] is even smaller than the calculated spin moment. The unreliability of the experimental FeO moment is due to extreme sensitivity to stoichiometry in that case.) As exhibited in the erratum to Ref. 8, one can obtain insulating gaps for OP1 by boosting the coefficient of the correction, although these gaps are practically zero. For OP2, this is not necessary, and for FeO one obtains a gap of 0.1 eV and for CoO a gap of 1.3 eV. The resulting orbital moments, though, are too large (by a factor of two for CoO). This is easy to understand, since such a correction is based on an atomic limit state, and thus one is obtaining a value for the orbital moment close to the appropriate Hund's rule value.

It is interesting to consider how one might correct the above results so as to reduce the orbital moment and yet maintain a gap. For the case of CoO and NiO, the moments do not actually lie along $\langle 001 \rangle$. In fact for CoO (SO case), the author has calculated the L_x and L_y components of the orbital moment and found that the actual moment is canted 27° off the $\langle 001 \rangle$ axis, in agreement with experiment [11]. The L_x and L_y components could be included in the OP2 calculations, but it is obvious that their effect will be to increase the moment further (if one takes the orbital moment of $2.53 \mu_B$ for OP2 and divides this by $\cos(27^\circ)$, one obtains $2.84 \mu_B$, close to the atomic limit value). On the other hand, one might expect that the Racah B parameter is somewhat reduced in the solid due to screening effects. In fact, comparing the value of B for NiO to that estimated by Brandow [2], one would have about a 25% reduction in the solid. A calculation was performed for CoO with a B reduced by 25%, but this

led to only a 3% reduction in the moment.

A more likely explanation is that the above correction is based on an atomic limit state and is diagonal in the m quantum number (if the quantization axis is orientated along the orbital moment direction). One could speculate that an analogous correction could be constructed utilizing crystal field basis states instead. Since such a basis has a quenched orbital moment, the resulting correction would be a paramagnetic version of the current correction, and may be useful in materials such as La_2CuO_4 . The problem with FeO and CoO is that their orbital moments are intermediate between the crystal field (zero) and free atom (Hund's rule) values, requiring a general correction which may be difficult to construct. The author has explored this problem by including the anisotropic part of the on-site d-d open shell Hartree Fock energy as a correction to the standard band calculations. Although such a correction reproduces the results in Table 1, the correction does not seem to work properly at the eigenvalue level (in the atomic case, occupying the correct m states leads to the correct total energy, but the eigenvalues obtained from functional differentiation give unoccupied m states which have lower energy than the occupied m states). More work, therefore, appears to be necessary in order to obtain a general orbital polarization correction applicable in all situations.

In conclusion, a formal version of a Hund's second rule correction in the atomic limit has been included in band structure calculations for FeO , CoO , and NiO , leading to insulating gaps in all three cases. The calculated orbital moments, though, are too large compared to experimental data, indicating the need for a more general correction valid away from the atomic limit.

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Table 1: Ground state energy, average energy of multiplet, energy difference, and calculated energy difference from OP1 and OP2 for the atomic configurations d^1 through d^5 . Energies are in units of the Racah parameter B.

State	E	E_{av}	ΔE	OP1	OP2
$d^1 \ 2D$	0	0	0	-2	0
$d^2 \ 3F$	-8	-3.5	-4.5	-4.5	-4.5
$d^3 \ 4F$	-15	-10.5	-4.5	-4.5	-4.5
$d^4 \ 5D$	-21	-21	0	-2	0
$d^5 \ 6S$	-35	-35	0	0	0

Table 2: Results of band structure calculations for FeO, CoO, and NiO. SO is spin-orbit only, OP1 and OP2 are the old and new versions of the orbital polarization correction. Tabulated are the spin and orbital moments (μ_B), the DOS at the Fermi energy ($\text{mJ/mol K}^2/\text{F.U.}$), and gap (eV).

	spin	orbital	DOS	gap
FeO - SO	3.47	0.16	5.2	-----
FeO - OP1	3.47	0.30	5.1	-----
FeO - OP2	3.64	1.17	0.0	0.1
CoO - SO	2.38	0.25	9.9	-----
CoO - OP1	2.39	1.12	9.4	-----
CoO - OP2	2.60	2.53	0.0	1.3
NiO - SO	1.08	0.15	0.0	0.3
NiO - OP1	1.10	0.35	0.0	0.4
NiO - OP2	1.40	1.37	0.0	0.1

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