Insulating gap in FeO: correlations and covalency

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We report calculations of the electronic structure of FeO in the LDA and LDA+U approximation with and without rhombohedral distortion. In both cases LDA renders an antiferromagnetic metal, and LDA+U opens a Hubbard gap. However, the character of the gap is qualitatively different in the two structure, and the difference can be traced down to underlying LDA band structure. An analysis of the calculations gives a new insight on the origin of the insulating gap in 3d monoxides and on the role of the $k$-dependency of U, missing in the contemporary LDA+U method.

It is a well-known fact that conventional band structure calculations incorrectly give metallic ground state for the intermediate 3d transition metal monoxides, CoO and FeO. Before the high-$T_c$ cuprates entered the scene, this had been often considered as the most notable failure of the Local Density Approximation (LDA). In the last decade a number of extensions of the density-functional theory were suggested, which, in different manners, led to insulating ground states for this compounds. Most successful were various flavors of the Self-Interaction Corrected (SIC) LDA\textsuperscript{1,2}, LDA+U\textsuperscript{3}, and the Orbital Polarization Correction in a crystal field basis\textsuperscript{4}. Interestingly, apart from the gap itself, LDA appears to do as good, and sometimes a better job, than these sophisticated extensions, especially when Generalized Gradient Correction to the conventional LDA is taken into account. Structural properties are reproduced very well, including rhombohedral distortion in FeO\textsuperscript{5}, and its increase with pressure\textsuperscript{6}. Moreover, angular resolved photoemission renders the bands more similar to the LDA bands, than to those in other calculational scheme (except for the narrow range near the gap)\textsuperscript{7}. The magnitude of the magnetic moment, which is often believed to be the first indication of an LDA failure, is nearly exact for the spin moment in CoO (2.4 $\mu_B$) and in FeO (3.5 $\mu_B$, assuming no orbital moment). On the contrary, the gap-improving calculation tend to overestimate the Fe moment, especially when the orbital moment is included (i.e., there is a tendency to underestimated the crystal field quenching of the orbital moment). It seems, then, that the main problem in the LDA is purely spectroscopical (quite in the spirit of the density functional theory), namely non-existence of the gap. It is worth noting that an important common feature of the LDA and the corrected schemes mentioned above is substantial width of the metal $d$-bands (for instance, in LDA the width of Fe $t_{2g}$ band at normal pressure is about 1.4 eV). This should be contrasted with the popular analysis of the electronic structure of 3$d$-oxides in terms of separate levels of a width less than Jan-Teller energy and spin-orbital coupling\textsuperscript{8}. The fact that LDA gaps are always too small is well understood. Mathematically it appears as the density-derivative discontinuity of the Kohn-Sham potential in the DFT. The physics of this discontinuity may be different, but for transition metal oxides (NiO, MnO) it is usually associated with the Mott-Hubbard repulsion. In view of this, it has always been much more disturbing to have wrongly a metallic behavior in LDA calculation, than just to have a wrong gap. As formulated by Norman\textsuperscript{9}, “one would like to obtain a gap at the level of a density functional calculation (no matter how small) so as to define the Mott-Hubbard correction in an unambiguous fashion”. Moreover, even in a case when LDA does not give a gap, but gives reasonable band structure except for the immediate vicinity of the Fermi level, and correctly describes delicate features of the ground state, like magnetoelastic interactions, it is desirable to have a correction scheme which does not destroy the LDA bands completely, but rather corrects them in a systematic manner. Unfortunately none of the schemes above acts in such a way. In this paper we shall analyze the results of the rotationally invariant LDA+U calculations for FeO in more details than is usually done, and compare them with the standard LDA calculations, paying particular attention to the process of the LDA+U gap opening in cubic and rhombohedral structure. We will see that the ground state in the LDA+U approach is intimately related with the underlying LDA band structure, although LDA+U cannot fully account for the bands hybridization effects, which seem to be quite important here. We will argue that none of the existing “corrected LDA” schemes (nor the straight LDA) correctly describes the insulating ground state in FeO and similar compounds. On the other hand, non-local schemes similar to the GW approximation may be able to provide a qualitatively correct description. It is worth noting that none of the existing “extended-LDA” calculations has taken into account such an important factor as the distortion from the ideal cubic NaCl-type structure, which is associated in 3$d$-monoxides with the onset of magnetic ordering.
Electronic structure of an isolated Fe$^{3+}$ ion in a cubic field is described in the high-spin state by the following scheme. The spin-up $d$-states are all filled, and separated from the spin-down states by the exchange splitting $E_{ax}$. The partially occupied spin-down states are split by the crystal field, so that $\epsilon(e_g) - \epsilon(t_{2g}) = \Delta \ll E_{ax}$. There is one electron in the $t_{2g}$ state, which is triply degenerate. Antiferromagnetic FeO has close-packed (111) planes of Fe ions with the same spin, which alternate with the similar planes with the opposite spin, thus lowering the symmetry to rhombohedral one. In the rhombohedral field, there is one linear combination of the $t_{2g}$ states, namely $A_{1g} = (xy + yz + zx) / \sqrt{3}$, which can also be written as $3Z^2 - r^2$, where $Z$ is parallel to [111] (here and below we shall use lower case symbols for the states classification in cubic symmetry and upper case symbols for the rhombohedral nomenclature). The four other states have the same symmetry $E_g$ (in the rhombohedral nomenclature), but when the deviation from the cubic symmetry is small one can speak about the upper two levels, $E_g^1$, and the lower two levels, $E_g^2$, which are close to the $A_{1g}$ also originate from the cubic $t_{2g}$ states, and are separated from $E_g^0$ by approximately $\Delta$. In the LDA calculation, when the crystal symmetry is still cubic, although the magnetic ordering is rhombohedral, the splitting between $E_g^1$ and $A_{1g}$ is small, much smaller than their bandwidths, so that they merge into one band (corresponding to the cubic $t_{2g}$ band), which is necessarily metallic. Note that although the magnetism in this system appears due to the indirect exchange and is determined by the O-Fe $pd$ interaction, the width of the $t_{2g}$ band is mainly due to the Fe-Fe $dd\sigma$ overlap. Fe-O hopping for this band is mainly $pd\pi$ and weak. The situation in CoO with two $t_{2g}$ electrons is very similar.

There were several successful attempts to obtain an insulating state in FeO. Interestingly, all these approaches give insulating gap in a fair agreement with the experiment, but all because of different reasons. SIC calculations favor $d-$bands in pure orbital states, that is, undermining the role of crystal field and quenching of orbital moment. The effect on the occupied $d$-states is thus extremely strong (of the order of 1 Ry) and all four oxides come out as pure charge transfer insulators. This is in contradiction with the general experimental indication that the character of the band gap changes from predominantly Mott-Hubbard to predominantly charge-transfer when going from MnO to NiO. Large orbital moment is obtained for FeO, in contradiction with the experiment (an argument is usually made that the experimental number may be incorrect because poor sample quality). It is also worth noting that the SIC formalism was initially invented as a remedy of the LDA in the direction of the exact, self-interaction free density functional. It is hard to imagine, however, that the exact density functional theory with its orbital-independent one-electron potential can unquench the orbital moment. The orbital-corrected functional used by Norman has a similar problem. The correct many-body solution for an isolated ion with unfilled $t_{2g}$ shell in a cubic field has an energy contribution proportional to the total angular momentum. This term, however, does not favor a specific direction of the momentum, that is, does not include the projections. The only interaction which does unquench the orbital momentum is spin-orbit, and it is relatively weak. Norman’s correction has the same functional form as the exact quantum chemical expression, but substitutes the total momentum by its projection on the quantization axis. This orbital moment projection dependent term acts in a way similar to the spin-orbit coupling, but with a much larger magnitude (of the order of exchange splitting $J$). Thus in FeO the occupied spin-down $d$-band is too close to a pure $m = 1$ state, that is, $xz + iyz$.

![FIG. 1. (a) LDA band structure without a rhombohedral distortion. The bars show the relative $A_{1g}$ character of the corresponding states; (b) LDA+U bands for the same crystal structure. Note the bottom of the Fe($s$) band at the \Gamma point.](image)
strongly mixed, the $A_{1g}$ (in rhombohedral notations) orbital being slightly more occupied than each of the two $E'_g$ orbitals. When formulated in rotationally invariant form, LDA+U tends to apply the positive $U$ correction to less occupied $E'_g$ orbitals, making them less and less filled (potential $U$ correction for more filled $A_{1g}$-orbital is negative), and eventually splits off the $A_{1g}$ band, forming a gap between it and the $E'_{g}$ bands. Sufficiently large $U$ (we used the empirical value of $U=5.1$ eV), which gives a good value for the gap; constrain LDA calculations yield a somewhat larger $U=6.8$ eV) pushes the occupied $A_{1g}$ band down close to, and for $U=6.8$ eV right into, the $O(p)$-bands manifold, and the unoccupied $E'_g$ bands up above the bottom of the Fe($s$) band. This seems to be in qualitative agreement with the photoemission experiments, which show the top of the valence band to be of the mixed O2$p$-Fe3$d$ character and with the optical experiments, which indicate a weak absorption between 0.5 and 2.0 eV, assigned to the ($pd$) – $s$ transitions, and strong absorption edge at 2.4 eV due to transitions into the Fe($d$) bands. In our calculations, the minimal gap opens between the $O(p)$–Fe($d$) band and the Fe($s$) band at 1.5 eV and transitions into the Fe($d$) bands start at 2.2 eV.

LDA and the LDA+U bands refer to the cubic FeO (here and below we show results of the ASA LMTO calculations with the unit cell volume 256 bohr$^3$/FeO, close to the LDA equilibrium volume $^{19}$). Since only 1 orbital, $A_{1g}$, is occupied (see Table $^2$), there is no orbital moment. One can expect that including weak (a few mRy) spin-orbit coupling will create a small orbital moment, but hardly one comparable with the spin magnetization.

It is interesting that the way the gap opens in LDA+U in the cubic structure is very "LDA-like": The only way to open a gap in an effective one-electron approximation is to split the $t_{2g}$ band by (magnetic, in this case) rhombohedral symmetry and to occupy the $A_{1g}$ orbital for FeO and the two $E'_g$ orbital in CoO. In fact, this is exactly what happened in the LDA calculations of Dufek et al. $^4$, who used an exotic LDA functional, which gave poor total energies but did open gaps in both compounds.

Overall this seems to be a physically satisfactory description of the gap opening. However, this is not as straightforward as one may think. To show the problem, let us compare the calculations in the cubic structure with those in the rhombohedrally distorted structure (Fig. $^2$ we used the LDA equilibrium distortion, calculated in Refs. $^2$ experimental distortion is smaller, but increases with the pressure). To understand the result, one should keep in mind that dispersion of the $t_{2g}$ bands is mainly due to direct $dd\sigma$ hopping between the like spins, which can be easily verified in the LMTO-TB method by removing oxygen orbitals from the basis set, or by looking directly on the corresponding elements of the LMTO-TB Hamiltonian. We observe that the distortion increases the $t_{2g}$ bandwidth (due to decreased distance between the like-spin ions), but mainly at the expense of the $E'_{g}$-like bands. The dispersion of the $A_{1g}$ band decreases instead, thus leading to a decreased occupancy of the $A_{1g}$-like state (because the whole $t_{2g}$ manifold is less than half filled). One can see this by comparing the occupancy matrices in the cubic (Table $^1$) and in the distorted (Table $^2$) structure on the first iteration, i. e., before the effect of $U$. While in the cubic structure the $A_{1g}$ state was the mostly occupied one (with the two $E'_g$ states close next), in the distorted structure the $E'_{g}$ states are twice more occupied than the $A_{1g}$ one.

![Graph](image-url)
it a separate band and to open a gap between this band and the rest of the spin-minority $d$-bands (Table IV).

One may feel it unphysical that the method converges to qualitatively different ground states with and without distortion. This fact suggests that probably the correct solution should be intermediate between the two LDA+U stationary points, a completely full and a completely empty solution should be intermediate between the two LDA+U distortion. This fact suggests that probably the correct and the rest of the spin-minority it a separate band and to open a gap between this band and the LDA+U opens gaps, but these gaps are of completely different character in the two structures, and also different from the gaps appearing in other “corrected-LDA” schemes, which, in turn, differ by their physical nature from each other. We believe that this is a consequence of the local character of the Mott-Hubbard correction in the conventional LDA+U method, and neither straight LDA, nor “corrected-LDA” methods provide a proper physical description of the gap formation. We argue that the ultimate method must take into account the non-local character of the Coulomb repulsion.

We are thankful to O.K. Andersen, R.E. Cohen, D.I. Khomskii, A.I. Lichtenstein, and W.E. Pickett for useful discussion. We acknowledge the hospitality of the Max-Planck-Institut für Festkörperforschung, where most of this work was performed. One of us (VIA) was in part supported by Russian Foundation for Fundamental Research (grant RFFI 96-02-16167).

To summarize, we report conventional LDA calculations and rotationally-invariant LDA+U calculations for antiferromagnetic FeO, both in the cubic and in a rhombohedrally distorted structure. In both cases LDA+U opens gaps, but these gaps are of completely different character in the two structures, and also different from the gaps appearing in other “corrected-LDA” schemes, which, in turn, differ by their physical nature from each other. We believe that this is a consequence of the local character of the Mott-Hubbard correction in the conventional LDA+U method, and neither straight LDA, nor “corrected-LDA” methods provide a proper physical description of the gap formation. We argue that the ultimate method must take into account the non-local character of the Coulomb repulsion.

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TABLE I. Orbitals and their occupations without rhombohedral distortion, for $U = 0$. Coordinates system corresponds to the rhombohedral symmetry: $z$-axis is perpendicular to the ferromagnetic Fe planes, $y$-axis points towards the nearest neighbor Fe with the like spin. The character of the orbitals is, in the order of the table, $2 \times E'_{g}$, $2 \times E''_{g}$, $A_{1g}$

| occupation | $xy$ | $yz$ | $3z^2 - 1$ | $xz$ | $x^2 - y^2$ |
|------------|------|------|-----------|------|-----------|
| 0.17       | -0.03| 0.03 | 0.00      | -0.65| 0.76      |
| 0.17       | 0.75 | -0.66| 0.00      | -0.03| 0.03      |
| 0.31       | 0.60 | 0.69 | 0.00      | 0.30 | 0.26      |
| 0.33       | -0.26| -0.30| 0.00      | 0.69 | 0.60      |
| 0.39       | 0.00 | 0.00 | 1.00      | 0.00 | 0.00      |

TABLE II. Orbitals and their occupations without rhombohedral distortion, for $U = 5.1$. The character of the orbitals is $2 \times E''_{g}$, $2 \times E'_{g}$, $A_{1g}$

| occupation | $xy$ | $yz$ | $3z^2 - 1$ | $xz$ | $x^2 - y^2$ |
|------------|------|------|-----------|------|-----------|
| 0.04       | -0.10| -0.10| 0.00      | 0.68 | 0.72      |
| 0.04       | 0.72 | 0.68 | 0.00      | 0.10 | 0.10      |
| 0.10       | 0.53 | -0.57| 0.00      | -0.46| 0.43      |
| 0.10       | -0.43| 0.46 | 0.00      | -0.57| 0.53      |
| 0.90       | 0.00 | 0.00 | 1.00      | 0.00 | 0.00      |

TABLE III. Orbitals and their occupations with 6% rhombohedral distortion, for $U = 0$. The characters are $2 \times E'_{g}$, $A_{1g}$, $2 \times E''_{g}$

| occupation | $xy$ | $yz$ | $3z^2 - 1$ | $xz$ | $x^2 - y^2$ |
|------------|------|------|-----------|------|-----------|
| 0.17       | -0.55| 0.84 | 0.00      | -0.02| 0.01      |
| 0.17       | -0.01| 0.02 | 0.00      | 0.83 | -0.56     |
| 0.19       | 0.00 | 0.00 | 1.00      | 0.00 | 0.00      |
| 0.38       | 0.84 | 0.55 | 0.00      | 0.00 | 0.00      |
| 0.39       | -0.01| -0.01| 0.01      | 0.56 | 0.83      |

TABLE IV. Orbitals and their occupations with 6% rhombohedral distortion, for $U = 5.1$. The characters are $A_{1g}$, $E'_{g}$, $2 \times E''_{g}$, $A_{1b}$, $E''_{g}$

| occupation | $xy$ | $yz$ | $3z^2 - 1$ | $xz$ | $x^2 - y^2$ |
|------------|------|------|-----------|------|-----------|
| 0.04       | -0.02| 0.00 | 0.99      | 0.14 | 0.04      |
| 0.04       | 0.96 | 0.28 | 0.02      | 0.01 | 0.01      |
| 0.10       | -0.28| 0.96 | 0.00      | 0.02 | -0.01     |
| 0.10       | 0.01 | -0.02| -0.09     | 0.83 | -0.56     |
| 0.86       | -0.01| 0.00 | -0.12     | 0.55 | 0.83      |