Insulating Ground States of Transition-Metal Monoxides from Exact Exchange

E. Engel and R. N. Schmid*

Institut für Theoretische Physik, J.W. Goethe-Universität Frankfurt, Max-von-Laue-Strasse 1 D-60438 Frankfurt/Main, Germany

(Received 26 February 2009; published 17 July 2009)

The exact exchange of density functional theory is used to calculate the electronic structure of the antiferromagnetic (type II) phases of the transition-metal monoxides MnO, FeO, CoO, and NiO at $T = 0$. In contrast with the local density approximation (LDA) and generalized gradient approximation, the exact exchange (combined with LDA correlation) correctly yields insulating ground states for all four compounds. The values for the band gaps and magnetic moments obtained with this parameter-free *first principles* method are in good agreement with the experimental data. While correlation plays a major role for the electronic structure, these results demonstrate that the mere opening of a gap in FeO and CoO is already obtained on the level of density functional theory, if the exact, multiplicative exchange potential is combined with a full potential method. State-dependent potentials are not required for obtaining a gap.

DOI: 10.1103/PhysRevLett.103.036404 PACS numbers: 71.15.Mb, 31.15.E−, 71.20.Be, 71.27.+a

The treatment of strongly correlated systems is one of the great challenges for density functional theory (DFT). Prototype systems of this class are the transition-metal monoxides MnO, FeO, CoO, and NiO. Neither the local density approximation (LDA) nor the generalized gradient approximation (GGA) reproduce the antiferromagnetic (type II—AF II) ground states of FeO and CoO [1–3]. In addition, the gaps predicted for MnO and NiO are marginal and therefore far from experiment. This has prompted the application of semiempirical modifications of the LDA and GGA, as the self-interaction corrected (SIC) LDA [4,5], the LDA + U approach [6] and various hybrid schemes [7]. Alternatively, the LDA is combined with explicitly correlated methods, as in the LDA + DMFT method [8]. All these approaches yield insulating ground states for the four monoxides and predict gaps of the right order of magnitude. In detail, however, the results differ significantly.

The success of the SIC-LDA, LDA + U and hybrid schemes primarily stems from their improved cancellation of the electronic self-interaction in the direct Coulomb potential. A complete and parameter-free cancellation of the self-interaction is provided by the exact exchange (EXX) of DFT (for an overview see [9]). In this contribution we demonstrate that this *ab initio* DFT approach resolves the problems of the LDA and GGA with the insulating ground states and predicts band gaps and magnetic moments in good agreement with experiment. In particular, the EXX gaps and moments follow the experimental trends through the 3d series.

First attempts to apply the exact exchange to the transition-metal monoxides were made a decade ago. An LMTO-ASA calculation for MnO [10] demonstrated that the EXX scheme provides an improved density of states for this compound. On the other hand, an EXX calculation for FeO [11] did not lead to the desired insulating behavior (see Fig. 1). However, in this work the multiplicative EXX potential was evaluated in the Krieger-Li-Iafrate (KLI) approximation [12]. While the KLI approximation reproduces the exact EXX potential of atoms and diatomic molecules quite well [13], it has recently become clear that it does not accurately account for directional information in the exchange potential [14].

In the present contribution we therefore apply the exact EXX potential, which is obtained from the optimized potential method (OPM) [15]. All calculations are per-

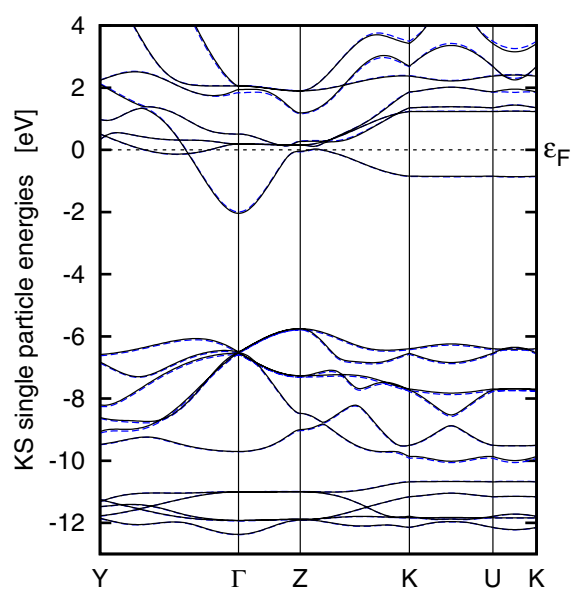

FIG. 1 (color online). Band structure of FeO in AF II phase obtained by plane-wave-pseudopotential calculations with the exact exchange and LDA correlation, utilizing the KLI approximation: Hard pseudopotential for iron with cutoff radii of $r_{c,s} = r_{c,p} = r_{c,d} = 0.8$ bohr and plane-wave cutoff energy of $E_{\rm cut} = 300$ Ry [11] (solid, black lines) versus soft pseudopotential with $r_{c,s} = 0.86$ bohr, $r_{c,p} = 1.0$ bohr, $r_{c,d} = 1.15$ bohr and $E_{\rm cut} = 160$ Ry (dashed, blue lines).

 © 2009 The American Physical Society

TABLE I. Technical parameters of PWPP-OPM calculations: Cutoff radii r_c for $3d$ atoms, experimental lattice constant a (as cited by [7]), plane-wave cutoff E_{cut}, cutoff X_{cut} for v_x. For oxygen $r_{c,s} = r_{c,p} = 1.0$ bohr has been applied.

	r_c [bohr]			a [Å]	E_{cut} [Ry]	X_{cut} [Ry]
	s	p	d			
MnO	0.86	1.05	1.35	4.445	140	96
FeO	0.86	1.00	1.15	4.334	160	96
CoO	0.80	1.00	1.15	4.254	160	96
NiO	0.75	0.95	1.15	4.171	160	96

formed within the plane-wave pseudopotential (PWPP) approach for the exact exchange [16], utilizing norm-conserving, relativistic EXX pseudopotentials [17]. The valence space of Fe includes the $4s$ state as well as the complete M shell: In spite of the energetic separation of the $3s$, $3p$ from the $3d$ state, EXX pseudopotential calculations necessarily have to be based on the complete shell, as the overlap (interaction) of the semicore states with the $3d$-states is too large to be neglected in the Fock integral. The corresponding cutoff radii are given in Table I, together with the associated plane-wave cutoffs E_{cut}. The sensitivity of the results to the cutoff radii and energies has been checked by variation of these parameters. Figure 1 demonstrates that the values of Table I lead to converged results. As the exchange potential is much smoother than the nuclear Coulomb potential, a reduced energy cutoff (X_{cut}) has been applied for v_x. The value of 96 Ry used gives essentially the same results as a cutoff of only 80 Ry.

All calculations have been done for the rocksalt structure, thus ignoring the rhombohedral distortion of the unit cell. For the lattice constants the experimental values have been chosen (see Table I). The exact exchange has been combined with the LDA for correlation (VWN) [18]. In the self-consistent calculations 20 special k points have been used for integration over the first Brillouin zone. Essentially the same results are obtained with 10 special k points. Spin-orbit coupling of the valence electrons has been neglected—it has no relevant effect on the properties considered [7].

The band structures and densities of states (DOS) resulting from this approach are shown in Figs. 2–5. All four compounds are found to be insulating. In the case of MnO the EXX-DOS, which agrees very well with the corresponding LMTO-ASA result [10], has some similarity with the SIC LDA, LDA + U, and hybrid data [5,7]. One finds strong hybridization of the Mn $3d$ and O $2p$ states, with the latter contributing about 50% to the DOS just below the Fermi energy. This observation is consistent with the experimental findings that the band gap is of mixed Mott-Hubbard–charge-transfer character [19–21] (the net charge in a sphere of radius 2.6 bohr around an oxygen atom is about 1.7). The EXX-DOS also shows the very

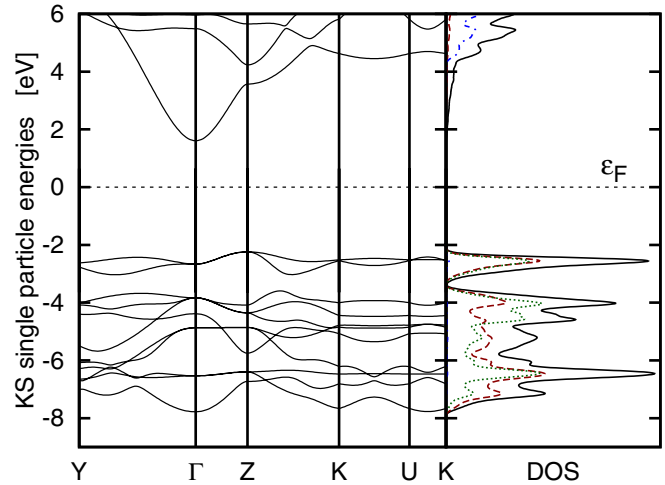

FIG. 2 (color online). Band structure of MnO (AF II) obtained by PWPP calculation with the exact exchange in combination with LDA correlation [18], using the full OPM for the evaluation of the exchange potential. Also shown are the total (solid, black line) and partial densities of states: O$2p$—dashed, red line; Mn$3d$ with majority ↑—dotted, green line; Mn$3d$ with majority ↓—dash-dotted, blue line.

slow rise above the Fermi level found with the LDA + U approach.

The agreement between EXX and LDA + U results [7] is less close for FeO, although the basic structure of the DOS is again similar. The most pronounced feature is an extremely narrow valence band, which is separated by more than 2 eV from the hybridized majority-spin Fe $3d$ and O $2p$ states below (the charge transfered to the oxygen atoms is again about 1.6). The small band width is a result of the enhanced $3d$ localization, resulting from the exact SIC. The nature of this narrow valence band is illustrated in Fig. 6, which shows the corresponding orbital density for the spin-up channel at the Γ point. As indicated by the

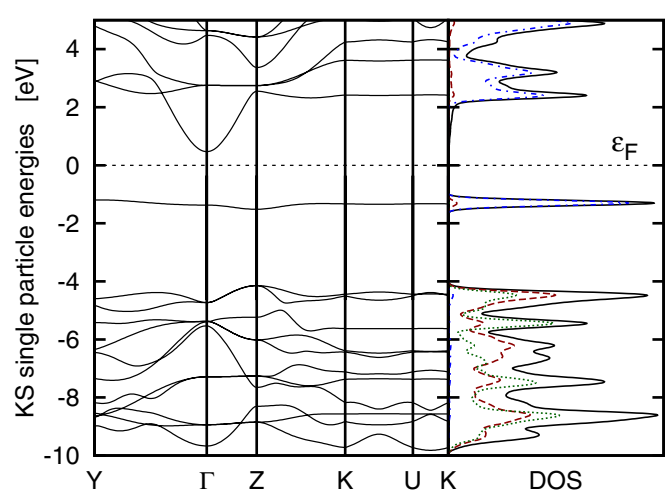

FIG. 3 (color online). As Fig. 2 for FeO.

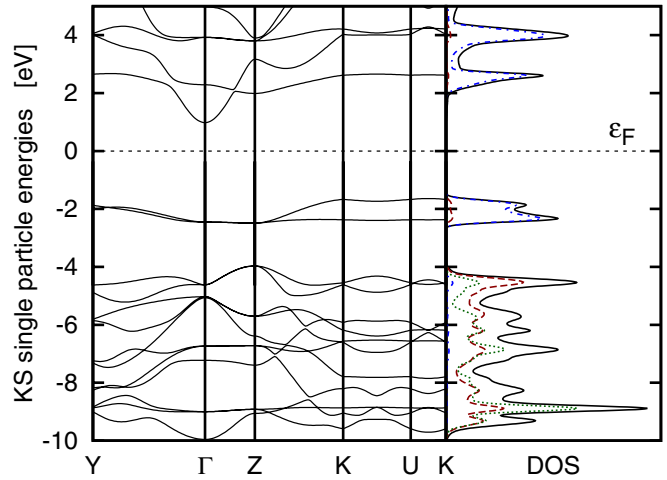

FIG. 4 (color online). As Fig. 2 for CoO.

majority spins at the iron sites, the valence state belongs to the minority-spin channel at the site at which it is located. Closer inspection of Fig. 6 demonstrates that this state has rather pure $3(z')^2 - r^2$ character in the coordinate system with the z' axis perpendicular to the AF II planes ($|3(z')^2 - r^2\rangle = (|xy\rangle + |yz\rangle + |zx\rangle)/\sqrt{3}$ [1]). This a_{1g} state (in the rhombohedral nomenclature) has exactly the same orbital character and the same symmetry as the corresponding LDA + U band [22]. As indicated by the LDA + U results, the proper elimination of the self-interaction stabilizes this t_{2g} state (with respect to the cubic axis) so much that a population imbalance of three t_{2g} states is energetically favorable and a gap emerges.

Two minority-spin t_{2g} states are filled in the case of CoO. These bands are separated from the majority-spin bands by about 1.5 eV, in contrast to the situation in all other approaches, in which these states merge with the majority-spin bands. A similar picture is observed for NiO, where the minority-spin t_{2g} states are now completely filled. While their separation from the majority-spin bands shrinks to about 0.5 eV, the gap between these occupied bands is still clearly visible. For both compounds the width of the minority-spin t_{2g} bands is rather small, in line with the very small admixture of O $2p$ states to these bands. At the same time, the exchange splitting resulting from the EXX (2.2 eV for the Ni atom, 3.3 eV for Co) dominates over the ligand field splitting, unlike the situation in the LDA, for which no clear energetic ordering is obtained [1]. As a result of the small band width and the large exchange splitting the minority-spin t_{2g} states separate from the majority-spin bands.

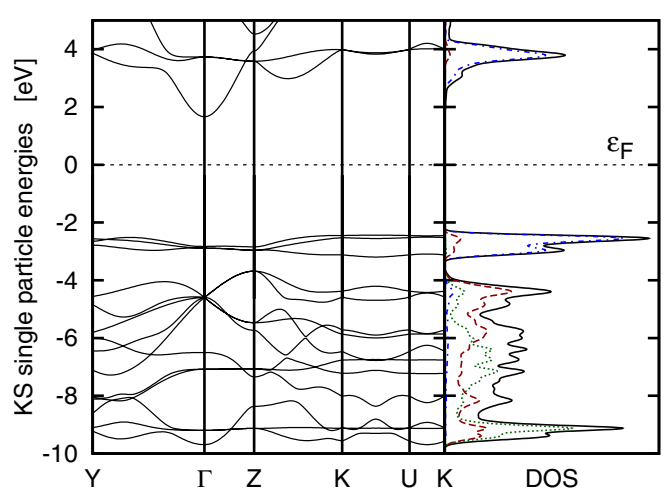

FIG. 5 (color online). As Fig. 2 for NiO.

While the narrow width of the minority-spin e_g band is no longer crucial for the formation of a gap in NiO (as it is in the LDA), the basic mechanism behind the gap still is the intersublattice coupling of the AF II structure [1]. This picture is confirmed by EXX results for completely unpolarized NiO, i.e., for the phase in which all local magnetic moments are suppressed (this phase should not be mixed up with the experimental paramagnetic phase above the Néel temperature in which local magnetic moments persist). The corresponding ground state is found to be metallic and 9 eV (per NiO molecule) higher in energy than the AF II state. This emphasizes the predominant role of the magnetic ordering for the ground state of NiO within DFT.

The (fundamental) band gaps and spin magnetic moments obtained with the EXX scheme are listed in Table II. The agreement of the EXX + VWN results with the experimental data is surprisingly good, given the fact that the LDA for correlation is not a particularly well-suited functional for use with the exact exchange [9] (concerning the magnetic moments of FeO and CoO one should note that

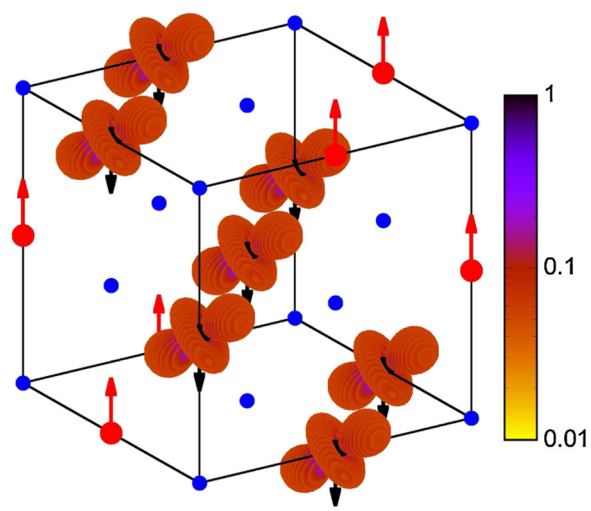

FIG. 6 (color online). Orbital density of highest occupied spin-up Bloch state for FeO in AF II phase (for $\boldsymbol{k} = \boldsymbol{0}$, the density is truncated below 0.05 Bohr^{-3}). The arrows at the Fe positions (large dots) indicate the majority spin of the corresponding site (small dots = O sites).

TABLE II. Fundamental band gap Δ_{fund} (in eV) and (spin) magnetic moment μ (in μ_B) of AF II phases of MnO, FeO, CoO, and NiO: EXX (+VWN) results versus LDA + U, hybrid (Fock-0.5) [7], SIC LDA [5] and experiment (as cited by [7]). All theoretical values for μ are spin moments, the experimental data correspond to the total magnetic moments.

		Expt.	EXX	LDA + U		hybrid	SIC
Δ_{fund}	MnO	3.9	3.85	3.5[a]	1.9[b]	1.7	3.57
	FeO	2.4	1.66	3.2[a]	1.7[b]	2.2	3.25
	CoO	2.5	2.62	3.2[a]	2.7[b]	2.3	2.51
	NiO	4.0,4.3	4.10	3.1[a]	3.2[b]	3.0	2.66
μ	MnO	4.58,4.79	4.81	4.61[a]	4.50[b]	4.46	4.64
	FeO	3.32,4.2	3.85	3.62[a]	3.60[b]	3.64	3.55
	CoO	3.35,3.98	2.88	2.63[a]	2.69[b]	2.77	2.59
	NiO	1.64,1.90	1.89	1.59[a]	1.72[b]	1.81	1.49

[a]Ref. [6]
[b]Ref. [7]

one finds an orbital magnetic moment of the order of $0.7\mu_B$ for FeO and $1\text{–}2\mu_B$ for CoO [7,23–25], which has to be added to the spin moments listed, when comparing with experimental data). Clearly, one would expect significant modifications, when replacing the LDA by some orbital-dependent correlation functional, as the RPA [10,26,27]. Any more detailed comparison with experiment therefore has to wait until corresponding results are available.

One should also note that the Kohn-Sham spectra in Figs. 2–5 correspond to an energy-independent self-energy. It is obvious that the transition to some energy-dependent approximation, e.g., in the sense of the GW approach, will lead to further modification. Our results nevertheless show that the mere opening of a gap in these materials can be obtained with the standard multiplicative potential of DFT, if an appropriate exchange-correlation potential and a full potential method are used. The EXX + VWN states should provide a better starting point for GW or DMFT calculations than LDA bands.

We would like to thank D. Ködderitzsch for very helpful discussions. Financial support by the Deutsche Forschungsgemeinschaft within the priority programs *Relativistic Effects in Heavy-Element Chemistry and Physics* and 1145 (Grant No. Dr 113/20-3 and No. EN 265/4-2) is gratefully acknowledged. The calculations for this work have been performed on the computer cluster of the Center for Scientific Computing of J. W. Goethe-Universität Frankfurt.

*Present address: Siemens AG, Corporate Technology, Otto-Hahn-Ring 6, 81739 München, Germany.

[1] K. Terakura, T. Oguchi, A. R. Williams, and J. Kübler, Phys. Rev. B **30**, 4734 (1984).
[2] T. C. Leung, C. T. Chan, and B. N. Harmon, Phys. Rev. B **44**, 2923 (1991).
[3] P. Dufek, P. Blaha, V. Sliwko, and K. Schwarz, Phys. Rev. B **49**, 10 170 (1994).
[4] A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990).
[5] Z. Szotek, W. M. Temmerman, and H. Winter, Phys. Rev. B **47**, 4029 (1993).
[6] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).
[7] F. Tran, P. Blaha, K. Schwarz, and P. Novak, Phys. Rev. B **74**, 155108 (2006).
[8] S. Y. Savrasov and G. Kotliar, Phys. Rev. Lett. **90**, 056401 (2003).
[9] S. Kümmel and L. Kronik, Rev. Mod. Phys. **80**, 3 (2008).
[10] T. Kotani, J. Phys. Condens. Matter **10**, 9241 (1998).
[11] R. Schmid, E. Engel, and R. M. Dreizler, in *NIC Symposium 2001*, NIC-Serie, Vol. 9, edited by H. Rollnik and D. Wolf (NIC-Directors, Jülich, 2002), p. 213.
[12] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Lett. A **146**, 256 (1990).
[13] E. Engel, A. Höck, and R. M. Dreizler, Phys. Rev. A **62**, 042502 (2000).
[14] E. Engel (unpublished).
[15] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).
[16] M. Städele, J. A. Majewski, P. Vogl, and A. Görling, Phys. Rev. Lett. **79**, 2089 (1997).
[17] E. Engel, A. Höck, R. N. Schmid, R. M. Dreizler, and N. Chetty, Phys. Rev. B **64**, 125111 (2001).
[18] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
[19] J. van Elp, R. H. Potze, H. Eskes, R. Berger, and G. A. Sawatzky, Phys. Rev. B **44**, 1530 (1991).
[20] J. van Elp, Ph.D. thesis, University of Groningen (1991).
[21] A. Fujimori, N. Kimizuka, T. Akahane, T. Chiba, S. Kimura, F. Minami, K. Siratori, M. Taniguchi, S. Ogawa, and S. Suga, Phys. Rev. B **42**, 7580 (1990).
[22] I. I. Mazin and V. I. Anisimov, Phys. Rev. B **55**, 12 822 (1997).
[23] I. V. Solovyev, A. I. Liechtenstein, and K. Terakura, Phys. Rev. Lett. **80**, 5758 (1998).
[24] I. V. Solovyev, A. I. Liechtenstein, and K. Terakura, J. Magn. Magn. Mater. **185**, 118 (1998).
[25] Z. Fang, I. V. Solovyev, H. Sawada, and K. Terakura, Phys. Rev. B **59**, 762 (1999).
[26] F. Furche, Phys. Rev. B **64**, 195120 (2001).
[27] M. Fuchs and X. Gonze, Phys. Rev. B **65**, 235109 (2002).