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Application of the self-interaction correction to transition-metal oxides

Z. Szotek and W. M. Temmerman
SERC Daresbury Laboratory, Warrington WA4 4AD, United Kingdom

H. Winter
Kernforschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik, P. O. Box 3640, D-7500 Karlsruhe, Germany

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We have implemented the self-interaction-corrected local-spin-density approximation within the standard linear-muffin-tin-orbital–atomic-sphere-approximation band-structure method making use of a unified Hamiltonian concept. We have used this *ab initio* band-structure scheme to study the electronic structure of MnO, FeO, CoO, NiO, and CuO. We find them to be wide-gap insulators, where the top of the valence band, of predominantly oxygen *p* character, shows a substantial hybridization with the metal *d* states.

It has been indicated that at least some of the failures of the local-spin-density approximation (LSDA) to describe the ground-state properties of some strongly correlated systems may be due to an unphysical interaction of an electron with itself.[1] The LSDA is known to fail particularly badly for transition-metal oxides giving much too small or zero band gaps and in some cases also too small magnetic moments.[2] However, subtracting explicitly each electron's self-interaction leads to self-interaction corrected (SIC) –LSDA theory,[1,3,4] which proves very useful for describing wide-gap insulators. This is because it results in a splitting of occupied and unoccupied states by the substantial on-site Coulomb interaction, which is an essential aspect of the physics of Mott insulators.

Recently, Svane and Gunnarsson have implemented the SIC-LSDA formalism within the linear-muffin-tin-orbital (LMTO) method in its tight-binding representation and have applied it to the 3*d* monoxides.[5] Their *ab initio* results greatly improve the description of the physics of these systems proving them to be wide-gap charge-transfer insulators, in agreement with experiment. Moreover, as has been shown by Svane,[6] the SIC-LSDA also leads to a correct antiferromagnetic and semiconducting ground state for La_2CuO_4 with the gap and magnetic moment in good agreement with experiment.

In this paper we concentrate on a different *ab initio* implementation of the SIC-LSDA theory, within the standard LMTO–atomic-sphere-approximation (ASA) method,[7] making use of a unified Hamiltonian concept[4] while seeking the solutions of the SIC-LSDA equations. We then apply this new band-structure scheme, SIC-LMTO-ASA, to calculate band gaps and spin magnetic moments for some transition-metal oxides in the observed magnetic ordering, namely, in the antiferromagnetic structure of the second kind where the magnetic order is along the (111) direction.

In the SIC-LSDA formalism a general one-electron state $\varphi_\alpha(\mathbf{r})$ satisfies the following wave equation:

$$H_\alpha^{\rm tot}\varphi_\alpha(\mathbf{r})=[H^{\rm LSDA}-\delta V_\alpha(\mathbf{r})]\varphi_\alpha(\mathbf{r})=\sum_{\alpha'}\varepsilon_{\alpha\alpha'}\varphi_{\alpha'}(\mathbf{r})\ , \qquad (1)$$

where $H^{\rm LSDA}$ is the conventional LSDA Hamiltonian, the Lagrange multipliers $\varepsilon_{\alpha\alpha'}$ ensure the orthogonality of $\varphi_\alpha(\mathbf{r})$'s, violated by the state dependence of the Hamiltonian.

The explicit form of the SIC potential δV_α is

$$\delta V_\alpha(\mathbf{r})=2\int\frac{|\varphi_\alpha(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+V_{\rm xc}^{\rm LSDA}(|\varphi_\alpha(\mathbf{r})|^2,0) \qquad (2)$$

with $V_{\rm xc}^{\rm LSDA}$ being the LSDA exchange and correlation potential. Due to the orbital dependence of the SIC potential, its value and total energy depend on how well localized the orbitals $\varphi_\alpha(\mathbf{r})$ are and for Bloch states, extending over the whole crystal, the SIC turns out to be insignificant, in which case one is brought back to the conventional local-density formalism.

Exploiting the translational symmetry of a crystal and reformulating the problem in terms of the unified Hamiltonian[4] one can transform Eq. (1) into the wave equation for the Bloch states $\psi_{\mathbf{k},\lambda}(\mathbf{r})$ with the wave vector $\mathbf{k}$ and band index λ. When implemented within the LMTO-ASA band-structure method[7] the matrix elements of the unified Hamiltonian H_u, expressed in the basis set of the muffin-tin orbitals $\chi_L^{\mathbf{k}}(\mathbf{r})$, read as follows:

$$\begin{aligned}\langle\chi_L^{\mathbf{k}}(\mathbf{r})|H_u|\chi_{L'}^{\mathbf{k}}(\mathbf{r})\rangle=&\langle\chi_L^{\mathbf{k}}(\mathbf{r})|H^{\rm LSD}|\chi_{L'}^{\mathbf{k}}(\mathbf{r})\rangle-\sum_{\lambda\lambda'(\lambda\neq\lambda')}^{\rm corr}M_{L,\lambda}^{\mathbf{k}}\langle\psi_{\mathbf{k},\lambda}(\mathbf{r})|H^{\rm LSD}|\psi_{\mathbf{k},\lambda'}(\mathbf{r})\rangle M_{L',\lambda'}^{\mathbf{k}*}\\&+\sum_{\lambda}^{\rm corr}M_{L,\lambda}^{\mathbf{k}}\langle\psi_{\mathbf{k},\lambda}(\mathbf{r})|\delta\tilde{V}_{\mathbf{k},\lambda}(\mathbf{r})|\psi_{\mathbf{k},\lambda}(\mathbf{r})\rangle M_{L',\lambda}^{\mathbf{k}*}+\sum_{\lambda}^{\rm corr}\sum_{\lambda'}^{\rm noncorr}M_{L,\lambda'}^{\mathbf{k}}\langle\psi_{\mathbf{k},\lambda'}(\mathbf{r})|\delta\tilde{V}_{\mathbf{k},\lambda}(\mathbf{r})|\psi_{\mathbf{k},\lambda}(\mathbf{r})\rangle M_{L',\lambda}^{\mathbf{k}*}\\&+\sum_{\lambda}^{\rm corr}\sum_{\lambda'}^{\rm noncorr}M_{L,\lambda}^{\mathbf{k}}\langle\psi_{\mathbf{k},\lambda}(\mathbf{r})|\delta\tilde{V}_{\mathbf{k},\lambda}(\mathbf{r})|\psi_{\mathbf{k},\lambda'}(\mathbf{r})\rangle M_{L',\lambda'}^{\mathbf{k}*}\ ,\end{aligned} \qquad (3)$$

where $M^{\mathbf{k}}_{L,\lambda}=\langle \chi^{\mathbf{k}}_L(\mathbf{r})|\psi_{\mathbf{k},\lambda}(\mathbf{r})\rangle$; L is the combined index for the site, orbital l, and magnetic m quantum numbers; and all real space integrals are performed over the central unit cell. Here by "corr" we mean all self-interaction corrected states, and by "noncorr" the rest of the states which are not self-interaction corrected, because not for all the occupied states the SIC potential is significant. A very useful feature of the unified Hamiltonian [Eq. (3)] is the fact that at a particular $\mathbf{k}$ point one obtains *all* the bands just by one matrix diagonalization. Moreover, the self-interaction corrected solutions, as well as the non-self-interaction corrected solutions, are obtained from the same diagonalization, and they are automatically orthogonal. In other words, it is a great advantage of the unified Hamiltonian to secure the orthogonality of the wave functions without the need of evaluating the Lagrange multipliers matrix. Equation (3) forms the essence of our SIC-LMTO-ASA band-structure method.

In the present implementation the Bloch wave functions are expressed in terms of the one-particle orbitals $\varphi_\alpha(\mathbf{r})$,

$$\psi_{\mathbf{k},\lambda}(\mathbf{r})=\sum_{n,\alpha} A^{-1}_{\lambda,\alpha}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}_n}\varphi_\alpha(\mathbf{r}-\mathbf{R}_n)\ , \tag{4}$$

where $\mathbf{R}_n$'s define the positions of the unit cells and the $\mathbf{k}$- and band-dependent SIC potential has the form

$$\delta\tilde{V}_{\mathbf{k},\lambda}(\mathbf{r})=\sum_{\alpha,n} A^{-1}_{\lambda,\alpha}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}_n}\delta V_\alpha(\mathbf{r}-\mathbf{R}_n)\frac{\varphi_\alpha(\mathbf{r}-\mathbf{R}_n)}{\psi_{\mathbf{k},\lambda}(\mathbf{r})}\ . \tag{5}$$

The orbital unitary transformation matrix $A_{\alpha,\lambda}(\mathbf{k})$ ensures the most optimal choice of the localized orbitals which minimize the ground-state energy. This matrix is the most important quantity in the application of the SIC to solids. In our formalism we start from orbitals completely localized in the central unit cell ensured by the following choice of the A matrix:

$$A_{\alpha,\lambda}(\mathbf{k})=\langle\psi_{\mathbf{k},\lambda}(\mathbf{r})|\psi_{\mathbf{k}=0,\alpha}(\mathbf{r})\rangle/N\ , \tag{6}$$

where N is a normalization factor. During the self-consistency (SCF) cycle, to reach convergence of the total energy and wave functions $\psi_{\mathbf{k},\lambda}$, the orbitals $\varphi_\alpha(\mathbf{r})$ have a freedom to relax towards the self-consistent solution with the most optimal degree of localization. This is accomplished through an additional set of unitary transformations operating on them in every iteration of the SCF cycle till the set of equations

$$\langle\varphi_\alpha|\delta V_\alpha-\delta V_{\alpha'}|\varphi_{\alpha'}\rangle=0 \tag{7}$$

is satisfied for every pair α,α'. The A matrix is transformed accordingly to comply with the back and forth transformations between $\psi_{\mathbf{k},\lambda}$ and φ_α. The above set of equations is often referred to as localization criterion since it ensures that the set of mutually orthogonal orbitals φ_α which minimizes the total energy has the most optimal degree of localization. This criterion follows from the requirement that the SIC-LSD total-energy functional is stationary with respect to unitary transformations among the occupied orbitals φ_α. It also implies the Hermiticity of the Lagrange multipliers matrix, so that one can diagonalize it to obtain the SIC-LSD eigenvalues. The SIC-LSD eigenvalues obtained by diagonalizing the unified Hamiltonian matrix are in a very good agreement with those provided by the diagonalization of the Lagrange multipliers matrix.

In all practical applications we have found the orbitals $\varphi_\alpha(\mathbf{r})$ to be nearly completely localized within the central unit cell, and therefore we have only considered the $n=0$ term in Eq. (5) for the construction of $\delta\tilde{V}_{\mathbf{k},\lambda}(\mathbf{r})$. Moreover, we only retain the spherically symmetric terms in the SIC potential expansion with respect to the angular momentum components. With respect to the basis functions we have performed calculations when s, p, and d muffin-tin orbitals have been placed on every transition-metal and oxygen site. However, in order to check convergence with respect to basis functions we have also performed calculations in the case when only s and p basis functions on the oxygen sites have been considered. Moreover, in the latter case we have performed both one and two energy-panel calculations with respect to the O $2s$ states. In all calculations we have assumed such ASA sphere radii which would give nearly charge neutral spheres. In the case of CuO we have chosen a lattice parameter of 8.022 a.u. after Ref. 8 and for the other compounds we have used the lattice parameters quoted in Ref. 9.

We have applied the self-interaction correction only to the occupied transition-metal $3d$ states. Applying SIC also to the oxygen $2p$ states has turned out to be energetically unfavorable. The criterion for the choice of the bands to be self-interaction corrected has been such that the spin moment has been maximized, in accordance with experiment and Hund's first rule. Therefore, for MnO we have corrected the five majority-spin bands, and for FeO, CoO, NiO, and CuO we have corrected additionally one, two, three, and four minority-spin bands, respectively. In any case the lowest subband contains exactly the number of bands that are self-interaction corrected, and these are further split into majority and minority subbands. There are of course other possible choices. For example, in CoO we have also tried to correct four majority and three minority bands to minimize the spin moment. However, it has turned out to be energetically unfavorable and led also to a decrease of the band gap by 1 eV.

Our *ab initio* results for band gaps and spin magnetic moments, corresponding to one energy-panel calculation with s, p, and d basis functions placed on all sites, are given in Table I, where the respective LSDA and experimental[10–13] values are also quoted for comparison. They indicate, in agreement with experiment,[10,14,15] that SIC-LSDA theory predicts MnO, FeO, CoO, NiO, and CuO to be strongly correlated wide-gap charge-transfer insulators, and therefore SIC-LSDA appears to be a better approximation to the density-functional theory than LSDA. This remains true independently of the number of energy panels or basis functions considered since the numbers from all the calculations we have performed compare very favorably. The influence of the d-oxygen muffin-tin orbitals has been reflected on the band gap through its decrease by typically 0.2–0.3 eV as compared to the case when only s and p basis functions have been placed on every oxygen site. Similar observation is true with

TABLE I. One-panel calculations with s,p,d orbitals on transition-metal and oxygen sites.

	Band gap (eV)			Spin magnetic moment (μ_B)			Total energy difference	SIC energy
System	LSDA	SIC-LSDA	Expt.	LSDA	SIC-LSDA	Expt. (total)	(eV)	(eV)
MnO	1.45	3.57	3.6–3.8	4.49	4.64	4.79,4.58	3.14	3.86
FeO	0.00	3.25		3.46	3.55	3.32	3.75	5.17
CoO	0.00	2.51	2.4	2.38	2.59	3.35,3.8	5.17	7.15
NiO	0.40	2.66	4.3,4.0	1.06	1.49	1.77,1.64,1.90	8.12	9.37
CuO	0.00	1.00	1.37	0.00	0.64	0.65	10.23	11.81

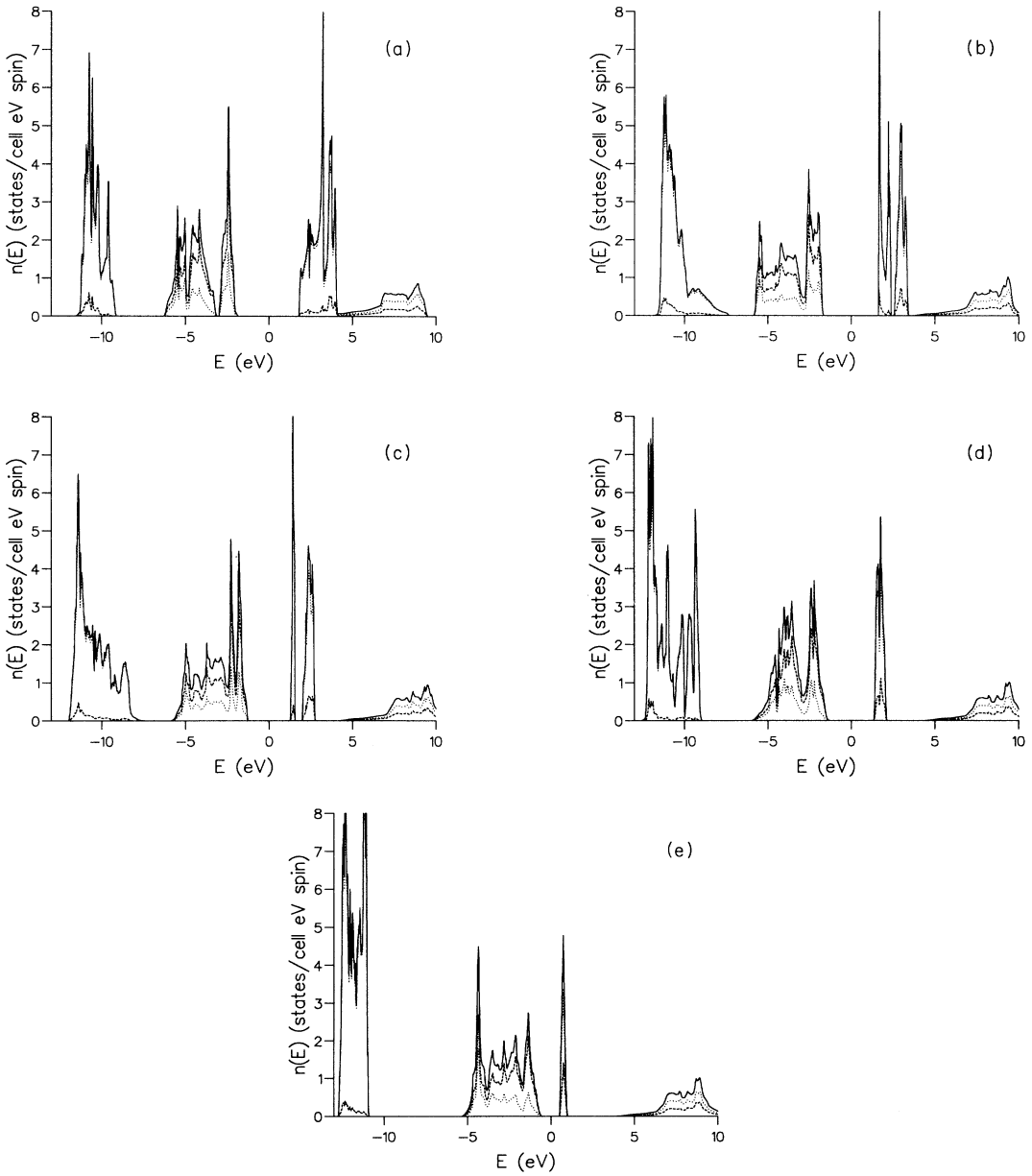

FIG. 1. SIC-LSDA density of states for (a) MnO, (b) FeO, (c) CoO, (d) NiO, and (e) CuO. Solid curves correspond to the total densities, dotted curves describe the transition-metal contributions to the density of states, and dashed curves are due to the oxygens.

respect to energy panels. For all monoxides the SIC-LSDA occupied $3d$ bands lie substantially below the oxygen bands, and the latter strongly hybridize with the transition-metal $3d$ states. Also, it is very reassuring that, in spite of a very different implementation of the SIC formalism, our results appear to be in good agreement with the results of Svane and Gunnarsson.[5]

From the last two columns of Table I one can see that the SIC-LSDA energy functional gives a substantially lower total energy than the LSDA energy functional, and that the relation

$$E_{\mathrm{SIC}} \simeq E_{\mathrm{LSDA}} - E_{\mathrm{SIC\text{-}LSDA}} \tag{8}$$

very well fulfilled in the case of atoms,[3] is obviously not true in the case of oxides. Here E_{SIC} is the expectation value of the SIC energy operator evaluated for the self-consistent SIC-LSDA wave functions, $E_{\mathrm{SIC\text{-}LSDA}}$ is the total energy of the self-consistent SIC-LSDA calculation, and E_{LSDA} is the total energy of the self-consistent LSDA calculation. We also note that the average SIC energy per orbital increases from 0.39 eV in MnO, to 0.43 eV in FeO, 0.52 eV in CoO, 0.59 eV in NiO, and 0.66 eV in CuO as the transition-metal d orbitals become more localized.

To gain more insight into the charge-transfer nature of the band gap in Fig. 1 we show the SIC-LSDA total densities of states and their decomposition into the metal and oxygen components for all studied oxides. They have been calculated on the basis of the results from one-panel calculations with s, p, and d muffin-tin orbitals placed on transition-metal and oxygen sites. The most striking feature is that in the SIC-LSDA scheme the *occupied* metal d states are well separated from the predominantly O p character valence band by an energy gap of a few eV. For NiO the *occupied* Ni d peak occurs about 9 eV below the valence-band edge which is in good agreement with the position of the experimentally observed d^7 satellite.[10] This is also supported by the parametrized many-body calculation.[16]

A substantial band gap occurs between the valence band and the remaining, *unoccupied*, transition-metal d states. Even though the band gap is between non-SIC corrected bands, its value is affected by the SIC through the orthogonalization of the respective wave functions to the wave functions of the SIC corrected bands. We note that in each of the lowest two subbands there are an integer number of electron states. The "transition-metal subband" contains five, six, seven, eight, and nine states for MnO, FeO, CoO, NiO, and CuO, respectively. The valence band contains six states, which are roughly populated by four O p electrons and two transition-metal electrons. Therefore, from the partial density of states one sees a substantial hybridization of the oxygen states with the metal states. The details of this hybridization determine the position of the O bands with respect to the metal bands and hence the energy band gap. These results differ dramatically from the corresponding local-density results where the top of the valence bands and the bottom of the conduction bands are the metal d states. Therefore, in the LSDA the band gaps occur, if at all, between metal d states, in variance with experimental evidence.

The substantial d-band splitting in the SIC-LSDA occurs because the self-interaction matrix element $\langle \varphi_\alpha | \delta V_\alpha | \varphi_\alpha \rangle$ is about 10 eV, leading to a 10-eV splitting of the d bands. The O p bands lie in this 10-eV gap. These matrix elements are so substantial, firstly because the application of the localization criterion transforms, by a unitary transformation, the localized state $\varphi_\alpha(\mathbf{r})$ to a new localized state $\bar{\varphi}_\alpha(\mathbf{r})$ whose weight is fully concentrated on only one of the transition-metal sites in the unit cell, and secondly due to the localized nature of the basis functions for the d channel on the metal sites. For the O sites these matrix elements are not substantial because the basis functions are not so localized as in the metal d channel. Therefore, it is not energetically favorable to self-interaction correct the O $2p$ states. For example, we obtain an SIC energy gain of 0.66 eV per metal d electron in CuO, while if we were to self-interaction correct also the O p bands we would lose energy.

Summarizing, we would like to stress a very good agreement of our results with the work of Svane and Gunnarsson,[5] in spite of a very different implementation of the SIC formalism. Both sets of results agree well with experiment: the band gap is between the occupied $2p$ oxygen states, strongly hybridizing with the transition-metal $3d$ bands, and the unoccupied transition-metal $3d$ states. This proves that these systems are not Mott-Hubbard insulators in a simple sense but charge-transfer insulators as seen in experiment.[10,14,15] Finally, our results prove that the SIC plays an important role in description of the electronic properties of transition-metal monoxides.

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[1] R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).
[2] K. Terakura *et al.*, Phys. Rev. B **30**, 4734 (1984).
[3] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[4] R. A. Heaton *et al.*, Phys. Rev. B **28**, 5992 (1983); M. R. Pederson *et al.*, J. Chem. Phys. **80**, 1972 (1984); M. R. Pederson and C. C. Lin, *ibid.* **88**, 1807 (1988).
[5] A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990).
[6] A. Svane, Phys. Rev. Lett. **68**, 1900 (1992).
[7] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); H. L. Skriver, *The LMTO Method* (Springer-Verlag, Berlin, 1984).
[8] N. G. Schmahl and G. F. Eikerling, Z. Phys. Chem. **62**, 268 (1968).
[9] L. F. Mattheiss, Phys. Rev. B **5**, 290 (1972).
[10] G. A. Sawatzky and J. W. Allen, Phys. Rev. Lett. **53**, 2339 (1984).
[11] H. A. Alperin, J. Phys. Soc. Jpn. Suppl. B **17**, 12 (1962).
[12] B. E. F. Fender *et al.*, J. Chem. Phys. **48**, 990 (1968).
[13] A. K. Cheetham and D. A. O. Hope, Phys. Rev. B **27**, 6964 (1983).
[14] J. Zaanen *et al.*, Phys. Rev. Lett. **55**, 418 (1985).
[15] J. van Elp *et al.*, Phys. Rev. B **44**, 1530 (1991).
[16] A. Fujimori *et al.*, Phys. Rev. B **29**, 5225 (1984); A. Fujimori and F. Minami, *ibid.* **30**, 957 (1984).