

Transition-Metal Oxides in the Self-Interaction-Corrected Density-Functional Formalism

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We present a method for performing fully self-consistent, *ab initio*, self-interaction-corrected, local-spin-density calculations. We demonstrate that the formalism correctly predicts that MnO, FeO, CoO, NiO, and CuO are antiferromagnetic insulators, and that VO is a nonmagnetic metal. The band gaps and moments are drastically improved compared with the local-spin-density approximation.

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The local-spin-density (LSD) approximation¹ of the spin-density-functional (SDF) formalism has been shown to give a good description of the ground-state properties for many systems with moderately strong correlation effects. However, for systems where the electron-electron interaction is strong enough to change the nature of the ground state, the LSD approximation often fails. Examples are provided by the occurrence of antiferromagnetism in the high- T_c -related compound La_2CuO_4 , the α - γ transition in Ce, and the insulating, antiferromagnetic transition-metal (TM) oxides. The TM oxides have been studied intensively for several decades, because of the controversial nature of their band gap. The LSD approximation describes certain aspects of the loss of the $3d$ contribution to cohesion,² but the band gaps are much too small or zero and the magnetic moments are in some cases also too small.³

We have recently applied the self-interaction-corrected (SIC) LSD approximation^{4,5} to the Hubbard model^{6,7} and to a model of La_2CuO_4 ,⁷ and demonstrated that this approximation greatly improves the LSD results for both the band gap and the moment. The LSD approximation leads to a Stoner theory, which gives a good description of the ground-state properties for the $3d$ metals.⁸ For more localized systems, however, the resulting Stoner parameter I is too small to give proper moments. Moreover, since I splits the spin-up and spin-down bands, it often fails to give a gap for systems where the band is not half filled. In the SIC-LSD approximation, on the other hand, the Coulomb interaction U splits the occupied and the unoccupied states. This is the correct physics for both the Hubbard model and the TM oxides, and it leads to a band gap also for localized systems where the band is not half filled.⁶ Since $U > I$, the SIC-LSD approximation also leads to larger moments than

the LSD approximation.

The SIC-LSD approximation provides a mechanism which allows the wave functions to localize for systems where the hopping integrals are small relative to the Coulomb interactions. It is therefore crucial that the SIC-LSD equations are allowed to determine the spatial extent of the wave functions in a self-consistent way.⁶ The solutions of these equations are not automatically orthogonal, since the potential is state dependent. The orthogonality has to be imposed explicitly, and the results depend crucially on this being done properly.⁹ The energy functional must, furthermore, be stationary with respect to unitary mixing of the occupied states, which in the SIC-LSD approximation is highly nontrivial.¹⁰ Therefore, to our knowledge, no fully self-consistent, *ab initio*, SIC-LSD calculation for solids has been published.¹¹ There have been a number of *ab initio* SIC-LSD calculations for rare gas and ionic insulators.¹² In these calculations, however, the spatial extent of the SIC-LSD solutions was not determined self-consistently, which for these wide-gap insulators may be a justifiable approximation. Because of the complexity of the problem, our earlier work^{6,7} was performed for simple models, where the SIC-LSD equations can more easily be solved exactly.

In this paper we present a technique which makes self-consistent, *ab initio*, SIC-LSD calculations possible, with a numerical effort which is not much greater than what is needed for a standard LSD band calculation. We find that the results for the band gaps and the moments of the TM oxides are greatly improved compared with the LSD results.

In the LSD approximation, each electron has a non-physical interaction with itself. In the SIC-LSD approximation⁵ this interaction is subtracted, leading to the energy expression

$$E_{\text{XC}}^{\text{SIC}}[n] = E_{\text{XC}}^{\text{LSD}}[n] - \sum_i^{\text{occ}} \left[\int d^3r d^3r' \frac{n_i(\mathbf{r})n_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int d^3r n_i(\mathbf{r})\epsilon_{\text{XC}}(n_i(\mathbf{r}),0) \right],$$

where $n_i(\mathbf{r})$ is the charge density corresponding to the solution i of the SIC-LSD equation and $\epsilon_{XC}(n_\uparrow, n_\downarrow)$ is the exchange-correlation (XC) energy of a homogeneous system with the spin densities n_\uparrow and n_\downarrow . The second term subtracts the nonphysical Coulomb interaction of an electron with itself as well as the corresponding LSD XC energy. The corresponding XC potential is state dependent, which allows the wave functions to localize.^{5,6,10,12}

For TM oxides, the solutions of the SIC-LSD equations have the following form. On each TM atom there are localized $3d$ -like solutions, while the oxygen $2p$ states form extended Bloch solutions. The solutions centered on one atom are described by using a large supercell with 512 atoms (128 unit cells), and periodically continuing the solution in all other supercells. Because of the large supercell, the solution can be rather extended without any appreciable (unphysical) overlap with its periodic continuation. The SIC part of the potential, seen by a particular localized solution, then has the periodicity of the supercell. The solutions are expressed as linear combinations of linear muffin-tin orbitals (LMTO).¹³ We use the steepest-descent method¹⁴ to minimize the total energy. Thus the gradient of the energy is calculated in the space of the coefficients of the LMTO's. This gradient is projected onto the hypersurface where all solutions (also solutions centered on different sites) are strictly orthogonal, and the coefficients are changed along this projected gradient. The energy is, furthermore, made stationary due to unitary mixing of the occupied states: If at a particular iteration an infinitesimal unitary mixing lowers the total energy, a small unitary mixing is performed. These steps are repeated until the energy is stationary with respect to all variations. The unitary mixing turns out to be important for the final result. By expressing the problem in reciprocal space, we use the periodicity of the non-SIC part of the problem to obtain matrices with a size which corresponds to the unit cell. This leaves us with sums over the full supercell involving products of matrix elements of the SIC potential and coefficients of a localized solution. Since the localized solutions in different unit cells are identical apart from a translation, there are only a few different localized solutions. The effort in performing the sums over the supercell therefore only grows linearly with the size of the supercell. The iterations are started by assuming that certain $3d$ orbitals are occupied (e.g., all but the E_g spin-down $3d$ orbitals for NiO). Different starting assumptions are used to assure that the absolute minimum of the total energy is found. For instance, localized oxygen $2p$ solutions were also considered, but they were found to be rather extended, leading to a positive SIC energy for these orbitals and hence an increase in the total energy in comparison with bandlike oxygen $2p$ states.

In the SIC approximation the effects of nonspherical contributions to the potential are more important than in the LSD approximation. These nonspherical compo-

nents are therefore taken into account, but the Wigner-Seitz cells are still approximated by spheres. The solutions are allowed to be any complex linear combination of cubic harmonics. The time requirement for one iteration is comparable (a few times slower) to that for a traditional band-structure problem.

The requirement that the solutions have to be orthogonal is fulfilled by introducing a matrix of Lagrange parameters. To obtain the SIC-LSD band structure for the occupied bands, this matrix is diagonalized.¹⁰ The unoccupied (extended) states are obtained directly by solving the SIC-LSD equations with the subsidiary condition that they are orthogonal to the occupied solutions. Below we use this band structure to estimate the band gap. A more accurate estimate could be obtained from total-energy differences.

In Table I, the results for the band gaps and the magnetic moments for VO, CrO, MnO, FeO, CoO, NiO, and CuO are compared with the LSD results and experimental results when available. For VO, localized solutions do not form in the SIC-LSD approximation, at least not for the size of the supercell used here (512 atoms). The solution then goes over to the LSD result, since the SIC correction goes to zero for extended states. Thus VO is correctly a metal in the SIC-LSD approximation. MnO, FeO, CoO, NiO, and CuO are correctly predicted to be insulators, while the LSD approximation gives no band gap for FeO,³ CoO,³ and CuO.¹⁵ For MnO and NiO the LSD band gaps are much too small, while the SIC-LSD approximation gives rather good band gaps for these systems.

The nature of the band gap has attracted much interest in the past. Recently, the understanding has greatly increased due to the comparison of many-body model calculations and spectroscopic experiment.¹⁶⁻¹⁸ For NiO it is found that the highest hole state has most of its weight on the O atoms;¹⁶ i.e., it has mainly $3d^8L^{-1}$ character with some mixture of d^7 character, where L^{-1} stands for a ligand (O $2p$) hole. Since the lowest electron state is a d^9 state, NiO is closer to being a charge-transfer insulator.¹⁶⁻¹⁸ This conclusion was supported by Norman and Freeman,¹⁹ who used a supercell technique for calculating the important parameters in the model-Hamiltonian approach. The LSD approximation predicts that both the highest occupied and the lowest unoccupied states have primarily $3d$ character. The character of the states is therefore of the same type as in a Mott-Hubbard insulator, although the LSD approximation in other respects is more similar to the Slater picture. In the SIC-LSD calculation, the lowest unoccupied states have primarily $3d$ character as in most other theories. The occupied part of the $3d$ density of states has most of its weight below the O $2p$ band, but there is also some $3d$ weight mixed into this band. The highest hole state in SIC-LSD, therefore, is a mixture of $3d^8L^{-1}$ and $3d^7$ states, as in the model calculation, and NiO is a charge-transfer insulator. For NiO, the SIC-

TABLE I. The LSD, SIC-LSD, and experimental energy band gaps (in eV) and spin magnetic moments (in μ_B) for VO, CrO, MnO, FeO, CoO, NiO, and CuO. The moments in parenthesis include the orbital contribution. The last column shows the energy difference ΔE (in eV) between the LSD and the SIC-LSD calculation.

Compound	Band gap			Magnetic moment			ΔE
	LSD	SIC-LSD	Expt.	LSD	SIC-LSD	Expt.	
VO	0.0	0.0	0.0	0.0	0.0	0.0	
CrO	0.0	1.01		2.99	3.49 (3.44)		1.0
MnO	0.8	3.98	3.6–3.8 ^a	4.39	4.49 (4.49)	4.79, ^b 4.58 ^c	3.9
FeO	0.0	3.07		3.42	3.54 (4.55)	3.32 ^d	4.6
CoO	0.0	2.81	2.4 ^e	2.33	2.53 (3.72)	3.35, ^f 3.8, ^d 3.8 ^g	6.6
NiO	0.2	2.54	4.3, ^h 4.0 ⁱ	1.04	1.53 (1.80)	1.77, ^b 1.64, ^j 1.90 ^c	9.5
CuO	0.0	1.43	1.37 ^k	0	0.65 (0.78)	0.65 ^l	14.7

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LSD calculation seems to exaggerate the charge-transfer character of the gap, while the LSD approximation greatly overestimates the Mott-Hubbard character, compared with the many-body calculations.¹⁶ We note that for a system with a localized degenerate level with a large Coulomb interaction, the degeneracy effectively enhances the hopping between different configurations.²⁰ This effect is not included in a one-particle treatment, i.e., neither in the SIC-LSD nor in the LSD approximations. Although the effect is moderate for the states considered in a many-body treatment of NiO,¹⁶ due to the few 3*d* holes in NiO, it should explain most of the SIC-LSD tendency to overestimate the charge-transfer character of the gap compared with the many-body calculation.¹⁶ An alternative scheme has been proposed by Anisimov, Korotin, and Kirmaev²¹ where the unoccupied states are shifted upwards in contrast to the downward shift of the occupied states in SIC-LSD. In the scheme of Anisimov, Korotin, and Kirmaev the highest occupied state has 3*d* character in contrast to the model calculations and our result.

Table I also shows the magnetic moments. The LSD approximation fails to give a moment for CuO, as might have been expected from its failure for the high- T_c -related compound La₂CuO₄.²² For the other antiferromagnetic oxides (except VO) the LSD approximation gives a moment, but it is too small for NiO. For both CuO and NiO the SIC-LSD approximation gives good magnetic moments. For FeO and CoO the orbital mo-

ment plays a substantial role. We therefore include the spin-orbit coupling $\mathbf{S} \cdot \mathbf{L}$ approximated as $S_z L_z$. Because of the nonlinear behavior of the XC contribution to the SIC, the nonspherical part of the XC energy tends to favor spherical orbitals. Thus the formalism tends to favor orbitals mainly built up from a spherical harmonic over one built up from a cubic harmonic. This tendency is stronger than the tendency of the crystal field to quench the orbital moments. For the calculation of the orbital moments, we therefore make a spherical approximation for the energy and potential. As expected, the orbital moments are important for FeO (1.01 μ_B) and for CoO (1.19 μ_B), but are small for CrO ($-0.05\mu_B$), MnO (0.00 μ_B), NiO (0.27 μ_B), and CuO (0.13 μ_B). The results in parenthesis in Table I show the total moments. In the LSD approximation, the orbital moments are small. For CoO it is essential to include the orbital moment to obtain a sensible total moment.²³

We presented an efficient method for solving the SIC-LSD equations, which makes *ab initio* SIC-LSD calculations feasible even for rather complicated systems. We find that the SIC-LSD approximation correctly predicts that MnO, FeO, CoO, NiO, and CuO are antiferromagnetic insulators, and the gaps and moments agree rather well with experimental results when available. For the metallic, nonmagnetic VO, on the other hand, no localized solutions are formed in the SIC-LSD approximation, which therefore correctly predicts a nonmagnetic metal. The results are in strong contrast to the results in

the LSD approximation, where the gaps are much too small or zero and the moments are often too small.

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