

Comment on “Taming multiple valency with density functionals: A case study of defective ceria”

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We show that two all-electron methods, the full-potential linearized augmented wave method and the projector augmented wave method, yield a metallic groundstate for Ce_2O_3 , as opposed to the experimentally observed insulating groundstate. This is in contrast to previous pseudopotential calculations [Phys. Rev. B **71**, 041102(R) (2005)], which suffered from an erroneous overestimation of the spin-enhancement factor and a resulting overestimation of the exchange splitting.

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Ab initio density functional theory has been very successful in the prediction of the magnetic properties of itinerant systems. Its application to materials with strongly localized electrons, for instance, $3d$ transition metal oxides and the oxides of lanthanides, has been only partly successful, since spurious self interactions in the present density functionals prevent the localization of $3d$ and $4f$ electrons. Concomitantly the electrons remain itinerant, and many oxides are predicted to be metals instead of the experimentally observed insulators.

In the past, calculations for Ce_2O_3 have been plagued by this problem: Three of the four Ce valence electrons are “donated” to oxygen, and the remaining one is distributed roughly equally among the seven $4f$ orbitals resulting in an almost spherical f -charge distribution and a metallic ground state.¹ Recently this observation has been challenged by S. Fabris *et al.*² In the local density approximation (LDA) and the generalized gradient approximation (GGA), they determined an antiferromagnetic (AF) insulating groundstate which is roughly 0.36 and 0.99 eV lower in energy than the AF metallic state, respectively. Using two all-electron (AE) methods, we show that the pseudopotential result cannot be sustained, i.e., it does not correctly describe the AE LDA limit. Both the projector augmented wave (PAW) method,³ as implemented in the VASP package,⁴ and the full-potential linearized augmented wave (FLAPW) method, implemented in the WIEN2K program,⁵ predict a metallic ferromagnetic (FM) ground state in LDA (in agreement with earlier calculations, see, e.g., Ref. 1) and only LDA+ U yields the correct AF insulating state.²

The electronic ground state was determined by using an LDA+ U approach⁶ and lowering the U until the effective U' becomes zero. We have used a simple LDA+ U version where the local part is described by the Ceperley-Alder functional⁷ and the one-center Coulomb and exchange interactions are treated by a single effective parameter $U' = U - J$.⁸ Figure 1 shows the electronic density of states for $U' = 1$ and 0 eV for the FLAPW and the PAW method. Since the U operates in the atomic spheres only and the PAW spheres are

larger than the FLAPW spheres, the effect of U is somewhat stronger in the PAW method. Otherwise both methods yield identical results. An insulating AF groundstate is observed even for a relatively modest U' , and the localized electron occupies a single f orbital which is a hybrid of the two real spherical harmonics f_{z^3} and $f_{y(y^2-3x^2)}$ in agreement with Ref. 2. When U' decreases, the gap decreases as well, until an AF metallic state is reached at roughly $U' = 0.4$ eV. In this state, and in the FM-LDA ground state, one electron is distributed among different f orbitals. Furthermore, the FM state is ~ 0.1 eV lower in energy than the AF metallic state.

The previous pseudopotential result—an insulating ground state for $U' = 0$ —could be reproduced using ultrasoft

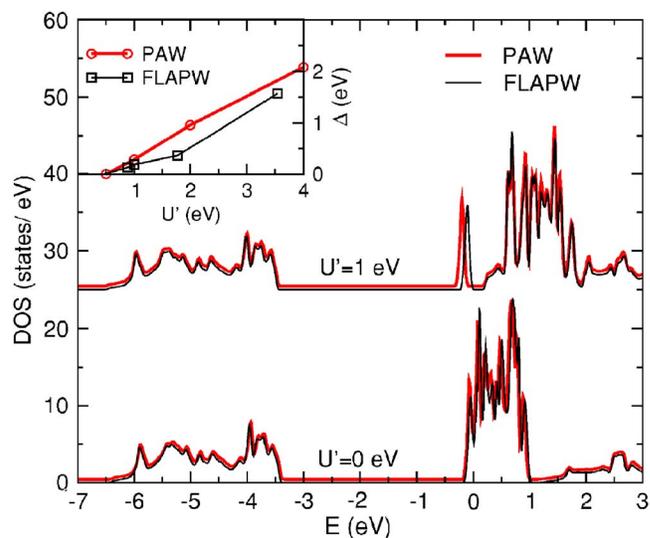


FIG. 1. (Color online) Electronic density of states for Ce_2O_3 calculated using the PAW and the FLAPW method for $U' = 1$ and 0 eV. The Brillouin zone was sampled at $14 \times 14 \times 8$ k points using the tetrahedron method. To improve visibility the final results have been smoothed using a Gaussian with a width of $\sigma = 0.12$ eV. Inset shows the band gap Δ versus U' .

pseudopotentials, if the core radius for the reconstruction of the charge density (augmentation radius) was set to $r_c > 0.7 \text{ \AA}$. The reason for the failure of these pseudopotentials to reproduce the AE results is an outward shift of the maximum of the $4f$ pseudowave function, causing a reduction of the core-valence overlap, and in turn, a too large value for the spin enhancement factor

$$\xi(r) = \frac{m(r)}{\rho_{\text{core-charge}}(r) + \rho_{\text{valence-charge}}(r)} \quad (1)$$

in the region where the magnetization density $m(r)$ reaches its maximum. As a result, the exchange splitting is significantly overestimated leading to an incorrect lowering of one specific $4f$ orbital. The problem has been amply discussed in

literature and can lead to artifacts, such as the overestimation of the magnetic moment in bcc Fe (pseudopotential GGA calculations in Ref. 9 obtain a moment of $2.44 \mu_B$, whereas the AE value is $2.2 \mu_B$, see, e.g., Ref. 4) or the incorrect prediction of a magnetic $V(001)$ surface.¹⁰

In conclusion, all-electron local density functional calculations do not yield the proper insulating ground state for Ce_2O_3 . The previous pseudopotential calculations suffer from an erroneous overestimation of the spin-enhancement factor and a resulting overestimation of the exchange splitting. In passing, we note that another recent pseudopotential study seems to suffer from similar pseudopotential deficiencies.¹¹ In general we believe that the application of pseudopotentials to magnetic systems is therefore problematic, and values must be checked against AE calculations.

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