

Predicting d^0 magnetism: Self-interaction correction scheme

A. Droghetti, C. D. Pemmaraju, and S. Sanvito

School of Physics and CRANN, Trinity College, Dublin 2, Ireland

(Received 9 September 2008; published 17 October 2008)

Predicting magnetism originating from $2p$ orbitals is a delicate problem, which depends on the subtle interplay between covalency and Hund's coupling. Calculations based on density-functional theory and the local spin-density approximation fail in two remarkably different ways. On one hand the excessive delocalization of spin-polarized holes leads to half-metallic ground states and the expectation of room-temperature ferromagnetism. On the other hand, in some cases a magnetic ground state may not be predicted at all. We demonstrate that a simple self-interaction correction scheme modifies both these situations via an enhanced localization of the holes responsible for the magnetism and possibly Jahn-Teller distortion. In both cases the ground state becomes insulating and the magnetic coupling between the impurities becomes weak.

DOI: [10.1103/PhysRevB.78.140404](https://doi.org/10.1103/PhysRevB.78.140404)

PACS number(s): 75.10.-b, 75.50.Pp

Conventional magnetism is associated with a narrow region of the periodic table, namely, that of the $3d$ and $5f$ series. In these atomic shells strong Hund's coupling results in a high-spin configuration and therefore in the formation of localized magnetic moments. Then one also needs a mechanism for coupling those local moments. This is not universal and generally depends on the details of the compound investigated. Importantly the formation of magnetic moments does *not* imply a macroscopic magnetic state. Furthermore, the orbital composition of the moment is crucial for establishing the microscopic nature of the coupling mechanism.

Following the criterion of having large Hund's coupling one should expect to find high-spin configurations and possibly magnetism also in materials with partially filled $2p$ orbitals. This situation takes the name of d^0 magnetism.¹ Oxygen is the prototypical case. O_2 has a triplet ground state and solid O orders in a complex antiferromagnetic structure at low temperature.² Another remarkable example is that of Rb_4O_6 , which was predicted to be an anionogenic half-metal,³ and measured spin glass.⁴ Away from molecular solids however the situation is less clear. Two properties of standard solids conspire against p -type magnetism. First, the p shells are usually fully filled and therefore cannot sustain a magnetic moment. Second the $2p$ hopping integrals are usually large and so are the typical bandwidths, meaning that the chances of moment formation are reduced by the large kinetic energy.

Despite these complications the experimental claims for d^0 ferromagnetism are numerous and include graphitic carbon⁵ and both defective⁶ and doped oxides.⁷ An explanation of these findings however remains controversial to date. The formation of the magnetic moment is usually attributed to holes localized at the defect site, either this being the molecular orbital associated to cation vacancies^{8,9} or p dopants at the O sites.^{10,11} Then the magnetic coupling is justified with the degree of delocalization of the same $2p$ shell responsible for the moment in a scheme similar to the Zener model for standard magnetic semiconductors.¹² Critically most of the predictions are based on density-functional theory (DFT) using local approximations of the exchange-correlation potential [local spin-density approximation (LSDA) or generalized gradient approximation (GGA)]. These notoriously underestimate Coulomb repulsion and

tend to overdelocalize the charge density. It is then no surprise that most of the calculations return a metallic (half-metallic) ground state and, usually, a large magnetic interaction.

In this Rapid Communication we demonstrate that, when strong correlation is introduced at the level of self-interaction correction (SIC), the picture changes drastically and even the formation of a local moment becomes a delicate issue. Consequently the mechanism for magnetic interaction can be completely different from that described by the LSDA. We prove this idea by presenting three prototypical cases. First we look at F centers in SiO_2 for which LSDA predicts a delocalized hole sustaining magnetic interaction instead of a paramagnetic self-trapped center.^{13,14} Then we look at B, C, and N substituting for O in MgO , for which LSDA correctly predicts a magnetic ground state but fails in capturing the orbital order and the insulating state. Finally we look at the case of Ga vacancy and dopant Zn in GaN . The former case is similar to that of F centers in SiO_2 , while in the latter LSDA now fails in predicting a high-spin state.

Our calculations are performed using the standard DFT code SIESTA with LSDA functional¹⁵ and a development version implementing the atomic SIC (ASIC) scheme.¹⁶ We treat core electrons with norm-conserving Troullier-Martin pseudopotentials, while the valence charge density and all the operators are expanded over a numerical orbital basis set, including multiple- ζ and polarized functions.¹⁵ The real-space grid has an equivalent cutoff larger than 500 Ry. Calculations are performed with supercells of various sizes including k -point sampling over at least ten points in the Brillouin zone. Relaxations are performed with standard conjugate gradients until the forces are smaller than $0.04 \text{ eV}/\text{\AA}$.

We begin our analysis by considering the famous prototypical case of the F center in SiO_2 , i.e., Al substituting Si (Al_{Si}). In Table I we summarize the results of our LSDA and ASIC calculations. These have been obtained with a 36-atom unit cell containing a single Al impurity. The LSDA local geometry of Al_{Si} has four Al-O bonds of equal length of 1.73 \AA , and the $S=1/2$ hole spreads uniformly over the four O atoms. However relaxation with ASIC produces a distortion. Three of the Al-O bonds relax to 1.67 \AA , while the fourth gets considerably longer (1.94 \AA). Such a distortion is associated with the localization of the Al-induced hole,

TABLE I. Summary of the LSDA and ASIC calculated bond lengths d (in Å) and magnetic moments μ (in μ_B) for the various defects investigated in SiO_2 , MgO , and GaN . In parentheses the number of bonds of a given length is given.

System	d_{LSDA}	μ_{LSDA}	d_{ASIC}	μ_{ASIC}
SiO_2 : Al_{Si}	1.73 (4)	1	1.67 (3), 1.94 (1)	1
MgO : B_{O}	2.19 (6)	3	2.20 (6)	3
MgO : C_{O}	2.18 (2), 2.15 (4)	2	2.18 (4), 2.15 (2)	2
MgO : N_{O}	2.10 (6)	1	2.15 (2), 2.10 (4)	1
GaN : V_{Ga}	2.10 (4)	3	2.14 (2), 2.28, 2.31	3
GaN : Zn_{Ga}	2.0 (4)	0	1.96 (3), 2.4 (1)	1

which occupies the orbital along the elongated bond. This picture is consistent with the experimentally found hole self-trapping and demonstrates the importance of SIC in the self-trapping problem.¹⁴

If one now calculates the magnetic interaction between two Al_{Si} , a remarkable result is found. By using a 72 atom supercell containing two Al impurities placed as second-nearest neighbors, we have calculated the energy difference $\Delta E = E_{\text{FM}} - E_{\text{AF}}$ between the ferromagnetic (FM) and antiferromagnetic (AF) configurations of the cell. This is about -120 meV for LSDA, meaning that for Al concentrations around 8%, LSDA predicts SiO_2 :Al to be a ferromagnet with a remarkably high coupling strength. This result must be viewed with suspicion however since the local electronic structure of Al_{Si} in LSDA is incorrect. When the same calculation is repeated with ASIC, which accurately describes the hole self-trapping around Al_{Si} , the magnetic coupling is negligible (~ -1 meV). This is consistent with the fact that no ferromagnetism has to date been observed in SiO_2 :Al at any Al concentration. We conclude therefore that the LSDA result is an artifact of hole delocalization.

Next we analyze the case of O substitutional defects A_{O} ($\text{A}=\text{B}, \text{C}, \text{N}$) in rocksalt MgO . These introduce, respectively, 3, 2, and 1 holes so that the filling of the A_{O} $2p$ shell is, respectively, $1/2$, $2/3$, and $5/6$. In Fig. 1 we report on the density of states for a 96 atom supercell doped with a single A_{O} and projected over the A_{O} $2p$ orbitals. For all the impurities both the LSDA and ASIC return a spin-polarized ground state with a magnetic moment as large as the number of holes. The details of the charge distribution around A_{O} are however profoundly different in LSDA and ASIC.

Let us look at the single acceptor N_{O} first. A magnetic ground state means that the hole is fully spin polarized. The problem then is the distribution of a single hole among the three $2p$ orbitals forming the chemical bonds with the Mg cations. As for SiO_2 also in this case LSDA predicts a spin-polarized ground state with the Fermi level cutting across a $2/3$ filled minority N- $2p$ impurity band. LSDA atomic relaxation is isotropic with a N-Mg bond length slightly larger (2.10 Å) than that between O and Mg of 2.08 Å. This half-metallic ground state, together with the considerable energy overlap between the O $2p$ and N $2p$ orbitals (see Fig. 1), is suggestive of a N ferromagnetic order via an impurity band Zener mechanism. In fact the calculated ΔE for a 96 atom cell and second-nearest neighbors is -120 meV and thus ferromagnetic.

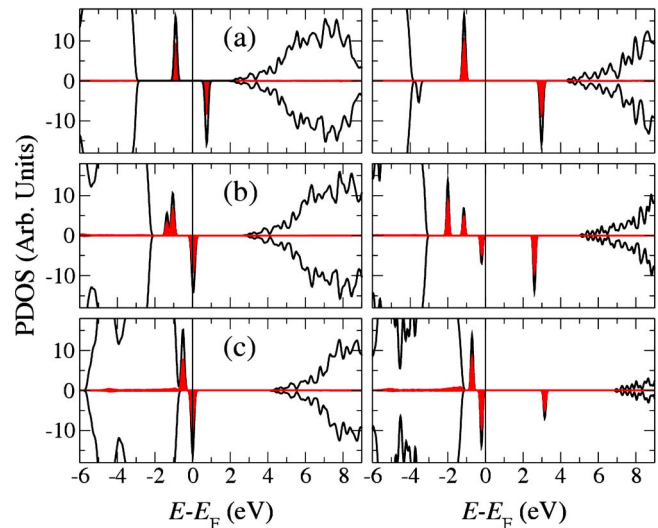


FIG. 1. (Color online) Total density of states (black line) and density of states projected over the $2p$ shells of the anion acceptor (fill shaded) for MgO doped, respectively, with (a) B, (b) C, and (c) N. The left-hand (right-hand) side plots correspond to LSDA (ASIC). The majority (minority) density of states (DOS) is plotted in the upper (lower) half of each panel.

Note however that this partially filled degenerate p configuration is sensitive to Jahn-Teller distortion. This is not captured by LSDA due to the erroneous over-delocalization of the hole, but it can be described by an ASIC calculation. ASIC in fact leads to the expansion of two of the six N-Mg bonds (2.15 Å) with the consequent N- $2p$ levels splitting into a doubly degenerate occupied level just above the MgO valence band and an empty singlet. These are separated by a crystal-field energy of approximately 3 eV. In this distorted configuration the magnetic moment is entirely localized over the longer p bonds as it can be clearly seen from Fig. 2 where we present the ASIC magnetization isosurface.

As it is, $\text{MgO}:\text{N}$ is an insulator and the only mechanism left for magnetic coupling between N_{O} is superexchange. This is expected to be extremely weak since the first avail-

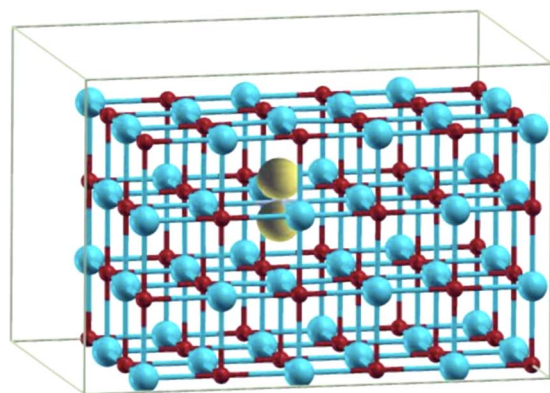


FIG. 2. (Color online) Magnetization isosurfaces calculated with ASIC for N_{O} in MgO . Note that the $S=1/2$ hole is completely localized along the p_y orbital and it is not evenly distributed along all the bonds. The large spheres are Mg and the smaller spheres are O ions. N is not displayed for clarity.

able Mg-filled shells to mediate the virtual transition necessary for superexchange are $2p$, which are extremely deep, leading practically to no coupling. In fact the calculated coupling at second-nearest neighbor is only 1 meV. Note also that, at variance to the standard Jahn-Teller distortion for d orbitals, the p -type distortion investigated here is frustrated, and each of the three degenerate $2p$ orbitals can transform into the singlet. This introduces an additional complication to the superexchange mechanism since only orbitals sharing the same angular momentum about the bonding axis can participate to the coupling. Pardo and Pickett¹⁷ recently studied N-doped MgO with GGA and LSDA+U. Their results with GGA are in accord with our LDA ones. In addition, turning on the U term, they find a scenario characterized by lattice distortion and orbital ordering which agrees with our ASIC results. Finally we note that a similar Jahn-Teller distortion was also predicted by Elfimov *et al.*¹¹ for N-doped SrO.

Let us now move to MgO:C. This time the minority C- $2p$ shell is singly occupied leading to a magnetic moment of $2\mu_B$ for both LSDA and ASIC. For C_O LSDA also predicts Jahn-Teller distortion with four 2.15-Å- and two 2.18-Å-long Mg-C bonds. One hole distributes entirely over the $2p$ orbital associated to the long bond but the second spreads evenly over the remaining orbitals again giving a half-metallic ground state [Fig. 1(b)]. ASIC changes the Jahn-Teller distortion into two short (2.15 Å) and four long (2.18 Å) bonds, basically reversing the LSDA geometry. In addition the ASIC level occupation is also different with a filled singlet (shorter bond) separated by about 2.5 eV from an empty doublet.

The triple acceptor B_O presents a somewhat less critical situation. Now the B- $2p$ impurity band is half filled and positioned completely within the MgO band gap. The strong Hund's interaction produces a magnetic ground state with a magnetic moment of $3\mu_B/B$ for both LSDA and ASIC. For such an occupation the Jahn-Teller mechanism does not operate and the LSDA and ASIC band structures are qualitatively similar.

When we look at the magnetic coupling we find for both N and C a situation very similar to that of Al in SiO₂, i.e., a large magnetic coupling in LSDA and practically no coupling in ASIC. The situation is rather different for B where even LSDA does not predict magnetic coupling. Does this mean that ferromagnetism cannot exist in these compounds? The answer to this question is not simple and essentially relates to the behavior of the impurities with additional doping. For instance by adding a fractional electronic charge to C_O one should find a situation intermediate between that on C_O and N_O. Such a charge however feels a weaker nuclear potential and certainly localizes less. Although it is likely that it will occupy one of the empty C_O p orbitals, leading once again to a half-metallic band structure, the quantitative details of its exact localization are not easy to predict. Since the ferromagnetism is the result of the subtle interplay between localization, which is necessary for the magnetic-moment formation and delocalization, which is necessary for the magnetic coupling, we believe that a more accurate electronic structure method capable of taking all these factors into account is needed.

We finally move our attention to Ga vacancy (V_{Ga}) and of

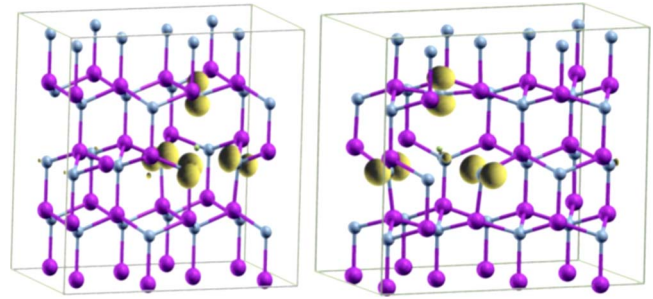


FIG. 3. (Color online) Isosurface of the three holes (the magnetization) associated to V_{Ga} in GaN as calculated with LSDA (left) and ASIC (right). In LSDA the holes are distributed uniformly over all the four N ions surrounding the vacancy, while they localize around the longer three bonds in ASIC.

Zn substitutional for Ga (Zn_{Ga}) in GaN. The first is again a triple acceptor and it was recently proposed as a possible source of d^0 ferromagnetism,¹⁸ while the second introduces only one hole, which is predicted nonmagnetic by LSDA. Our results, obtained with a 64-atom supercell are summarized again in Table I, where we can observe that LSDA and ASIC agree on the magnetic ground state of V_{Ga} but give, respectively, a nonmagnetic and a magnetic $S=1/2$ state for Zn_{Ga} . The nonmagnetic state found in LSDA is resistant to supercell size and persists to cells as large as 256 atoms, which are already large enough to decouple the impurities located in the periodic mirror cells.

Let us consider first the case of V_{Ga} . Here the situation is somehow similar to that of MgO:N, where the magnetic state is reproduced already at the level of LSDA, but the spatial distribution of the moment changes radically when SIC is considered. In LSDA, in fact, the four N's surrounding the vacancy move outward, so that the distance with the vacant site is 2.1 Å, which is about 8% longer than that between Ga and N. Such displacement is isotropic and the three holes spread uniformly over the four available bond directions of the wurtzite lattice (see Fig. 3). Thus the material turns out to be half metallic.¹⁸ The ASIC picture is however rather different. Also in this case the SIC allows the hole to be localized. The ASIC relaxation leads to two bonds of 2.14 Å and two longer of bonds of slightly different lengths. The longest of the four is fully filled and the three holes localize on the remaining three (Fig. 3). Such a situation reminds that of Al_{Si} and it is a further demonstration of the effects of self-trapping. Also for GaN: V_{Ga} self-trapping massively suppresses the magnetic coupling energy which reduces from 145 meV (antiferromagnetic) in LSDA (for two V_{Ga} placed at 6.3 Å from each other) to 1 meV for ASIC.

The situation for the single acceptor Zn_{Ga} is dramatically different with LSDA giving a nonmagnetic ground state with the hole evenly distributed over the four almost tetrahedrally coordinated bonds. These are just slightly expanded to about 2 Å. ASIC again captures the Jahn-Teller distortion. Three Zn-N bonds readjust to a distance of 1.96 Å, while the fourth expands considerably to 2.4 Å (Fig. 4). The hole now completely localizes over the longest bond; and due to the enhanced degree of localization, Hund's coupling spin splits the energy level in forming a spin 1/2 ground state. The

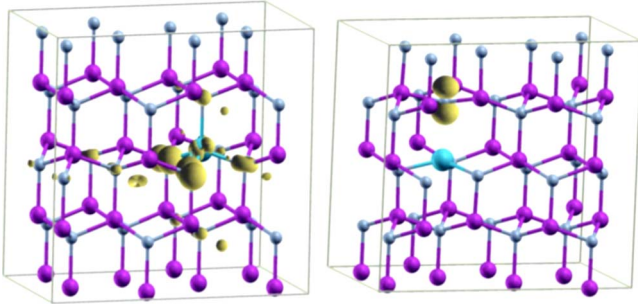


FIG. 4. (Color online) Isosurface of the hole (the magnetization) associated to Zn_{Ga} in GaN as calculated with LSDA (left) and ASIC (right). In LSDA the hole is unpolarized and distributed uniformly over all the four N ions surrounding the vacancy, while it spin splits and localizes around the longer bond in ASIC.

ASIC electronic structure is then that of Zn_{Ga} being a paramagnetic deep trap instead of a shallow nonmagnetic acceptor.

In conclusion we have demonstrated that the problem of predicting the magnetic ground state of p -type impurities is

an extremely delicate one. In general standard LSDA is unable to capture Jahn-Teller distortion and systematically underestimates the electron localization. As a consequence Hund's coupling is also underestimated. In some cases a magnetic ground state is still predicted, but the spatial distribution of the magnetic moment is inaccurate. This typically leads to a metallic (via impurity band) ground state, strong exchange coupling between the magnetic impurities, and the expectation of room-temperature ferromagnetism. The removal of the self-interaction error results in Jahn-Teller distortion and the creation of an insulating ground state with little to no magnetic coupling between the impurities. A more drastic situation is however encountered when the erroneous LSDA delocalization strongly suppresses Hund's coupling and produces a nonmagnetic ground state. Also in this case ASIC predicts a nonvanishing magnetic moment localized at distorted bonds.

This work was sponsored by the Science Foundation of Ireland under Grants No. 07/IN.1/I945 and No. 07/RFP/MASF238. Computational resources have been provided by ICHEC and the HEA IITAC project managed by TCHPC.

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