

## Self-interaction correction and contact hyperfine field

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(Received 18 January 2003; published 28 April 2003)

The hyperfine field is a precise and essential probe of the magnetic state of a solid, and of the quality of theoretical core wave functions, but its accurate evaluation has proven challenging from first principles. In this work, the self-interaction *free* potential, suggested recently by Lundin and Eriksson, is applied to the core states in the calculation of the hyperfine field for 3d transition metal ferromagnets Fe, Co, and Ni, and for three Fe compounds. Compared to the local spin density approximation and to its conventional self-interaction corrected form, the new potential functional is found to increase substantially the core contribution to the Fermi contact term, leading to good agreement with measurements for Fe and Co, and significantly better results for iron compounds. Our results strongly suggest that the new functional is more suitable for generating realistic core wave functions to high accuracy for a wide range of materials. The subtle effects resulting from the change of potential functional are also addressed.

DOI: 10.1103/PhysRevB.67.140403

PACS number(s): 76.30.Fc, 71.15.Mb, 71.70.Jp

The local spin density approximation (LSDA) to density functional theory proved to be immensely valuable for understanding of the magnetic properties of solids. Yet there are well documented shortcomings of LSDA when applied to the magnetic systems. In the present paper we concentrate on one of them—the contact hyperfine field  $B_c$  is consistently underestimated by LSDA, as first noticed by Blügel *et al.*<sup>1</sup> and emphasized in several other papers since then.<sup>2,3</sup> From the good agreement between measured and calculated hyperfine field in special cases when  $B_c$  is dominated by the transferred hyperfine interaction (e.g., in Cu impurities in Fe, Co, and Ni (Refs. 1,4,5)  $B_c$  originates mainly from the spin polarization of Cu 4s valence states via interactions with the magnetic neighbors) it can be concluded that the underestimation of  $B_c$  results mainly from the on-site contribution of the 1s, 2s, and 3s core states to the contact hyperfine field, reflecting serious inadequacy of LSDA for the core states.

This defect of LSDA in the description of the core states is not too surprising, considering the large nonphysical self-interaction (SI) these localized states suffer. Unexpectedly, while removing the SI via correction proposed by Perdew and Zunger (PZ-SIC)<sup>6</sup> does significantly improve the binding energy of the core states, the resulting  $B_c$  is almost unchanged and therefore still underestimated,<sup>3</sup> indicating insufficiency of PZ-SIC functional in properly describing the Kohn-Sham wave function of the core states. In light of the importance of magnetic systems in various applications and the fundamental scientific understanding of localized electronic states, it is crucial to identify the origin of the defect and improve the current schemes.

Recently, Lundin, and Eriksson<sup>7</sup> pointed out that the self-interaction is not fully removed in the PZ-SIC functional, since, due to the nonlinear dependence of LSDA  $V_{XC}(\rho_\sigma, \rho_{\sigma'})$  on  $\rho_\sigma$ , the potential  $V_{i\sigma}^{PZ}$  felt by state  $|i, \sigma\rangle$  still depends explicitly on the density of the same orbital:

$$V_{i\sigma}^{PZ} = V_{\text{ext}} + V_H(\rho) + V_{XC}(\rho_\sigma, \rho_{\sigma'}) - V_H(\rho_{i\sigma}) - V_{XC}(\rho_{i\sigma}, 0), \quad (1)$$

where  $V_{\text{ext}}$ ,  $V_H$ ,  $V_{XC}$  are external, Hartree, and exchange-correlation potential and  $\rho$ ,  $\rho_\sigma$ , and  $\rho_{i\sigma}$  correspond to total density, density of spin  $\sigma$ , and density of the orbital  $|i, \sigma\rangle$ , respectively. These authors proposed an alternative potential functional (denoted as LE-SIC hereafter)

$$V_{i\sigma}^{\text{LE}} = V_{\text{ext}} + V_H(\rho - \rho_{i\sigma}) + V_{XC}(\rho_\sigma - \rho_{i\sigma}, \rho_{\sigma'}) \quad (2)$$

that is explicitly SI-free by construction.

In this paper we show that the LE-SIC, when applied to the core states of ferromagnets Fe, Co, and Ni, and three Fe compounds, significantly removes the  $B_c$  underestimation systematically in all the cases studied. Especially for bcc Fe, this leads to an excellent agreement with experiments. These results strongly suggest that LE-SIC is practically much superior than LSDA or PZ-SIC for the description of the core state wave functions, in a wide range of materials. The subtle effects of changing the potential functional will then be discussed.

The hyperfine field  $B_{\text{hf}}$  may be written as a sum of four contributions

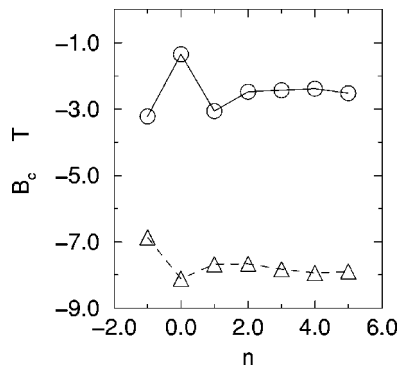


FIG. 1. Fcc Ni, LSDA method. Contribution of the valence states (full curve) and core states (dashed curve) to the contact hyperfine field as function of  $n$ . Number of the  $k$  points in the Brillouin zone  $N_k = 1000 \times 2^n$ .

$$B_{\text{hf}} = B_c + B_{\text{orb}} + B_{\text{dip}} + B_{\text{latt}}, \quad (3)$$

where  $B_c$  is the Fermi contact term,  $B_{\text{orb}}$  and  $B_{\text{dip}}$  are the contributions from the “on site” magnetic dipolar interaction of the nuclear magnetic moment with the electronic orbital and spin momentum, respectively.  $B_{\text{latt}}$  corresponds to the field from the magnetization density of the rest of the sample and it is zero for sites possessing cubic symmetry. For the systems of interest in this work,  $B_c$  is the dominant contribution, and is thus the focus of our study. The actual calculation of the hyperfine field follows the approach suggested by Blügel *et al.*<sup>1</sup>

While it is difficult to apply SIC to the valence electrons in a periodic crystal,<sup>8</sup> for the fully localized core electrons application of SIC is straightforward and simple. The weak violation of orthogonality, resulting naturally from the SIC functional, is removed via Schmidt procedure. As pointed out by Severin *et al.*,<sup>3</sup> the Fermi contact term is a trace of a Hermitean operator and thus it is independent of the particular choice of the basis states, once these are orthogonalized. Note, however, that because of the nonorthogonality no unambiguous way of assessing contribution of specific  $ns$  core state to  $B_c$  exists. The effects of SI of the valence states on  $B_c$  is assumed negligible.

The electronic structure is calculated with the full potential augmented plane waves + local orbitals (APW+LO) method, as implemented in the WIEN2k package.<sup>9</sup> The  $1s$ ,  $2s$ ,  $2p$ , and  $3s$  states of the  $3d$  metal atom were treated as core states, while  $3p$ ,  $3d$ ,  $4s$ , and  $4p$  were included as the valence states. The sensitivity of the results to the parameters of the APW+LO was checked and we found that for the metallic systems rather large number  $N_k$  of  $k$  points in the Brillouin zone must be taken in order to obtain reliable results. As an example the core and valence contributions to the contact field for fcc Ni are plotted as functions of  $N_k$  in Fig. 1.

A remark concerning  $B_{\text{orb}}$  should be made. Since the focus of this work is  $B_c$  and underlying core state wave functions, and only total  $B_{\text{hf}}$  can be accessed experimentally, a reliable estimation of  $B_{\text{orb}}$  is necessary for the comparison to be meaningful. Now,  $B_{\text{orb}}$  is to a good approximation proportional to the valence orbital momentum  $l_z$ , which, unfortu-

TABLE I. Hyperfine field for bcc Fe, hcp Co, and fcc Ni, comparison of LSDA, PZ-SIC, and LE-SIC methods.  $\kappa$  is the ratio  $l_z(\text{exp})/l_z$ . Experimental hyperfine field and orbital momentum were taken from Ref. 2. All hyperfine fields are in T. Lattice contribution  $B_{\text{latt}}$  is zero for Fe and Ni and it is very small for hcp Co:  $B_{\text{latt}} = -0.0004$  T.  $B_{\text{hf}}(\text{sc})$  is calculated from Eq. (3), but with  $B_{\text{orb}}$  scaled according to Eq. (4).

		$l_z$	$B_c$	$B_{\text{dip}}$	$B_{\text{orb}}$	$B_{\text{hf}}$	$\kappa$	$B_{\text{hf}}(\text{sc})$
bcc	LSDA	0.049	-30.13	0.00	2.79	-27.34	1.83	-25.04
	PZ-SIC	0.049	-30.12	0.01	2.73	-27.38	1.83	-25.11
Fe	LE-SIC	0.047	-38.04	0.01	2.50	-35.52	1.91	-33.23
	exp.	0.09						-33.9
hcp	LSDA	0.079	-26.68	-0.10	5.72	-21.07	1.90	-16.04
	PZ-SIC	0.079	-26.66	-0.10	5.72	-21.04	1.89	-16.04
Co	LE-SIC	0.076	-33.72	-0.11	5.43	-28.408	1.96	-23.28
	exp.	0.15						-21.8
fcc	LSDA	0.051	-10.42	0.00	4.53	-5.89	0.99	-5.95
	PZ-SIC	0.050	-10.39	0.00	4.47	-5.92	1.00	-5.93
Ni	LE-SIC	0.049	-13.36	0.00	4.27	-9.09	1.03	-8.98
	exp.	0.05						-7.5

nately, is also severely underestimated for bcc Fe and hcp Co within LSDA (Ref. 2) (another well-known failure of the LSDA). Instead of employing the *ad hoc* approach of orbital polarization,<sup>10</sup> we overcome the difficulty by empirically rescaling LSDA  $B_{\text{orb}}$  by the ratio of experimental<sup>2</sup> and calculated orbital momentum

$$B_{\text{orb}}(\text{scaled}) = \frac{l_z(\text{exp.})}{l_z(\text{calc.})} B_{\text{orb}}(\text{calc.}). \quad (4)$$

Scaling of  $B_{\text{orb}}$  is important (roughly a factor of 2) for bcc Fe and hcp Co (Table I), while it is insignificant for fcc Ni and for the iron compounds  $\text{FeF}_3$  and  $\text{Fe}_3\text{O}_4$  considered below. Similar difficulty occurs in estimating  $B_{\text{dip}}$ , which is also a (complex) function of the orbital momentum. Fortunately,  $B_{\text{dip}}$  is small in all cases considered here, and its uncertainty may be disregarded.

The results for bcc Fe, hcp Co, and fcc Ni using LSDA, PZ-SIC, and LE-SIC are summarized in Table I. The LE-SIC form increases  $|B_c|$  by 20–30 % in these magnetic metals and results in dramatically improved agreement with the experimental values, indicating a superb quality of the resulting core state wave functions. Note that the accidental success of LSDA and PZ-SIC in the case of hcp Co is destroyed, once the underestimation of  $B_{\text{orb}}$  is taken into account. Also note that the success story of PZ-SIC in increasing the binding energy of core states is retained (in all cases considered in this work) with LE-SIC, which produces a larger enhancement of the binding energy than the former.

To demonstrate the performance of the three above methods in the iron containing magnetic compounds we selected  $\text{FeF}_3$ , magnetite  $\text{Fe}_3\text{O}_4$  in its cubic phase and lithium nitridoferrate  $\text{Li}_2(\text{Li}_{1-x}\text{Fe}_x)\text{N}$ . Iron trifluoride is an antiferromagnetically ordered ionic compound, valence state of iron is  $3+$ . The ground state of  $\text{Fe}^{3+}$  is  ${}^6S$ , hence little orbital mo-

TABLE II. Hyperfine field for FeF<sub>3</sub>. Comparison of LSDA, PZ-SIC, and LE-SIC methods. Magnetic moments are along [111], then  $B_{\text{lat}}=0$  due to the symmetry.

	$B_{\text{orb}}$	$B_{\text{dip}}$	$B_c$	$B_{\text{hf}}$
LSDA	1.02	-0.23	-41.67	-40.88
PZ-SIC	1.04	-0.22	-41.60	-40.78
LE SIC	0.95	-0.29	-55.76	-55.10
$ B_{\text{hf}}(\text{exp.}) $				61.5

ment is expected. Among the stoichiometric iron compounds, FeF<sub>3</sub> has the highest hyperfine field with the magnitude  $B_{\text{hf}}=61.5$  T.<sup>11</sup> In magnetite iron enters two sublattices-tetrahedral (*A*) where its valence state is +3 and octahedral (*B*) with the formal valence of iron +2.5. Magnetite is a ferrimagnet with Fe(*B*) spins antiparallel to Fe(*A*) spins. The hyperfine fields extrapolated to 0 K are  $B_{\text{hf}}(\text{A})=50.8$  T,  $B_{\text{hf}}(\text{B})=48.6$  T.<sup>12,13</sup> Finally in lithium nitridoferrate the valence state of iron is 1+ and a huge hyperfine field was observed for selected iron centers.<sup>14,15</sup> The calculations were performed assuming ferromagnetic ordering. The supercell denoted as *hex2* in Ref. 15 that contains two iron centers Fe1 and Fe2 with different cation environment was used.

The results for FeF<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> are given in Tables II and III. It is seen that very large disagreement of LSDA and PZ-SIC is much improved when LE-SIC is used. For lithium nitridoferrate the situation is more complex — in this case positive  $B_{\text{orb}}$  gives the largest contribution to  $B_{\text{hf}}$ , while  $B_c$  is negative and smaller. We used the LDA+*U* method to explain unusual properties of this system;<sup>15</sup> this, however, brings considerable uncertainty in calculated  $B_{\text{hf}}$ , due to an uncertainty in the value of the *U* parameter and the fact that different versions of the LDA+*U* method may be employed. Nevertheless even in this case LE-SIC brings the theoretical results closer to experimental ones by enhancing the core contribution to  $B_c$  by 9.6 and 9.5 T for Fe1 and Fe2, respectively.

Physically, the contact hyperfine field is expected to be approximately proportional to the 3*d* spin magnetic moment  $m_S$ . Indeed, as shown in Fig. 2,  $B_c$  is found to be propor-

TABLE III. Hyperfine fields in the cubic phase of Fe<sub>3</sub>O<sub>4</sub>. Comparison of LSDA, PZ-SIC, and LE-SIC methods. Magnetization is along [001], then  $B_{\text{lat}}=0$  due to the symmetry.

	$B_{\text{orb}}$	$B_{\text{dip}}$	$B_c$	$B_{\text{hf}}$	
Fe(A)	LSDA	-0.49	0.01	31.20	30.72
	PZ-SIC	-0.49	0.00	31.11	30.62
	LE SIC	-0.47	0.00	43.34	42.87
	$ B_{\text{hf}}(\text{exp.}) $				50.8
Fe(B)	LSDA	0.74	0.57	-30.91	-29.60
	PZ-SIC	0.72	0.54	-30.80	-29.54
	LE SIC	0.68	0.53	-43.67	-42.46
	$ B_{\text{hf}}(\text{exp.}) $				48.6

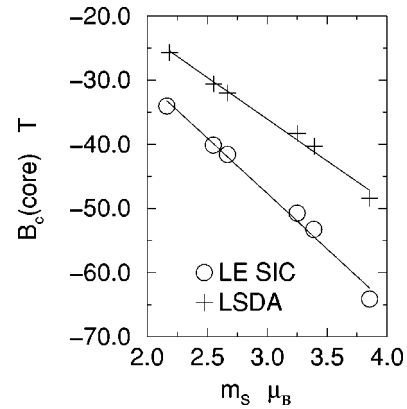


FIG. 2. bcc Fe and Fe compounds. Contribution of the core states to the contact hyperfine field as function of the 3*d* spin magnetic moment  $m_S$ . The points ordered according to increasing  $m_S$  correspond to bcc Fe; Fe2, Fe1 centers in *hex2* supercell of Li<sub>2</sub>(Li<sub>1-x</sub>Fe<sub>x</sub>)N; Fe(*A*), Fe(*B*) in Fe<sub>3</sub>O<sub>4</sub>, and to Fe in FeF<sub>3</sub>. The muffin tin radius of Fe was 1.9 a.u. The lines are linear fits to the data.

tional to  $m_S$  despite very different valence states of iron in the bcc Fe and in iron compounds considered above, with either LSDA or LE-SIC.

In order to understand the action of SIC we identify possible effects of the modified potential on the hyperfine field. Note that since one is dealing with tiny differences of large numbers (spin and charge densities in the core region), a quantitative estimation would be quite difficult. There are two ways to increase the spin density at the nucleus: (1) increase the degree of the spin polarization while keeping the charge density unchanged (increasing the exchange field) or (2) increase the charge density (more attractive potential) keeping the relative spin polarization constant. Our calculations showed that several counteracting mechanisms take place. First, the LSDA-SIC potential is more attractive than LSDA potential obtained with the same density resulting in contraction of the wave functions. Second, contraction of the *s* function reduces the effective exchange field due to reduced overlap with the *d* spin density. Third, contraction of the deeper lying functions leads to a better screening of the nuclear charge forcing an expansion of the higher lying orbitals (this mechanism is effective through the self-consistency). Fourth, different SIC schemes lead to different exchange field originating from the *s* spin density as is shown below. Numerical tests showed that all the above mechanisms are larger in magnitude in the LE scheme than for PZ. (In the latter case, the Hartree contribution to SIC is strongly compensated by the exchange-correlation term.) However, the final result is a delicate balance of all the four above mechanisms and none of them can be identified as the dominant one.

We now discuss how the LE-SIC differs from the PZ-SIC potential. Both PZ-SIC and LE-SIC handle the largest, self-Hartree term identically and exactly. The difference that is crucial for  $B_c$  arises only from the treatment of the XC self-interaction of the core orbitals. The difference in the potentials (exchange and correlation, either separately or together) is

$$\delta V^{\text{LE-PZ}} = V_{X(C)}(\rho_\sigma - \rho_{i\sigma}, \rho_{\sigma'}) - [V_{X(C)}(\rho_\sigma, \rho_{\sigma'}) - V_{X(C)}(\rho_{i\sigma}, 0)] \quad (5)$$

$$\approx -\rho_{i\sigma} f_{X(C)}(\rho_\sigma, \rho_{\sigma'}) + V_{X(C)}(\rho_{i\sigma}, 0), \quad (6)$$

where the  $X(C)$  interaction  $f_{X(C)}$  is the derivative of  $V_{X(C)}$  that arises in linear response formalisms. The Taylor expansion in  $\rho_\sigma - \rho_{i\sigma}$  should be good enough for illustrative purposes near the nucleus of atoms of interest here, where  $B_c$  arises primarily from  $2s$  and  $3s$  orbitals, for which 2nd order terms in  $\rho_{i\sigma}/(\rho_\sigma - \rho_{i\sigma})$  do not change the interpretation. Since  $V_{XC}$  scales as  $\rho^{1/3}$  the deviation between LE and PZ-SIC increases with increasing  $\rho$ . The XC part of PZ-SIC compensates to a large extent the Hartree part, while in LE-SIC is the Hartree part compensated much less resulting in mechanisms 1 – 3 to be larger in magnitude for LE-SIC. However, calculations neglecting the XC part of SIC (Hartree only) do not lead to improvement of the hyperfine field yielding only a moderate enlargement over the LSDA results.

If a Taylor expansion were also good for the last term, the difference would involve only one higher derivative of  $V_{X(C)}$  (and would be sensitive to parametrizations;  $f_{X(C)}$  already shows some such sensitivity). However, local density correlation functionals are not constructed to be accurate in the low density limit (where they are unphysical due to Wigner crystallization). Evaluating the difference of the exchange field  $B_{\text{ex}} = V_\uparrow - V_\downarrow$  between LE and PZ-SIC, i.e., the fourth mechanism, we obtain

$$\begin{aligned} \delta B_{\text{ex}}^{\text{LE-PZ}} &\approx -(\rho_{i\uparrow} - \rho_{i\downarrow}) f_{X(C)}(\rho_\uparrow, \rho_\downarrow) \\ &\quad + [V_{X(C)}(\rho_{i\uparrow}, 0) - V_{X(C)}(\rho_{i\downarrow}, 0)] \\ &\approx -(\rho_{i\uparrow} - \rho_{i\downarrow}) [f_{X(C)}(\rho/2, \rho/2) - f_{X(C)}(\rho_i/2, 0)]. \end{aligned} \quad (7)$$

Here the expansion of  $V_{X(C)}$  around zero argument has been avoided. It can be seen that LE-SIC–PZ-SIC difference is proportional to the (small) orbital polarization, but is non-zero only because the  $X(C)$  interaction  $f_{X(C)}$  is evaluated for a fully polarized single electron density (PZ) versus an (essentially) unpolarized all-electron density (LE).

In conclusion, we have shown that the SI-free potential functional proposed by Lundin and Eriksson, in addition to its conceptual attractiveness, provides a much needed increase in the core contribution to the contact hyperfine field in bcc Fe, hcp Co, and fcc Ni, as well as in several iron compounds. The improvement is closely related to the modification of the core  $s$  functions according to the employed potential, which strongly suggests the practical superiority of LE-SIC over LDA and PZ-SIC in describing the core state wave functions. The subtle modification can be traced back to both spin-independent and exchange-field parts of the potential, and can not be easily explained based merely on the stronger attraction in the field, or the enhancement of resulting charge density at the nucleus. We expect this correction for  $|B_c|$  to hold more generally, and are in the process of testing the LE-SIC functional for more systems and other properties.

This work was supported by Czech-USA Project No. KONTAKT ME547, by Grant No. A1010214 from the Academy of Sciences of the Czech Republic, by the NATO/NSF Grant No. DGE-0209264, and by NSF Grant No. DMR-0114818.

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