Theor Chem Acc (2005) 113: 191–196
DOI 10.1007/s00214-005-0631-6

REGULAR ARTICLE

Diana Guenzburger · D.E. Ellis · Joice Terra

Self-interaction correction and isotropic hyperfine parameter of light atoms

Received: 20 October 2004 / Accepted: 10 December 2004 / Published online: 18 March 2005

Abstract Numerical self-consistent field (SCF) calculations in density functional theory (DFT) and the local spin-density approximation (LSDA) were performed for the light atoms H, Li, B, C, N, O and F, in order to investigate the effect of the self-interaction correction (SIC) on the isotropic (or contact) hyperfine parameter A_{ISO}. In contrast to the findings for certain 3d-metals and compounds, results for light-atom SI-corrected A_{ISO} present no improvement over the LSDA values. We show that relatively modest changes to the correlation potential can lead to significant improvement of densities near the nucleus and the related A_{ISO}, suggesting a direction for future improvements in DFT functionals.

Introduction

Density functional theory (DFT) and the local spin-density approximation (LSDA) have had considerable success in recent years in calculating properties of magnetic molecules and solids. However, one property, which is particularly sensitive to the shape of the wave function in the core region of the atoms, has posed a challenge not yet resolved: the isotropic (or contact) hyperfine interaction parameter $\mathrm{A_{ISO}}$ [1]. This parameter, which depends on the electronic spin-density at the nucleus, was obtained for first-row atoms in molecular calculations employing the LSDA with rather poor results [2–5]. Inclusion of gradient corrections (GGA) to the LSDA has done little to improve the situation, particularly since the different forms of the GGA correction potentials give quite different results. Improved results were obtained by including in the corrections to the LSDA a fraction of the Hartree–Fock potential (HF) [4]; however, this procedure takes us out of the framework of DFT. With such an empirical mixture of two quite different theories, one has little hope of learning how to make fundamental improvements in theory. In any case, efforts to improve exchange-correlation potentials were largely directed toward binding energies and bond lengths, and not local wavefunction properties.

The core states of an atom are localized, and thus are very susceptible to an intrinsic error of DFT, which is the interaction of an electron with itself, or self-interaction. This spurious effect arises from the incomplete cancellation of the self-interaction contained in the Coulomb repulsion potential by the exchange-correlation potential; in other words, the electron feels the effect of itself in the self-consistent field. A self-interaction correction (SIC) was proposed by Perdew and Zunger and applied to binding energies of atoms with success, bringing theoretical and experimental values to a better agreement [6]. However, application to calculations of the core electrons contact hyperfine field of the metals Fe, Co and Ni had little success in improving the theoretical values [7]. More recently, a new formulation of SIC by Lundin and Eriksson was proposed [8], which is conceptually more satisfying than the original one, since it is explicitly entirely SIC-free by construction, which was not the case with the earlier proposition. With a firm theoretical foundation within the DFT formalism, and successful applications to molecules and solids (correction of the well-known LDA band-gap problem, for example) one may hope to find further improvements in the treatment of other more subtle properties. Application to calculations of the contact hyperfine fields of solid ionic Fe compounds, as well as metallic Fe, Co and Ni, showed significant improvement in the results, as compared with LSDA [9]; however, comparison with experiment is impaired since the orbital component of the hyperfine field was obtained by an empirical rule. It thus becomes highly interesting to see how well the model performs in prediction of hyperfine fields of lighter atoms.

We have recently been engaged in calculations of A_{ISO} for small molecules containing H, C, N and O, as well as A_{ISO} for N in large biological molecules [10]. Confronted by the difficulty posed by the use of LSDA in calculating this property, we decided to test the efficacy of SIC in obtaining A_{ISO} for the

D. Guenzburger · J. Terra
Centro Brasileiro de Pesquisas Físicas, rua Xavier Sigaud 150, 22290-180 Rio de Janeiro, RJ, Brazil

D.E. Ellis
Department of Physics and Astronomy and Materials Research Center, Northwestern University, Evanston, IL 60208, USA

Table 1 Atomic orbital contributions to $\Delta\rho_s(0)$ (in a_o^{-3})

		H	Li	B	C	N	O	F
LSDA	1s	0.302	0.004	−0.090	−0.279	−0.573	−0.506	−0.313
	2s	–	0.225	0.084	0.268	0.561	0.492	0.299
	Total	0.302	0.229	−0.006	−0.011	−0.012	−0.014	−0.014
SIC[a]	1s	0.315	0.490	−0.268	−0.664	−1.212	−0.766	−0.431
	2s	–	0.345	0.195	0.486	0.874	0.696	0.399
	Total	0.315	0.835	−0.073	−0.178	−0.338	−0.070	−0.032
SIC[b]	Total	0.315	0.736	−0.117	−0.271	−0.488	−0.174	−0.088

[a] Non-orthogonalized orbitals
[b] Orthogonalized orbitals

light atoms H, Li, B, C, N, O and F. In particular, for the case of the first-row atoms, it is well known that the LSDA gives poor results due to the unsatisfactory description of the 1s core spin-polarization by the 2p electrons. It was hoped that using SIC would correct for this deficiency to some extent. Results obtained with and without SIC were then assessed by comparison with available experimental data. Finally, we carried out an estimate of the effects of correlation on A_{ISO}, using an empirical scaling function.

Atomic calculations and SIC

All atomic calculations were performed on a numerical grid of 300 points, and thus the radial eigenfunctions R(r) obtained are numerical. The Kohn–Sham equations of LSDA are solved self consistently (in Hartree atomic units):

$$\left[-\nabla^2/2 + \int \rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|\mathrm{d}^3\mathbf{r}' + V_{xc}^{\sigma}(\mathbf{r}) + V_N(\mathbf{r})\right]\phi_i^{\sigma}(\mathbf{r}) = \varepsilon_i^{\sigma}\phi_i^{\sigma}(\mathbf{r}) \quad (1)$$

In Eq. (1), $V_N(\mathbf{r})$ is the external (nuclear) potential, the second term is the Hartree (effective Coulomb) potential and the electronic spin-density $\rho^{\sigma}(\mathbf{r})$ of spin σ is given by the sum over the atomic spin-orbitals $\phi_i^{\sigma}(\mathbf{r})$ with occupation n_i^{σ} and eigenvalues ε_i^{σ}:

$$\rho^{\sigma}(\mathbf{r}) = \sum_i n_i^{\sigma}|\phi_i^{\sigma}(\mathbf{r})|^2 \equiv \sum_i n_{\mathrm{i}}^{\sigma}\rho_i^{\sigma}(\mathbf{r}). \quad (2)$$

The total $\rho(\mathbf{r})$ is the sum of $\rho^{\sigma}(\mathbf{r})$ for both spins, and the spin density $\Delta\rho_s(\mathbf{r})$ is defined as $[\rho^{\uparrow}(\mathbf{r}) - \rho^{\downarrow}(\mathbf{r})]$, with ↑ (↓) pertaining to $m_s = +1/2(-1/2)$. The exchange and correlation potential V_{xc}^{σ} of Eq. (1) is decomposed in the usual manner as the sum of the Kohn–Sham exchange potential V_x^{σ} and the correlation potential V_c. The local exchange-correlation potential $V_{xc}^{\sigma}(\mathbf{r})$ employed here was that of Vosko, Wilk and Nusair (VWN) [11], which was obtained by fitting Ceperley and Alder's Green's function Monte-Carlo data [12].

In the Lundin–Eriksson SIC (LE-SIC) method, one uses a different potential for each $\phi_i^{\sigma}(\mathbf{r})$, constructed by subtracting the density pertaining to this orbital, $\rho_i^{\sigma}(\mathbf{r})$, from the total density:

$$V_{\text{SIC}}^{i\sigma} = V_N + V_H(\rho - \rho_i^{\sigma}) + V_{xc}(\rho^{\sigma} - \rho_i^{\sigma}, \rho^{\sigma'}), \quad (3)$$

where V_H is the Hartree-Coulomb potential.

The model described here is within the nonrelativistic spin-polarized framework, which is a subset of the more general spin- and orbital-polarized methodology. In the general case, one allows different radial wavefunctions for each m_l and m_s, which can produce a nonspherical charge and spin density. Desclaux et al. [13] have shown that, in spin- and orbital-polarized Hartree–Fock (SOPHF) calculations, the additional freedom of orbital polarization has only minor effects on the s-densities responsible for the isotropic hyperfine interaction. For example, SOPHF results for the 5d^n ions differ from spin-polarized results by only 0.2–0.5%.

After obtaining the self-consistent solutions, the isotropic hyperfine parameter may be calculated as:

$$A_{\text{ISO}} = (8\pi/3)\mathrm{g}_e\beta_e\mathrm{g}_N\beta_N\Delta\rho_s(0), \quad (4)$$

where g_e and g_N are the electron and nuclear gyromagnetic ratios, respectively, β_e is the Bohr magneton, β_N the nuclear magneton and $\Delta\rho_s(0)$ is the electron spin-density at the nucleus; in the non-relativistic approximation only s electrons penetrate the nucleus.

Results and discussion

In Table 1 are given the self-consistent values of $\Delta\rho_s(0)$ for the LSDA calculations with and without SIC, for the atoms H, Li, B, C, N, O and F. The individual contributions of the 1s and 2s orbitals are shown. In the case of SIC, the 1s and 2s orbitals are non-orthogonal and the density may be projected in an invariant manner as

$$\rho = \sum_{ij}\phi_i S_{ij}^{-1}\phi_j\sqrt{n_i n_j} \quad (5)$$

consistent with the Pauli exclusion principle; here S_{ij} is the overlap matrix element between orbitals i and j. This can be described as resulting from mutual orthogonalization of the orbitals within a single determinant wavefunction; however, the result given in Eq. (5) is independent of any particular choice of orthogonalization scheme [14]. Due to spin- and angular momentum-orthogonality the only nontrivial elements of S which enter in the present case are the 1s–2s overlaps of a given spin. The occupation-number factor is included in Eq. (5) to remind the reader that only occupied states enter into the calculation of ρ. In the Table, results

Table 2 Theoretical and experimental values of A_{ISO} (in MHz) for light atoms

	^{1}H	^{7}Li	^{11}B	^{13}C	^{14}N	^{17}O	^{19}F
LSD*A*[a]	1351	397	−8.84	−11.83	−3.93	+8.56	−59.73
SIC[a]	1409	1279	−168.5	−304.8	−157.5	+105.3	−370.0
DFT[b]	–	–	−32.37	1.45	15.70	−17.77	–
DFT[c]	–	–	–	12.66	23.29	−43.20	–
DFT[d]	–	–	17.5	24.6	10.3	−28.7	243.6
LSD*A*[e]	1296	390	12.6	23.6	16.4	−26.9	59.3
CCSD[f]	–	–	10.25	21.42	11.00	−33.16[g]	302.87
Exp.	1420[h]	401.8[h]	11.6[i] 18.7[j]	21.4[k] 22.5[i]	10.45[l]	34.5[g,m]	301.7[m]

[a] This work. $g_N(^1H) = 5.58556$, $g_N(^7\mathrm{Li}) = 2.17091$, $g_N(^{11}\mathrm{B}) = 1.79233$, $g_N(^{13}\mathrm{C}) = 1.4048$, $g_N(^{14}\mathrm{N}) = 0.40375$, $g_N(^{17}\mathrm{O}) = -0.75748$, $g_N(^{19}\mathrm{F}) = 5.2576$. All values of g_N from Ref. [15]

[b] From Ref. [3]. Gaussian basis, gradient-corrected functionals by Perdew, and Perdew and Wang [16]

[c] From Ref. [3], different Gaussian basis

[d] From Ref. [4]. Gaussian basis, mixed exchange-correlation functional DFT/Hartree–Fock (B3LYP)

[e] Employing V_c multiplied by factor F, with $a = 1$, $b = 1.5$, see Eqn. (6)

[f] From Ref. [17], Coupled-Cluster method

[g] The apparent sign discrepancy here is merely due to the negative nuclear g_N factor of ^{17} O; experimental value lacks determination of the sign (see text)

[h] From Ref. [15] and references therein

[i] From Ref. [18]

[j] From Ref. [19]

[k] From Ref. [20]

[l] From Ref. [21]

[m] From Ref. [22]

with SIC are given before and after the orthogonalization; after this procedure, however, one cannot speak of 1s and 2s individual contributions anymore, therefore only the total is given.

The electron spin density at the nucleus for H and Li is large and positive and, in the case of Li, due almost entirely to the valence 2s. In the case of the series B–F, the total $\Delta\rho_s(0)$ is much smaller, since it results from a delicate balance of the negative core (1s) contribution and the positive 2s. In this series, both the 1s and 2s orbitals are entirely filled, and the spin density results from the polarization by the unpaired electrons in the 2p orbital. The total positive spin (or spin up) of the 2p electrons attracts electrons of equal spin, since the exchange interaction does not exist between electrons of opposite spin. Since the 1s electrons are nearer to the core than the 2p, the latter will attract the 1s↑ electrons and thus a larger 1s↓ density will remain in the core region, resulting in negative total 1s contribution to $\Delta\rho_s(0)$. Conversely, the 2s electrons give a positive contribution since much of the 2s electron density lies outside the 2p. Observation of the LSDA results in Table 1 reveals that the two contributions of opposite sign almost cancel each other, resulting in very small negative values for $\Delta\rho_s(0)$. Inclusion of SIC increases the magnitudes of all contributions in all atoms; however, in the B–F series the magnitude of the 1s spin density is substantially increased relative to 2s, thus resulting in total negative $\Delta\rho_s(0)$ of larger magnitudes. The effect of orthogonalization is not negligible, apparently contrary to the case of heavy atoms [8,9], and increases the magnitudes of the negative $\Delta\rho_s(0)$ further.

In Table 2, the theoretical values of A_{ISO} in MHz, as well as other calculated and experimental values obtained from the literature are given. It is seen that the LSDA gives quite accurate values for H and Li, where no indirect effect of spin polarization by 2p electrons is involved. However, values for the B-F series have opposite signs to the experimental measurements. Inclusion of SIC brings the value for H closer to experiment; however, the value for Li is substantially overestimated, as are the magnitudes of the values for the B-F series, which become even more negative.

The third and fourth rows in Table 2 are results of reported DFT calculations, both employing the same GGA correction, but with different Gaussian basis sets [3]. It is seen that the choice of basis has a significant influence on the calculated A_{ISO}. Since our atomic orbitals are numerical, our results are free of spurious basis set effects. In the fifth row, reported values obtained with a large Gaussian basis and a mixed DFT/Hartree–Fock exchange-correlation functional (B3LYP) [4] are given. Results are fairly good compared to experiment; however, the degree of mixture is empirical and this approach, as mentioned in the Introduction, does not provide any basis for further improvements in basic DF theory. As an example of highly accurate atomic calculations of A_{ISO}, we include in row 7 of Table 2 the reported results obtained with the Coupled-Cluster method (CCSD) [17]. Comparison with experiment is very satisfactory; however, extension to polyatomic and solid-state systems is difficult.

It must be mentioned that experimental results are often obtained for atoms trapped in a matrix, and thus some residual matrix effects may be present.

To understand better the effect of SIC on $\Delta\rho_s(0)$, we have plotted on Fig. 1 (a) and (b) the spin densities of the orbitals 1s, 2s and 2p of nitrogen. We may see that the spin-polarized region of 1s and 2s is very close to the nucleus, and is enhanced strongly by the use of SIC (Fig. 1b). This increase in polarization may be understood by observing the increase of the 2p spin density near the core region, brought forth by SIC.

In conclusion, we have tested the effects of inclusion of LE-SIC in LSDA calculations of the isotopic hyperfine parameter A_{ISO}. We have found that this correction used together with the local exchange-correlation functional VWN increases substantially the spin polarization of the 1s and 2s electrons at the nuclear site. In the case of the B-F series, the increase in the magnitude of the 1s polarization is higher, and thus calculated A_{ISO} values become more negative. Overall, except for H the use of LE-SIC results in calculated values that are further away from experiment, compared to conventional LSDA.

Effect of correlation on $\Delta\rho_s(0)$

The failure of the LSDA to give accurate values of $\Delta\rho_s(0)$ was generally attributed to the local exchange potential, which presumably does not correctly describe the spin polarization of the core (and valence) electrons. However, little attention was given to the effects of the correlation potential on $\Delta\rho_s(0)$, perhaps because V_c and its corresponding energy E_c are typically of the order of 10% of the exchange potential V_x and energy E_x. Parametrization of LSDA correlation functionals is done to fit theoretical data (obtained via Quantum Monte Carlo for the homogeneous electron gas) for the valence-density region of the atoms, which is relevant to correctly describe molecular or metallic bonds, bond lengths and cohesion energies. The very high electron densities present at or near the atomic nucleus are harder to treat due to inadequacies of LDA itself; for example, the results of Ceperley and Alder [12] fitted to obtain the VWN potential are more accurate for low densities [11].

As described in Sect. 3, the LE-SIC corrections tend to increase the electron density in the core region, and thus also $\Delta\rho_s(0)$. As this happens, the correlation among the electrons will increase in this region, and an adequate correlation potential V_c would correctly compensate for this change. However, unfortunately, investigations of the behavior of V_c of LSDA and several GGA approaches for the He atom show large discrepancies, when compared to exact values, especially at the core region [23]. The same is true for Ne [24,25]. The VWN V_c is found to be too attractive (higher negative values) in the core region, as compared to the exact V_c; nevertheless, its behavior near the nucleus of He compares much better with the exact V_c than all the other GGA potentials tested, possibly because in its derivation, a constraint was imposed for approximately correct behavior at high densities [26]. As an indication of the complexity of analysis in this region, we note that the error in exchange, V_x, counterbalances the error in V_c to a certain extent. An extensive discussion of the accuracy of GGA functionals, divergence of the related potentials, and their behavior with respect to various asymptotic forms and boundary conditions is given in Ref. [24].

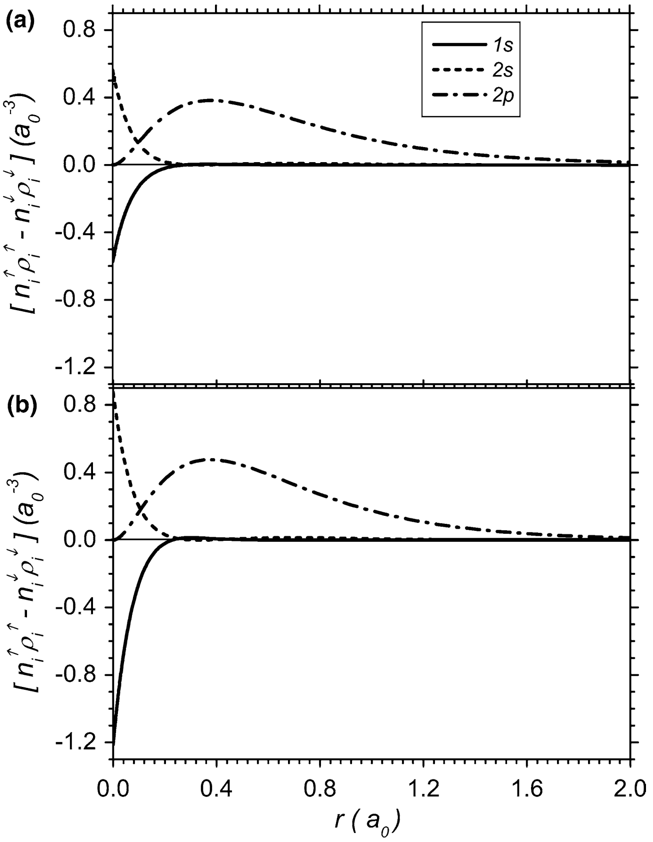

Fig. 1 Spin densities of nitrogen orbitals 1s, 2s and 2p along radial coordinate. **a** LSDA. **b** LSDA+SIC

The principal aim of the LE–SIC approach is to remove the spurious self-interaction effect from the exchange-potential V_x. However, the density $\rho^{\sigma} - \rho_i^{\sigma}$ is also carried over into V_c (Eq. (3)), resulting in some modifications as compared to standard LSDA. Therefore, a consistent formulation of the SI-corrected LSDA theory would have to take into account these changes, perhaps through a re-parametrization of V_c.

Here we make no attempt to propose a new correlation potential; instead, we wish to comment on the effects that changes on V_c might bring to $\Delta\rho_s(0)$. To do this, we have multiplied the V_c potential in the LSDA calculations by a factor:

$$\mathrm{F}V_c = (a - b/r_s)V_c, \qquad (6)$$

where r_s has the usual definition $r_s = [3/(4\pi\rho)]^{1/3}$. We have experimented with several of the popular versions of V_c; for the sake of brevity and clarity, we report here only on results obtained using the VWN parametrization which is fitted to the Gellman–Bruckner asymptotic form at high density [11]. In Eq. (6), the first parameter "a" will scale V_c linearly, and the second term will decrease (for $b > 0$) the magnitude of V_c by an amount proportional to the electron density, vanishing in the low-density region where V_c is believed to be accurate.

In Fig. 2 (a) and (b), we have plotted the effect of F on the LSDA values of $\Delta\rho_s(0)$ for Li and N. It is seen from these figures that if $b = 0$ (solid lines), $\Delta\rho_s(0)$ always increases as V_c is increased. When $a = 1$ (i.e., the first term in Eq. (6) is just V_c), for Li an increase in "b" will decrease $\Delta\rho_s(0)$; however, for N the opposite occurs. The reason for this is that in N the second term in Eq. (6) will be more important for the electrons with higher density (1s) which contribute with negative values to $\Delta\rho_s(0)$ (see Table 1), and thus as "b" increases the total $\Delta\rho_s(0)$ will tend towards positive values. Results for B, C, O and F are analogous to those for N.

As an example of the sizable effect on A_{ISO} induced by modest changes in V_c, we show in row 6 of Table 2 the results obtained for A_{ISO} with LSDA, using the modified correlation potential FV_c, for a given "approximately optimized" pair (a, b) in Eq. (6). It is seen that these changes in the correlation potential may in fact bring the values of the contact parameter much closer to experiment. In particular, the sign of A_{ISO}, which was opposite to the experimental values in the series B-F, is now corrected. The sign of A_{ISO} in general may not be determined in an EPR measurement, or sometimes it may be determined only if certain assumptions are made. For this reason, the experimental values in the last row of Table 2 are given without a sign. However, the theoretical values of A_{ISO} obtained for the B–F series, utilizing several highly-accurate, highly-correlated ab initio methods, are positive for all these atoms. The only exception is ^{17}O, for which a negative A_{ISO} is obtained, but this is merely due to the negative sign of the nuclear factor g_N in Eq. (4) (for a compilation of values of the isotropic hyperfine parameters obtained with different methods, see Ref. [17]). Therefore, one may safely assume, as has been done by other authors, that the signs obtained with these highly precise methods (such as the Coupled-Cluster method, from which results are given in Table 2) are correct. As for H and Li, since only the direct contribution is expected to have a significant value, the sign is positive for obvious reasons.

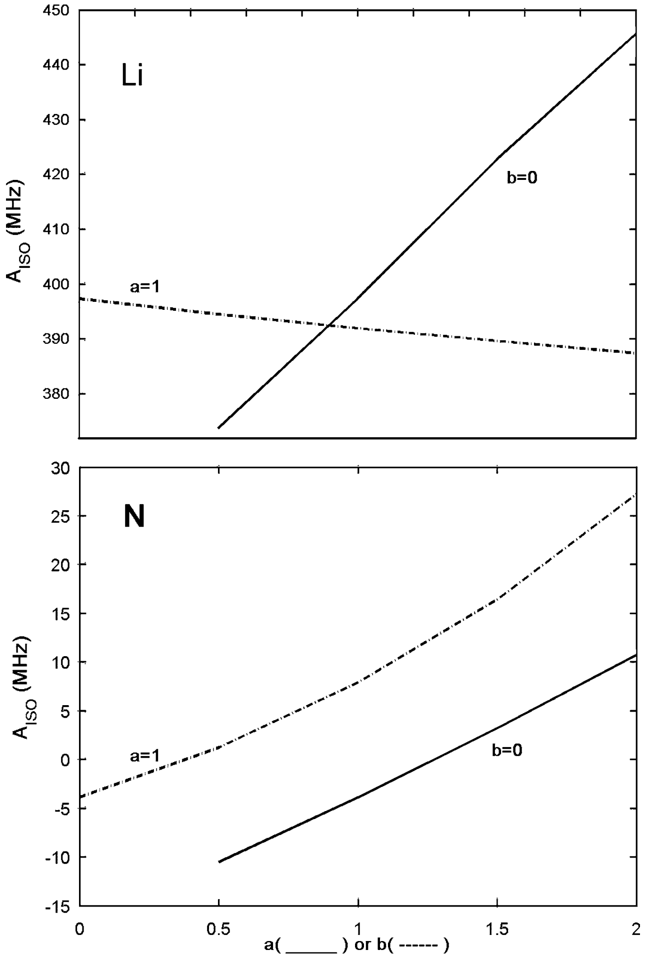

Fig. 2 Values of the isotropic hyperfine parameter A_{ISO} for Li and N, plotted against parameters "a" (or "b") of Eq. (6). Horizontal scale gives values of "a" for $b = 0$ (—), or values of "b" for $a = 1$ (- - - -)

Conclusions

We have carried out numerical LSDA atomic calculations for the light atoms H, Li, B, C, N, O and F, with and without the inclusion of the LE–SIC, to obtain the isotropic hyperfine parameter A_{ISO}. With the exception of H, all A_{ISO} values have their magnitudes increased considerably, such that comparison with experimental values becomes worse than values obtained with LSDA. It is suggested that a poor description of electron correlation in the high density region near the nuclei may play a role, and a simple empirical factor multiplying V_c is employed to illustrate the effect of V_c on $\Delta\rho_s(0)$. The results indicate that further work is needed in obtaining correlation functionals adequate for regions of very high electron densities. In fact, it was shown that for He, Be and Ne the local VWN correlation potential is considerably more negative in the core region than the exact V_c for these atoms [23–25]. Correction for the self-interaction of electrons is a physically well-founded concept – in fact, it was used by Hartree for the Coulomb interaction in his historic self-consistent method for atoms. It is possible that the use of correlation functionals more adequate for the high electron densities in the vicinity of the nuclei will lead to improved DFT results for the isotropic hyperfine parameter. Furthermore, the modified density used in LE-SIC suggests a need for re-parametrization of current V_c formulations. With a simple scaling approach, we demonstrated that modest changes in V_c have an enormous impact in the calculated values of A_{ISO}, capable of bringing them closer to experiment.

Acknowledgements This work was supported in part by the MRSEC program of the National Science Foundation (DMR-0076097) at the Materials Research Center of Northwestern University. The authors benefited from an interesting correspondence with W. E. Pickett and J. Kuneš.

References

1. Abragam A (1961) The principles of nuclear magnetism. Oxford University Press, Oxford
2. Engels B, Eriksson LA, Lunell S (1996) Advances Quant Chem 27:297, and references therein
3. Kong J, Eriksson LA, Boyd RJ (1994) Chem Phys Lett 217:24
4. Barone V (1994) J Chem Phys 101:6834
5. Eriksson LA, Malkina OL, Malkin VG, Salahub DR (1994) J Chem Phys 100:5066
6. Perdew JP, Zunger A (1981) Phys Rev B 23:5048
7. Severin L, Richter M, Steinbeck L (1997) Phys Rev B 55:9211
8. Lundin U, Eriksson O (2001) Int J Quant Chem 81:247
9. Novak P, Kuneš J, Pickett WE, Ku W, Wagner FR (2003) Phys Rev B 67:140403
10. Zeng Z, Guenzburger D, Ellis DE (2004) J Mol Struct THEOCHEM 678:145
11. Vosko SH, Wilk L, Nusair M (1980) Can J Phys 58:1200
12. Ceperley DM (1978) Phys Rev B 18:3126; Ceperley DM, Alder BJ (1981) Phys Rev Lett 45:566
13. Desclaux JP, Freeman AJ, Mallow JV (1977) J Magn Magn Mater 5:265
14. Löwdin P-O (1955) Phys Rev 97:1474; *ibid* 97:1490
15. Weltner W Jr (1989) Magnetic atoms and molecules. Dover, New York, and references therein
16. Perdew JP (1986) Phys Rev 33:8822; *ibid* (1986) 34:7406; Perdew JP, Wang Y (1986) Phys Rev B 33:8800
17. Perera SA, Watts JD, Bartlett RJ (1994) J Chem Phys 100:1425
18. Harvey JSM, Evans L, Lew H (1972) Can J Phys 50:1719
19. Graham WRM, Weltner W Jr. (1976) J Chem Phys 65:1516
20. McDonald JR, Golding RM (1978) Theoret Chim Acta 47:1
21. Holloway WW, Jr., Lüscher E, Novik R (1962) Phys Rev 126:2109
22. Harvey JSM (1965) Proc Roy Soc Lond Ser A 285:581
23. Umrigar CJ, Gonze X (1994) Phys Rev A 50:3827
24. (a) Filippi C, Umrigar CJ, Gonze X (1996) Phys Rev A 54:4810; (b) Filippi C, Gonze X, Umrigar CJ (1996) In: Seminario JM (ed) Recent developments and applications of density functional theory. Elsevier, Amsterdam, p1
25. Grabovski I, Hirata S, Ivanov S, Bartlett RJ (2002) J Chem Phys 116:4415
26. Gell-Mann M, Brueckner KA (1957) Phys Rev 106:364