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Polarizability of molecular chains: A self-interaction correction approach

C. D. Pemmaraju,[1] S. Sanvito,[1] and K. Burke[2]
[1]*School of Physics and CRANN, Trinity College, Dublin 2, Ireland*
[2]*Departments of Chemistry and of Physics, University of California at Irvine, Irvine, California 92697, USA*

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Standard density functional approximations greatly overestimate the static polarizability of long-chain polymers, but Hartree-Fock or exact exchange calculations do not. We show that simple self-interaction corrected approximations afford a viable alternative for accurate polarizability calculations within density functional theory.

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Ground-state Kohn-Sham (KS) density functional theory (DFT) has become extraordinarily popular for solving electronic structure problems in solid-state physics, quantum chemistry, and materials science.[1] The accuracy of modern generalized gradient approximations (GGAs) and hybrid functionals has proven sufficient for many applications, often with surprisingly small errors. Bond dissociation energies, geometries, phonons, etc., are now routinely calculated with errors of 10%–20%.

Local and gradient-corrected functionals overestimate massively the static polarizability and hyperpolarizability of molecular chains, especially conjugated polymers. This failure has been the subject of many studies over the last decade,[2–10] studies which highlight the important role played by the response field originating from the exchange-correlation (XC) potential. The exact induced XC field counteracts the applied external field, keeping the polarization low. In the local (or gradient-corrected) density approximation (LDA), this field erroneously points in the *same* direction as the applied field.[4–6] Such failures of standard functionals appear in other contexts, such as transport through single molecules[11] or the polarizability of large molecules.[3]

In contrast, these effects are easily captured within standard wave-function theory. In particular, Hartree-Fock (HF) theory does not greatly overestimate the polarizabilities and provides a good starting point for more accurate wave-function treatments, such as Møller-Plesset (MP) perturbation theory. Thus exact exchange (EXX) DFT, the KS-DFT method for minimizing the HF energy while retaining a single multiplicative potential, provides a promising alternative and indeed has been found to give results very similar to HF.[5,8,10] This improvement can be attributed to the orbital-dependence of EXX, and the lack of self-interaction error,[8] i.e., EXX is exact for one electron, unlike LDA or GGA.

However, EXX is only one among many possible self-interaction free functionals that one may construct. In fact any GGA can be corrected to become self-interaction free [self-interaction corrected (SIC)] by direct subtraction of the XC functional evaluated on each of the individual orbitals.[12] While this can be performed for either LDA or GGA, only LDA has significantly improved energetics from this procedure, but many investigators are searching for useful methods to correct GGAs for self-interaction.[13] So the question then becomes: does one really need EXX, or will any self-interaction free functional perform equally well?

We perform SIC calculations for the polarizabilities of hydrogenic chains using LDA and GGA. Our SIC potential is constructed using the optimized effective potential (OEP) framework within the Krieger-Li-Iafrate (KLI) approximation.[14] Using results from accurate wave-function methods as a benchmark, we find that the polarizabilities calculated with KLI-SIC are in better agreement than those obtained with KLI exact exchange (X-KLI), with the remaining error attributed to the KLI approximation.[10,15]

We start with a brief description of the SIC method used in this work. In DFT,[16] the total energy functional $E[\rho^{\uparrow},\rho^{\downarrow}]$ (ρ^{σ} is the spin $\sigma=\uparrow,\downarrow$ density, $\rho=\Sigma_{\sigma}\rho^{\sigma}$) can be written as

$$E[\rho^{\uparrow},\rho^{\downarrow}] = T_{\mathrm{S}}[\rho] + \int d^3\mathbf{r}\,\rho(\mathbf{r})v(\mathbf{r}) + U[\rho] + E_{\mathrm{xc}}[\rho^{\uparrow},\rho^{\downarrow}], \tag{1}$$

with T_S the kinetic energy of the noninteracting KS orbitals, $v(\mathbf{r})$ the external potential, U the Hartree energy, and E_{xc} the XC energy. For any GGA

$$E_{\mathrm{xc}}^{\mathrm{SIC}}[\{\rho_n^{\sigma}\}] = E_{\mathrm{xc}}^{\mathrm{GGA}}[\rho^{\uparrow},\rho^{\downarrow}] - \sum_{n\sigma}^{\text{occupied}} \left(U[\rho_n^{\sigma}] + E_{\mathrm{xc}}^{\mathrm{GGA}}[\rho_n^{\sigma},0]\right), \tag{2}$$

where $\rho_n^{\sigma}=|\psi_n^{\sigma}|^2$ is the density of the nth KS orbital. Levy's minimization[17] leads to a set of single particle KS-like equations for ψ_n^{σ} with corresponding eigenvalues $\epsilon_n^{\sigma,\mathrm{SIC}}$ and occupation numbers p_n^{σ} ($\rho^{\sigma}=\Sigma_n p_n^{\sigma}\rho_n^{\sigma}$),

$$\left[-\frac{1}{2}\boldsymbol{\nabla}^2 + v_{\mathrm{eff},n}^{\sigma}(\mathbf{r})\right]\psi_n^{\sigma} = \epsilon_n^{\sigma,\mathrm{SIC}}\psi_n^{\sigma}. \tag{3}$$

The effective potential $v_{\mathrm{eff},n}^{\sigma}(\mathbf{r})$ is now KS-orbital dependent and cannot be classified as a standard multiplicative KS potential. For instance, it is ambiguously defined for unoccupied KS orbitals since the SIC is only defined for the occupied ones. The solution of Eq. (3) has followed several approaches. The simplest one is to solve it directly under a normalization constraint with the resulting nonorthogonal orbitals undergoing an orthogonalization procedure.[12] This scheme, however, is not free of complications, since $E_{\mathrm{xc}}^{\mathrm{SIC}}$ is not invariant under a unitary transformation of the occupied $\{\psi_n^{\sigma}\}$. The solution[18] is then to work with an auxiliary set of localized orbitals $\{\phi_n^{\sigma}\}$ used for constructing $v_{\mathrm{eff},n}^{\sigma}(\mathbf{r})$ and related to $\{\psi_n^{\sigma}\}$ by a unitary transformation chosen so as to minimize $E_{\mathrm{xc}}^{\mathrm{SIC}}$.

A convenient alternative is offered by the OEP method[19] where the orbital-dependent $v^{\sigma}_{\text{eff},n}(\mathbf{r})$ is recast into a local multiplicative orbital-independent potential. In this way the SIC problem can then be solved as a normal KS problem. However the construction of an OEP is computationally demanding. Here we adopt the KLI approximation,[14] which is practically easy to construct and retains most of the advantages of the full OEP, being therefore well-suited to the SIC problem.[20] The orbital-independent KLI effective SIC Kohn-Sham potential takes the form

$$v^{\sigma}_{\text{KS}}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v^{\sigma,\text{GGA}}_{\text{xc}}(\mathbf{r}) + v^{\sigma,\text{SIC}}_{\text{xc}}(\mathbf{r}), \tag{4}$$

where v_{H} and $v^{\sigma,\text{GGA}}_{\text{xc}}$ are the Hartree and GGA-XC potentials. We define the SIC potentials by

$$u^{\sigma,\text{SIC}}_{n}(\mathbf{r}) = -v^{\sigma,\text{GGA}}_{\text{Hxc}}[\tilde{\rho}^{\sigma}_{n},0](\mathbf{r}), \tag{5}$$

where v_{Hxc} is the sum of the Hartree and GGA potentials, and their Slater average as

$$w^{\sigma,\text{SIC}}_{\text{xc}}(\mathbf{r}) = \sum_{n=1}^{N^{\sigma}} \tilde{f}^{\sigma}_{n}(\mathbf{r}) u^{\sigma,\text{SIC}}_{n}(\mathbf{r}), \tag{6}$$

where $\tilde{f}^{\sigma}_{n}(\mathbf{r}) = \tilde{\rho}^{\sigma}_{n}(\mathbf{r})/\rho^{\sigma}(\mathbf{r})$ is the auxiliary orbital density as a fraction of the spin-density of its spin. Then

$$v^{\sigma,\text{SIC}}_{\text{xc}}(\mathbf{r}) = w^{\sigma,\text{SIC}}_{\text{xc}}(\mathbf{r}) + \sum_{n=1}^{N^{\sigma}} \tilde{f}^{\sigma}_{n}(\mathbf{r})[\Delta v^{\sigma,\text{SIC}}_{n} - C^{\sigma}]. \tag{7}$$

The orbital densities $\tilde{\rho}^{\sigma}_{n}$ in Eqs. (5)–(7) are calculated from the auxiliary set of localized orbitals $\{\phi^{\sigma}_{i}\}$ instead of the canonical $\{\psi^{\sigma}_{i}\}$. Both sets of orbitals give the same total density ρ^{σ}. The response terms $\Delta v^{\sigma,\text{SIC}}_{n}$ (being a constant), are obtained by solving

$$\sum_{n=1}^{N^{\sigma}} (\delta_{nm} - \bar{\tilde{f}}^{\sigma}_{nm}) \Delta v^{\sigma,\text{SIC}}_{n} = \bar{w}^{\sigma,\text{SIC}}_{\text{xc},m} - \bar{u}^{\sigma,\text{SIC}}_{m}, \tag{8}$$

where $\bar{h}^{\sigma}_{m} = \int d\mathbf{r} \tilde{\rho}^{\sigma}_{m}(\mathbf{r}) h^{\sigma}(\mathbf{r})$. Furthermore,

$$\sum_{n=1}^{N^{\sigma}} \bar{\tilde{f}}^{\sigma}_{nm} = 1, \quad \sum_{n=1}^{N^{\sigma}} (\bar{w}^{\sigma,\text{SIC}}_{\text{xc},m} - \bar{u}^{\sigma,\text{SIC}}_{m}) = 0, \tag{9}$$

so that the linear system in Eq. (8) is of rank $(N^{\sigma}-1)$ and must be solved using a least-squares approach. The constant C^{σ} is set to $\Delta v^{\sigma,\text{SIC}}_{\text{HOMO}}$ (HOMO is the highest occupied molecular orbital). We have implemented this scheme in the DFT code SIESTA.[21]

To facilitate easy comparison with previous quantum chemistry and EXX-DFT calculations,[10] we chose as a test system the widely studied linear hydrogen chains H_n made up of n H atoms with alternating H-H distances of $2a_0$ and $3a_0$, with a_0 the Bohr radius. An optimized atomic orbital basis set consisting of double zeta polarized s and triple zeta polarized p functions is employed. The Pipek-Mezey localization scheme,[22] which minimizes the number of atoms over which a given molecular orbital is delocalized, is used to transform the canonical KS orbitals $\{\psi^{\sigma}_{n}\}$ into the localized set $\{\phi^{\sigma}_{n}\}$. As an example both the $\{\phi^{\sigma}_{n}\}$ and the $\{\psi^{\sigma}_{n}\}$ of H_6 are presented in Fig. 1. An algorithm based on pairwise Jacobi rotations is found to be convenient to obtain the localized orbitals with minimal computational overheads. However, for larger systems a localization procedure based on conjugate gradients might be necessary to optimize convergence. Finally the static polarizability $\alpha = \delta\mu_z/\delta F_z$ is calculated numerically using finite differences.

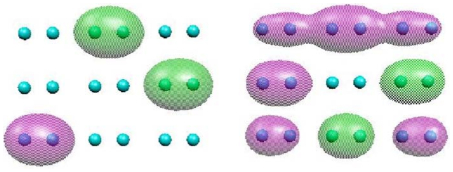

FIG. 1. (Color online) The Pipek-Mezey localized molecular orbitals $\{\phi^{\sigma}_{i}\}$ (left) and canonical Kohn-Sham orbitals $\{\psi^{\sigma}_{i}\}$ (right) for the occupied states of the H_6 molecule.

Before presenting the results for the polarizability, we comment on some interesting qualitative differences in the ground state density of the H chains between LSDA/GGA and KLI-SIC. We find that the semilocal functionals produce only spin-unpolarized ground state densities while KLI-SIC can lead to spin-polarized ground state solutions. In particular, the orbital densities of the auxiliary localized orbitals are seen to exhibit a clear spin-polarized symmetry with the spin components of each molecular orbital being localized over different spatial regions. This becomes more prominent especially as the interatomic distance between the H atoms in the H_2 molecular units is increased. However, in the system geometries considered for the polarizability calculations the spin-polarization of the electron density in KLI-SIC is negligible.

Table I contains the central results of this work. The first column contains highly accurate (MP4) quantum chemical results, which we take as exact. The next two columns show LDA and PBE results,[23] demonstrating the LDA overestimate (by about 100% for H_{12}) of α, an overestimate that is only slightly reduced by GGA. We checked several GGAs, and they all had the same features. Small finite systems, such as atoms, are well-known to overpolarize in LDA and GGA, because their XC potentials are too shallow, and do not decay with the correct asymptotic form, $-1/r$; but this is a distinct effect from that discussed here, which is due to the response to the electric field inside the molecule. Ours is a bulk effect, not depending on the end points. We checked this and found that the LB94 functional,[24] specifically designed to reproduce the correct asymptotic behavior, does not yield any better results than the other GGAs and in fact worsens the LDA α.

The next three columns in Table I list results of different types of calculations using the Fock integral, and no correlation. We note that HF slightly overestimates the polarizability, but by less than 10%. An exact OEP treatment of the same functional (X-OEP) yields essentially the same numbers. Our KLI scheme, applied to the same functional (X-KLI), makes a noticeable overestimate, but the error remains less than 20%, compared to OEP.

Now we focus on the SIC results. Regardless of the GGA functional used, the KLI-SIC polarizabilities show a drastic

TABLE I. Calculated polarizability α of H_n chains obtained by using the KLI-SIC method with different XC functionals. The subscript X indicates that correlation has been dropped from the XC potential. These are compared with MP4, HF, and exact exchange DFT (EXX) results from Ref. 10

	Exact	GGA		EXX			KLI-SIC		Exchange only			
H_N	MP4	LDA	PBE	HF	X-OEP	X-KLI	LDA	PBE	LDA_x	PBE_x	SIC-LDA_x	SIC-PBE_x
H_4	29.5	37.26	35.62	32.0	32.2	33.11	33.38	33.14	38.90	36.51	33.37	33.10
H_6	51.6	73.10	69.35	56.4	56.6	60.64	58.56	58.07	76.16	70.45	58.84	57.63
H_8	75.9	116.58	109.74	82.3	84.2	91.56	86.94	86.48	121.64	110.84	87.08	84.53
H_{10}		166.36	155.31			124.87	117.28	116.16	173.89	156.45	116.77	113.14
H_{12}	126.9	220.55	204.53	137.6	138.1	159.27	147.96	145.98	231.25	205.51	147.19	141.90

improvement with respect to those obtained with pure GGA. Furthermore, PBE results are very close to LDA results. There remains about $a \sim 15\%$ overestimate for H_{12} with respect to MP4, but this is probably due to the KLI approximation and a full OEP treatment of SIC might improve results further.[15]

We also checked if the inclusion of correlation was important for the excellent KLI-SIC results by running the calculations with correlation removed. For the pure functionals, LDA correlation slightly reduces the huge overestimate, whereas PBE correlation has almost no effect. On the other hand, for the KLI-SIC results, LDA correlation has almost no effect, while PBE correlation corrects the PBE_X result in the *wrong* direction. This is consistent with the general result that SIC-GGA includes some incorrect overcounting of gradient effects.[13]

The improved response obtained with orbital dependent functionals is due to the opposing XC field, already demonstrated in the literature for OEP exact exchange.[10] Here we verify that the same happens with the KLI-SIC scheme. In Fig. 2 we plot ΔV_{XC} defined as the difference between the XC potential with and without an applied electric field $\Delta V_{XC}(z) = V_{XC}^{E}(z) - V_{XC}$ for LDA, SIC-LDA, and X-KLI. We denote by a superscript S results obtained by including only the Slater average potential in Eq. (7), dropping the constant terms. Clearly both contributions are significant in the final XC potential. The Slater-only polarizabilities are shown in Table II and reflect this.

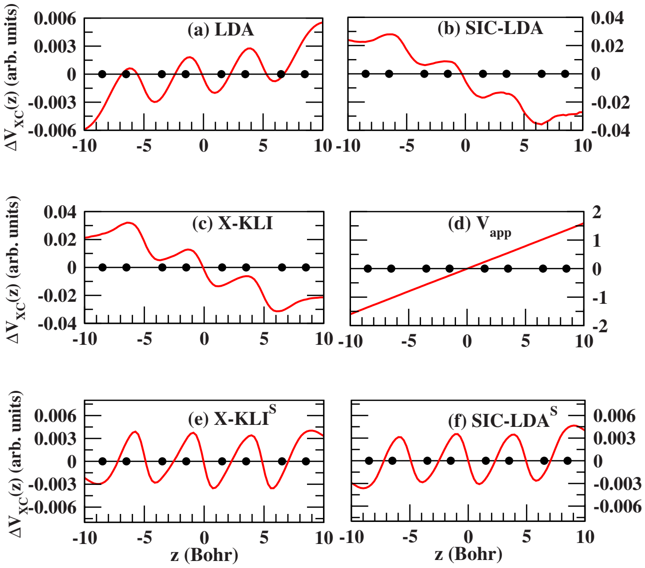

FIG. 2. (Color online) $\Delta V_{XC}(z) = V_{XC}^{E}(z) - V_{XC}$ for H_8 plotted against position (z) for (a) LDA, (b) SIC-LDA, (c) X-KLI, (e) X-KLI^S, and (f) SIC-LDA^S. The applied external field is shown in (d) and the black dots indicate the position of the H atoms.

By comparing the values of α in Tables I and II one may conclude that the Slater average already contains important corrections, but the bulk of the effect is contained in the response term. For example, if one considers the α calculated with LDA for H_{12} the polarizability is 220.5 for LDA, 193.9 for SIC-LDA^S, and 147.9 for SIC-LDA. It is also interesting to note that even at the level of the Slater average, SIC performs better than X-KLI. This can be understood by looking at the XC potential for SIC-PBE^S and X-KLI^S (Fig. 3) when no external field is applied. The SIC-PBE potential exhibits higher peaks in the intermolecular space between H_2 units than X-KLI. This explains the quantitative difference in α between the two cases. The improved performance of X-OEP over X-KLI can be attributed[10] to similar barriers in the intermolecular region which, however, arise from the response part of the X-OEP potential.

Finally we ask whether similar results can be obtained with atomiclike corrections, which have the effect of making the KS potential deeper at the atomic sites. We investigated both the LDA+U[25] and the atomic LDA-SIC (ASIC) methods[26,27] in this regard. The LDA+U results are extremely poor, as they provide polarizabilities larger than even those obtained with simple LDA. The ASIC results are far

TABLE II. Static polarizability α of H_n obtained from SIC and X-KLI where only the Slater term in the KLI potential is used (superscript S). Both XC and X-only results are shown for the SIC-LDA^S and SIC-PBE^S.

H_N	SIC-LDA^S	SIC-PBE^S	SIC-LDA$_X^S$	SIC-PBE$_X^S$	X-KLI^S
H_4	35.37	35.12	36.25	35.16	35.78
H_6	67.74	67.13	68.92	66.34	69.17
H_8	105.91	104.89	107.57	102.97	108.72
H_{10}	148.64	146.18	150.86	143.10	152.90
H_{12}	193.94	190.47	197.05	185.25	199.91

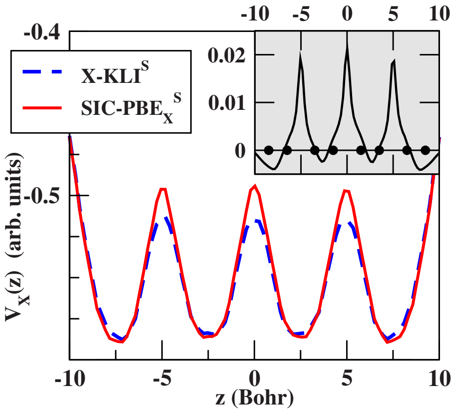

FIG. 3. (Color online) XC potential plotted against distance (z) for SIC-PBE^S (solid line) and X-KLI^S. The gray inset plots the difference between the two potentials.

more promising, being half-way between those of GGA and of SIC (α=33.95, 63.67, 98.39, 137.42, and 178.87 for H_n, respectively, with n=4, 6, 8, 10, and 12). In fact, if the ASIC corrections relative to pure LDA were double those we found, they would reproduce the HF results very accurately. The above can be understood by the way the atomic corrections are introduced. The H atoms are half-filled in the absence of an external field. Switching on the field produces a tiny charge transfer, which, however, is amplified by the LDA+U potential. As a result the already wrong LDA response field gets amplified. The same does not happen with ASIC, which improves the response over LDA by virtue of the higher intermolecular barriers.

Before we conclude, a few comments on the computational efficiency of the KLI-SIC approach are pertinent. In principle, the numerical cost in constructing the SIC potential scales only linearly with the number of occupied molecular orbitals as opposed to the quadratic scaling in EXX. However, KLI-SIC invloves a further localization step including a unitary transformation of the occupied set of orbitals which introduces additional numerical overheads. For the systems considered in this work, the computational effort involved in the Pipek-Mezey localization scheme was found to be negligible in comparison to the rate determining step which is the evaluation of the individual orbital self-Hartree potentials. Thus the KLI-SIC calculations were considerably less expensive compared to the X-KLI calculations especially for the longer hydrogen chains. In general, however, for systems that exhibit a complex molecular orbital structure, the overheads associated with the localization can be nontrivial and the relative efficiency of KLI-SIC and X-KLI is expected to be somewhat system dependent.

In conclusion, we have investigated the performance of explicitly self-interaction corrected DFT functionals in estimating the polarizabilities of molecular chains. We find that SIC functionals do exhibit a field counteracting term in the response part of the XC potential as a result of which the calculated polarizability is much improved in comparison to normal LDA/GGA. Furthermore, at the KLI level of approximation, the SIC functionals are also seen to perform better than KLI exact exchange at computing the static polarizability of hydrogenic chains. This difference is attributed to the presence of higher intermolecular barriers in the Slater term of the KLI-SIC potential.

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[1] *A Primer in Density Functional Theory*, edited by C. Fiolhais, F. Nogueira, and M. Marques (Springer-Verlag, New York, 2003).
[2] B. Champagne *et al.*, J. Chem. Phys. **109**, 10489 (1998).
[3] B. Champagne *et al.*, J. Phys. Chem. A **104**, 4755 (2000).
[4] S. J. A. van Gisbergen, P. R. T. Schipper, O. V. Gritsenko, E. J. Baerends, J. G. Snijders, B. Champagne, and B. Kirtman, Phys. Rev. Lett. **83**, 694 (1999).
[5] O. V. Gritsenko and E. J. Baerends, Phys. Rev. A **64**, 042506 (2001).
[6] M. Grüning, O. V. Gritsenko, and E. J. Baerends, J. Chem. Phys. **116**, 6435 (2002).
[7] H. Iikura, T. Tsuneda, T. Yanai and K. Hirao, J. Chem. Phys. **115**, 3540 (2001).
[8] P. Mori-Sanchez, Q. Wu, and W. Yang, J. Chem. Phys. **119**, 11001 (2003).
[9] S. Kümmel, J. Comput. Phys. **201**, 333 (2004).
[10] S. Kümmel, L. Kronik, and J. P. Perdew, Phys. Rev. Lett. **93**, 213002 (2004).
[11] C. Toher, A. Filippetti, S. Sanvito, and K. Burke, Phys. Rev. Lett. **95**, 146402 (2005); C. Toher and S. Sanvito, *ibid.* **99**, 056801 (2007).
[12] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[13] O. A. Vydrov, G. E. Scuseria, J. P. Perdew, A. Ruzsinszky, and G. I. Csonka, J. Chem. Phys. **124**, 094108 (2006).
[14] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **45**, 101 (1992).
[15] See T. Korzdorfer *et al.*, arXiv:0708.2870v1 (unpublished).
[16] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[17] M. Levy, Phys. Rev. A **26**, 1200 (1982).
[18] R. A. Heaton and C. C. Lin, J. Phys. B **16**, 2079 (1983); M. R. Pederson, R. A. Heaton, and C. C. Lin, J. Chem. Phys. **80**, 1972 (1984).
[19] S. Kummel and J. P. Perdew, Phys. Rev. B **68**, 035103 (2003).
[20] J. Garza, J. A. Nichols, and D. A. Dixon, J. Chem. Phys. **112**, 7880 (2000).
[21] J. M. Soler *et al.*, J. Phys.: Condens. Matter **14**, 2745 (2002).
[22] J. Pipek and P. G. Mezey, J. Chem. Phys. **90**, 4916 (1989).
[23] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[24] R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).
[25] M. Wierzbowska, D. Sánchez-Portal, and S. Sanvito, Phys. Rev. B **70**, 235209 (2004).
[26] A. Filippetti and N. A. Spaldin, Phys. Rev. B **67**, 125109 (2003).
[27] C. D. Pemmaraju, T. Archer, D. Sanchez-Portal, and S. Sanvito, Phys. Rev. B **75**, 045101 (2007).