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Scaling down the Perdew-Zunger self-interaction correction in many-electron regions

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Semilocal density functional approximations (DFAs) for the exchange-correlation energy suffer from self-interaction error, which is believed to be the cause of many of the failures of common DFAs, such as poor description of charge transfer and transition states of chemical reactions. The standard self-interaction correction (SIC) of Perdew and Zunger mends some of these failures but spoils such essential properties as thermochemistry and equilibrium bond lengths. The Perdew-Zunger SIC seems to overcorrect many-electron systems. In this paper, we propose a modified SIC, which is scaled down in many-electron regions. The new SIC has an improved performance for many molecular properties, including total energies, atomization energies, barrier heights of chemical reactions, ionization potentials, electron affinities, and bond lengths. The local spin-density approximation (LSDA) benefits from SIC more than higher-level functionals do. The scaled-down SIC has only one adjustable parameter. Rationalization of the optimal value of this parameter enables us to construct an almost-nonempirical version of the scaled-down SIC-LSDA, which is significantly better than uncorrected LSDA and even better than the uncorrected generalized gradient approximation. We present an analysis of the formal properties of the scaled-down SIC and define possible directions for further improvements. In particular, we find that exactness for all one-electron densities does not guarantee correct asymptotics for the exchange-correlation potential of a many-electron system. © *2006 American Institute of Physics*.
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I. INTRODUCTION

Practical applications of density functional theory (DFT) are typically performed within the Kohn-Sham framework,[1] which relies on approximations to the exchange-correlation (xc) energy $E_{xc}[\rho_\alpha,\rho_\beta]$. These approximations are assigned to various rungs of "Jacob's ladder,"[2] according to the number and kind of their ingredients. The lowest rung is the local spin-density approximation (LSDA), the second rung is the generalized gradient approximation (GGA), the third one is meta-GGA, and so on. The first three rungs, collectively known as semilocal approximations, are particularly popular due to their very favorable accuracy-to-computational cost ratio. For that reason, DFT is the method of choice to study relatively large systems, where wave function methods are unaffordable. As strange as it may sound, semilocal functionals are often more accurate for large many-electron systems than for systems with just one or a few electrons. A notorious example is the dissociation curve of the simplest one-electron molecule H_2^+, for which common functionals predict unphysical results.[3] This is one of the manifestations of a serious flaw in approximate xc functionals, known as self-interaction error (SIE). SIE arises when one (or both) of the following requirements are violated: for any one-electron density $\rho_i(\mathbf{r})$, an exchange functional E_x must obey

$$E_x[\rho_i,0]+J[\rho_i]=0, \tag{1}$$

and a correlation functional E_c must obey

$$E_c[\rho_i,0]=0. \tag{2}$$

$J[\rho]$ in Eq. (1) is the Coulomb interaction of an electron density with itself,

$$J[\rho]=\frac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \tag{3}$$

Because Eq. (3) is a fully nonlocal functional of the density, the requirement of Eq. (1) cannot be exactly satisfied on the first three rungs of the Jacob's ladder. The requirement of Eq. (2) can only be satisfied on the third or higher rungs.

If the SIE arose only in one-electron systems, it would be easy to correct: one can explicitly evaluate the spurious self-interaction terms and remove them. But the problem manifests itself in many-electron systems as well. Unfortunately, the SIE of a particular density functional approxima-

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tion (DFA) is much more difficult to quantify in a many-electron system. There is no unique definition of the SIE and no unique way to correct it.

In 1981, Perdew and Zunger[4] (PZ) proposed to use densities of occupied orbitals $\rho_{i\sigma}(\mathbf{r})=|\phi_{i\sigma}(\mathbf{r})|^2$ to define a self-interaction correction (SIC) for any density functional approximation:

$$E_{\mathrm{xc}}^{\mathrm{SIC\text{-}DFA}}=E_{\mathrm{xc}}^{\mathrm{DFA}}[\rho_\alpha,\rho_\beta]-\sum_{i\sigma}^{\mathrm{occ}}\left(J[\rho_{i\sigma}]+E_{\mathrm{xc}}^{\mathrm{DFA}}[\rho_{i\sigma},0]\right). \quad (4)$$

Although the PZ correction looks very simple, it is nontrivial to implement and apply, since Eq. (4) is not invariant under a unitary transformation of occupied orbitals. Orbitals minimizing the PZ self-interaction corrected energy are usually localized in shape. Reliable self-consistent implementations of the PZ-SIC for molecules have become available only recently, which made it possible to carry out systematic studies of its performance.[5–10] It was found that the Perdew-Zunger SIC improves the description of transition states of chemical reactions[6] and dissociation curves of odd-electron systems,[7,8] but it fails badly on some basic thermochemical tests[9,10] and predicts too short bonds in molecules.[5,11] Overall, PZ-SIC often seems to overcorrect many-electron systems.[9,10,12] Notwithstanding this, the work of Perdew and Zunger[4] remains a major landmark in the development of the density functional formalism. It was one of the sources of the later discovery[13] of the derivative discontinuity of the exact exchange-correlation functional.

Recently, it was observed[12] that scaling down the self-interaction correction of Eq. (4) by a factor of 0.4 improves the thermochemistry, although such a scaled SIC loses the property of being exact for any one-electron density. This problem is avoided in a more recent proposal[2] to scale down the SIC only in many-electron systems. Moreover, this alternative SIC is invariant under unitary transformations of orbitals. However, this nice feature comes at the price of a great increase in computational demand.

In this paper, we introduce a simple method to scale down the SIC in many-electron regions without a major increase in complexity or cost over the Perdew-Zunger SIC. We show that such a scaling improves many important properties of molecular systems.

II. METHODOLOGY

Aiming to scale down the Perdew-Zunger SIC in many-electron regions, we propose a dimensionless scaling factor evaluated for each orbital density $\rho_{i\sigma}(\mathbf{r})$:

$$X_{i\sigma}^{k}=\int\left(\frac{\tau_\sigma^W}{\tau_\sigma}\right)^k\rho_{i\sigma}(\mathbf{r})d\mathbf{r}, \quad (5)$$

where τ_σ is the noninteracting kinetic energy density of σ-spin electrons,

$$\tau_\sigma(\mathbf{r})=\frac{1}{2}\sum_i|\nabla\phi_{i\sigma}(\mathbf{r})|^2, \quad (6)$$

τ_σ^W is the von Weizsäcker kinetic energy density,

$$\tau_\sigma^W(\mathbf{r})=\frac{|\nabla\rho_\sigma(\mathbf{r})|^2}{8\rho_\sigma(\mathbf{r})}, \quad (7)$$

and k is a non-negative real number. τ_σ^W and τ_σ in Eq. (5) are evaluated at the total spin density ρ_σ

$$\rho_\sigma(\mathbf{r})=\sum_{i=1}^{N_\sigma}\rho_{i\sigma}(\mathbf{r}). \quad (8)$$

It is known that $\tau_\sigma(\mathbf{r})=\tau_\sigma^W(\mathbf{r})$ in regions containing only one electron of spin σ (or more generally containing only orbitals of spin σ with the same shape), and that $\tau_\sigma(\mathbf{r})\geqslant\tau_\sigma^W(\mathbf{r})$ otherwise. For a uniform density, $\tau_\sigma^W(\mathbf{r})=0$. The ratio $\tau_\sigma^W/\tau_\sigma$ is customarily used in construction of self-correlation-free [i.e., obeying Eq. (2)] meta-GGA functionals.[14,15] This ratio was also recently used as a mixing function in a local hybrid,[16] with intent to eliminate the self-interaction error in the exchange component. The scaling factor of Eq. (5) satisfies

$$0\leqslant X_{i\sigma}^k\leqslant 1. \quad (9)$$

The scaled-down self-interaction correction is defined as

$$E_{\mathrm{xc}}^{\mathrm{SIC\text{-}DFA}}=E_{\mathrm{xc}}^{\mathrm{DFA}}+E^{\mathrm{SIC}}, \quad (10)$$

$$E^{\mathrm{SIC}}=-\sum_{i\sigma}^{\mathrm{occ}}X_{i\sigma}^k\left(J[\rho_{i\sigma}]+E_{\mathrm{xc}}^{\mathrm{DFA}}[\rho_{i\sigma},0]\right). \quad (11)$$

The derivatives of Eq. (11) with respect to orbital variations can be easily obtained analytically, as shown in the Appendix. The self-consistent implementation of the new correction is straightforward and requires only minor changes in the previously developed PZ-SIC code.[9] The Perdew-Zunger SIC can be considered a special case of Eq. (11) with $k=0$. The SIC of Eq. (11) properly vanishes when $E_{\mathrm{xc}}^{\mathrm{DFA}}$ is replaced by the exact xc functional for any $k\geqslant 0$.

The scaling factor X_i^k with $k>0$ ensures that the correction vanishes for a uniform density, independent of the type of orbitals used. All the xc functionals we test in this work are exact in the uniform density limit, so that no correction is needed. In the limit of $k\to\infty$, X_i^k will become zero for any system other than a one-electron or a spin-compensated two-electron system.

$\tau_\sigma^W/\tau_\sigma$ was first proposed as a scaling factor for the self-interaction correction in Eq. (22) of Ref. 2, and our Eq. (11) was intended as a computationally practical test of the principle for that approach. We note that Eq. (5) is not the only possible choice of a scaling factor. An even simpler version[17] can be constructed by using $\rho_{i\sigma}/\rho_\sigma$ instead of $\tau_\sigma^W/\tau_\sigma$ in Eq. (5). This alternative choice, however, is not guaranteed to vanish in the uniform density limit.

III. COMPUTATIONAL DETAILS

All calculations were carried out with a developmental version of the GAUSSIAN program.[18] We tested several xc functionals, including LSDA in the Perdew-Wang 92 parameterization;[19] the GGA of Perdew, Burke, and Ernzerhof (PBE);[20] the meta-GGA functional of Tao, Perdew, Staroverov and Scuseria (TPSS);[15] and a hybrid of PBE with 25% of exact exchange (PBEh, also known as PBE0 or

TABLE I. Values of the X_i^k factor for different shells in the Ar atom. The 6-311+G(3*df*) basis set was used.

Functional	Shell 1	Shell 2	Shell 3
SIC-LSDA (k=1)	0.6749	0.4428	0.5278
SIC-PBE (k=1)	0.6738	0.4433	0.5266
SIC-TPSS (k=1)	0.6707	0.4434	0.5274
SIC-LSDA (k=2)	0.5137	0.2377	0.3502
SIC-PBE (k=2)	0.5112	0.2378	0.3494
SIC-TPSS (k=2)	0.5078	0.2381	0.3504

PBE1PBE).[21–23] All these functionals are nonempirical in the sense that they have no parameter fitted to data sets. TPSS correlation is already self-interaction-free, so only its exchange term is changed by Eq. (11). All calculations used a (99 590) unpruned integration grid. The 6-311+G(3*df*,2*p*) basis set is used in all tests, except atomic ionization potentials (IPs) and electron affinities (EAs), where the 6-311++G(*d*) basis set is used. All calculations on open shells are spin unrestricted. No spherical averaging of atomic orbital densities is used in the present work. Deviations are defined as "*theory-experiment*" and reported as mean errors (MEs), mean absolute errors (MAEs), and root mean square errors (RMSEs).

IV. RESULTS

A. Magnitudes of the correction

The scaling factor X_i^k does not explicitly include any dependence on the xc functional. Since SIC-minimizing orbitals look similar for different functionals, the X_i^k factor for corresponding orbitals will assume similar values. Table I shows values of X_i^k obtained in self-consistent calculations on the Ar atom using three different xc functionals, with $k=1$ and $k=2$. The dependence of the magnitude of E^{SIC} on the value of the parameter k is shown in Table II for the Ar atom and the LSDA functional. It is clearly seen that the magnitude of the correction is steadily scaled down as k increases.

B. Total energies of atoms

The nonrelativistic total energies of all the atoms up to Ar are known accurately.[24] For all the theoretical methods under investigation, we computed the errors in the total energies of 16 atoms from Li to Ar. The error for each atom was divided by the number of electrons N and averaged among the atoms in the set. After this division by N, the absolute error can still grow with N, but more slowly than before. The statistics thus obtained are presented in Table III. The individual values of total energies are given in Ref. 25 To estimate the effect of incompleteness of the 6-311+G(3*df*) basis set, we calculated total energies of several atoms with a much larger aug-cc-pVQZ basis set. We found that, for all theoretical methods studied, the increase of basis set size results in energy lowering of less than 0.002 hartree/electron, which will not dramatically change the qualitative trends observed in Table III.

TABLE II. Contributions to E^{SIC} from different shells in the Ar atom, computed with the SIC-LSDA functional and different values of k. The 6-311+G(3*df*) basis set was used. All values are in hartrees.

	Shell 1[a]	Shell 2[b]	Shell 3[b]	Total
k=0	−1.4878	−1.0131	−0.1221	−2.6231
k=1/2	−1.1926	−0.6491	−0.0817	−1.9234
k=1	−1.0016	−0.4450	−0.0612	−1.5078
k=2	−0.7626	−0.2370	−0.0402	−1.0398
k=3	−0.6127	−0.1383	−0.0292	−0.7801

[a] First shell (1*s*) includes two electrons.

[b] Second and third shells each include eight electrons in equivalent sp^3-hybrid orbitals.

TABLE III. Errors per electron in total energies of the atoms from Li to Ar computed with the 6-311+G(3*df*) basis set. All values are in hartrees.

Functional	ME	MAE	RMSE
LSDA	0.073	0.073	0.074
SIC-LSDA (k=0)	−0.033	0.033	0.037
SIC-LSDA (k=1/2)	−0.014	0.014	0.014
SIC-LSDA (k=1)	−0.001	0.004	0.005
SIC-LSDA (k=2)	0.014	0.015	0.018
SIC-LSDA (k=3)	0.022	0.023	0.028
PBE	0.009	0.009	0.009
SIC-PBE (k=0)	0.014	0.014	0.016
SIC-PBE (k=1/2)	0.011	0.011	0.012
SIC-PBE (k=1)	0.010	0.010	0.010
SIC-PBE (k=2)	0.008	0.008	0.008
SIC-PBE (k=3)	0.007	0.007	0.007
TPSS	−0.002	0.002	0.002
SIC-TPSS (k=0)	0.021	0.021	0.025
SIC-TPSS (k=1/2)	0.014	0.014	0.016
SIC-TPSS (k=1)	0.010	0.010	0.012
SIC-TPSS (k=2)	0.005	0.006	0.006
SIC-TPSS (k=3)	0.003	0.003	0.004
PBEh	0.008	0.008	0.008
SIC-PBEh (k=0)	0.013	0.013	0.014
SIC-PBEh (k=1/2)	0.011	0.011	0.012
SIC-PBEh (k=1)	0.009	0.009	0.009
SIC-PBEh (k=2)	0.007	0.007	0.008
SIC-PBEh (k=3)	0.007	0.007	0.007

It is clear that scaling down the SIC reduces the errors in total energies as compared to the original Perdew-Zunger SIC (k=0). The most remarkable improvement is observed in the case of LSDA. The uncorrected LSDA functional predicts total energies that are too high, and the deviation (*calculated-exact*) increases with the atomic number. On the other hand, SIC-LSDA (k=0) energies are too low with an increasingly negative deviation. With the scaled-down SIC, total energies fall in between LSDA and SIC-LSDA (k=0), and thus much closer to the accurate values. Figure A of Ref. 25 illustrates the errors in total energies for SIC-LSDA functionals with different k. The lowest MAE corresponds to SIC-LSDA (k=1), but the errors of SIC-LSDA (k=1/2) are more systematic: its error per electron is almost constant. However, these particularly good atomic energies do not lead

TABLE IV. Errors in atomization energies for the AE6 test set set computed with the 6-311+G($3df,2p$) basis set. All values are in kcal/mol.

Functional	ME	MAE	RMSE
LSDA	77.3	77.3	92.2
SIC-LSDA ($k=0$)	57.7	60.3	79.4
SIC-LSDA ($k=1/2$)	31.3	34.0	42.9
SIC-LSDA ($k=1$)	18.6	21.0	25.1
SIC-LSDA ($k=2$)	6.7	8.6	10.0
SIC-LSDA ($k=3$)	0.8	7.2	8.7
PBE	12.4	15.5	17.8
SIC-PBE ($k=0$)	−13.6	17.0	21.7
SIC-PBE ($k=1/2$)	0.7	8.6	12.4
SIC-PBE ($k=1$)	7.8	12.6	14.7
SIC-PBE ($k=2$)	13.5	16.0	19.3
SIC-PBE ($k=3$)	14.8	17.2	20.6
TPSS	4.1	5.9	6.6
SIC-TPSS ($k=0$)	−28.8	34.7	39.2
SIC-TPSS ($k=1/2$)	−8.6	15.0	17.5
SIC-TPSS ($k=1$)	1.3	9.9	10.6
SIC-TPSS ($k=2$)	9.4	11.3	12.4
SIC-TPSS ($k=3$)	11.9	12.4	14.1
PBEh	0.6	6.2	6.6
SIC-PBEh ($k=0$)	−19.2	19.8	25.6
SIC-PBEh ($k=1/2$)	−6.1	10.7	13.8
SIC-PBEh ($k=1$)	0.2	8.1	11.2
SIC-PBEh ($k=2$)	5.1	10.3	11.9
SIC-PBEh ($k=3$)	6.3	10.9	12.1

to the best atomization energies, as we show in the next section.

C. Atomization energies

A benchmark set of molecular atomization energies or enthalpies of formation is one of the standard tests habitually applied to a newly developed density functional. To assess the thermochemical performance of the new SIC scheme, we computed atomization energies for the AE6 set developed by Lynch and Truhlar.[26] This set includes only six molecules [SiH_4, S_2, SiO, C_3H_4 (propyne), $C_2H_2O_2$ (glyoxal), and C_4H_8 (cyclobutane)], but it is quite diverse and was constructed to be representative, that is, to reproduce errors in much larger sets. We used QCISD/MG3 molecular geometries suggested by the authors of the set.[26,27] The deviations of the theoretical methods from the best estimates of atomization energies are summarized in Table IV. The deviations for individual molecules can be found in Ref. 25.

Note that an error in an atomization energy is equal to the negative of the error in the enthalpy of formation for the same molecule. Thus, MEs reported in Table IV for the PZ-SIC ($k=0$) have opposite signs to the ones reported in Ref. 9 for enthalpies of formation.

As compared to the Perdew-Zunger SIC ($k=0$), the corrections with $k>0$ provide much better thermochemical performance. The improvement is particularly noticeable in the case of LSDA. The optimal value of the parameter k happens to be around 1/2 for PBE. TPSS and PBEh seem to require $k=1$, whereas LSDA needs higher values of k, such as $k=2$ or $k=3$.

The strong LSDA overbinding of molecules (Table IV) arises largely because the self-interaction error of LSDA raises the energies of the separated atoms more than it raises the energy of the molecule. Reducing this error in the atoms (as in Table III, or in the more empirical approach of Ref. 28) strongly reduces the LSDA error of the atomization energy of the molecule. However, as mentioned in the previous section, the best total energies for the atoms arise when $k\sim 1$, while the best SIC atomization energies arise when $k\sim 2$ or 3.

D. Barrier heights of chemical reactions

Barrier heights of chemical reactions are seriously underestimated by semilocal functionals. In fact, barrier heights are often predicted to be negative, erroneously suggesting that the transition state is more stable than either reactants or products. Self-interaction error is often taken to be responsible for this fault. Hybrid functionals specifically designed for thermochemical kinetics usually contain a large fraction of exact exchange,[29,30] which reduces the SIE. Although the Perdew-Zunger SIC does improve barrier heights,[6] it cannot compete with specialized hybrids.

To assess the performance of the new SIC, we computed barrier heights for the BH6 benchmark set,[26] which consists of the forward and reverse barriers for three reactions: $OH+CH_4\rightarrow CH_3+H_2O$, $H+OH\rightarrow H_2+O$, and $H+H_2S\rightarrow H_2+HS$. Like the AE6 set, this small data set was optimized to be representative. Geometries of all species as well as the best estimates of barrier heights were taken from Refs. 26 and 27. The summary of deviations is given in Table V and the detailed tables can be found in Ref. 25.

Table V shows that the scaled-down SIC performs better than the PZ-SIC, if $k=1/2$ or $k=1$ is chosen. For all self-interaction corrected methods, the largest error corresponds to the reverse barrier of the first reaction. That is not surprising since this reaction has the CH_3 radical as one of the products. We used the planar geometry for CH_3, optimized in a high-level quantum chemistry method. However PZ-SIC erroneously predicts CH_3 to be pyramidal.[7] Scaling the SIC down alleviates but does not completely solve this problem. The SIC also produces an unwanted large correction to the reaction energy of the first reaction. Besides the aforementioned inconsistency in the CH_3 geometry, another contribution to this problem appears to come from the difference in shapes of localized orbitals between OH and H_2O, resulting in considerably different magnitudes of E^{SIC} for the reactants and products.

E. Ionization potentials and electron affinities

We have recently tested[10] the Perdew-Zunger SIC for atomic and molecular IPs and EAs. For IPs and EAs evaluated as differences in total energies (the ΔSCF method), we found that PZ-SIC provides a little improvement for LSDA, whereas the performance of beyond-LSDA functionals is deteriorated by the PZ-SIC.

TABLE V. Errors in barrier heights for the BH6 test set computed with the 6-311+G($3df,2p$) basis set. All values are in kcal/mol.

Functional	ME	MAE	RMSE
LSDA	−17.9	17.9	18.8
SIC-LSDA ($k=0$)	−5.2	5.2	6.6
SIC-LSDA ($k=1/2$)	−3.8	3.8	5.0
SIC-LSDA ($k=1$)	−3.2	3.5	4.7
SIC-LSDA ($k=2$)	−2.8	4.7	5.4
SIC-LSDA ($k=3$)	−2.9	5.7	6.3
PBE	−9.5	9.5	10.0
SIC-PBE ($k=0$)	−0.1	4.2	5.4
SIC-PBE ($k=1/2$)	−2.5	2.9	4.9
SIC-PBE ($k=1$)	−4.2	4.3	5.8
SIC-PBE ($k=2$)	−6.5	6.5	7.7
SIC-PBE ($k=3$)	−7.7	7.7	8.9
TPSS	−8.5	8.5	8.8
SIC-TPSS ($k=0$)	−0.2	5.7	6.5
SIC-TPSS ($k=1/2$)	−2.8	4.4	5.5
SIC-TPSS ($k=1$)	−4.6	5.0	6.0
SIC-TPSS ($k=2$)	−6.8	6.8	7.6
SIC-TPSS ($k=3$)	−7.9	7.9	8.5
PBEh	−4.8	4.8	5.0
SIC-PBEh ($k=0$)	1.3	4.1	4.8
SIC-PBEh ($k=1/2$)	−0.6	2.9	3.6
SIC-PBEh ($k=1$)	−2.0	2.4	3.7
SIC-PBEh ($k=2$)	−3.6	3.7	4.7
SIC-PBEh ($k=3$)	−4.5	4.5	5.3

TABLE VI. Deviations from experiment of ΔSCF ionization potentials and electron affinities for atoms from H to Ar computed with the 6-311++G(d) basis set. All values are in eV.

	18 IPs		12 EAs	
Functional	ME	MAE	ME	MAE
LSDA	0.17	0.30	0.29	0.29
SIC-LSDA ($k=0$)	0.21	0.24	−0.15	0.18
SIC-LSDA ($k=1$)	0.07	0.15	−0.08	0.11
SIC-LSDA ($k=2$)	0.00	0.13	−0.05	0.09
SIC-LSDA ($k=3$)	−0.04	0.14	−0.03	0.10
PBE	0.10	0.15	0.09	0.13
SIC-PBE ($k=0$)	−0.34	0.39	−0.57	0.57
SIC-PBE ($k=1$)	−0.14	0.22	−0.29	0.29
SIC-PBE ($k=2$)	−0.06	0.15	−0.15	0.15
SIC-PBE ($k=3$)	−0.01	0.12	−0.07	0.10
TPSS	0.08	0.12	0.03	0.05
SIC-TPSS ($k=0$)	−0.28	0.34	−0.45	0.47
SIC-TPSS ($k=1$)	−0.08	0.17	−0.22	0.24
SIC-TPSS ($k=2$)	0.00	0.12	−0.10	0.12
SIC-TPSS ($k=3$)	0.05	0.11	−0.03	0.08
PBEh	0.06	0.12	−0.02	0.09
SIC-PBEh ($k=0$)	−0.30	0.33	−0.53	0.53
SIC-PBEh ($k=1$)	−0.14	0.19	−0.31	0.31
SIC-PBEh ($k=2$)	−0.07	0.14	−0.20	0.20
SIC-PBEh ($k=3$)	−0.03	0.12	−0.13	0.15

We have tested the performance of the scaled-down SIC for IPs and EAs of atoms up to argon. The deviations of theoretical predictions from the experimental data[31] are summarized in Table VI and given in detail in Ref. 25.

We can clearly see that SIC with $k>0$ performs better than the Perdew-Zunger SIC ($k=0$) in all cases. The optimal values of k for IPs and EAs seem to be around $k=2,\ldots,3$, which is often higher than the optimal values for atomization energies or barrier heights. The EA of the boron atom is negative in Perdew-Zunger-corrected PBE, TPSS, and PBEh. But it becomes correctly positive if $k\geqslant 1$.

F. Bond lengths

We compiled a benchmark set of 11 small molecules for which the equilibrium bond lengths are known from experiment.[31] The set comprises the following species: LiH, BeH, BH, CH_4, $C_2(^1\Sigma_g^+)$, CO, N_2, OH, O_2, HF, and F_2. We optimized geometries of all the molecules in the set using self-interaction corrected and uncorrected functionals. Since analytic gradients with respect to nuclear displacements are not available in our SIC implementation, all the geometry optimizations with SIC functionals were done by means of bond length variation followed by quadratic interpolation. Table VII summarizes the deviations of equilibrium bond lengths from experiment, and the detailed errors are available in Ref. 25.

In agreement with previous observations,[5,11] we found that the PZ-SIC predicts too short bonds in molecules. The C_2 molecule is a notable exception since the C_2 bond is too long in all SIC methods.[25] C_2 has several low-lying spin states and thus is very problematic for single-reference methods, which often put the states in a wrong order.[32] In all our calculations, we treated C_2 as a closed shell singlet, since that is the experimental ground state. For all the molecules in the set, increasing the value of k of the SIC brings the bond lengths into a much better agreement with experiment. The SIC with $k=2$ is particularly successful.

TABLE VII. Deviations from experiment of equilibrium bond lengths for 11 molecules computed with the 6-311+G($3df,2p$) basis set. All values are in Å.

Functional	ME	MAE	RMSE
LSDA	0.005	0.012	0.015
SIC-LSDA ($k=0$)	−0.035	0.048	0.055
SIC-LSDA ($k=1$)	−0.010	0.018	0.024
SIC-LSDA ($k=2$)	−0.001	0.009	0.013
PBE	0.010	0.010	0.011
SIC-PBE ($k=0$)	−0.012	0.032	0.046
SIC-PBE ($k=1$)	−0.009	0.014	0.022
SIC-PBE ($k=2$)	−0.004	0.008	0.013
TPSS	0.007	0.007	0.008
SIC-TPSS ($k=0$)	−0.004	0.026	0.043
SIC-TPSS ($k=1$)	−0.006	0.012	0.020
SIC-TPSS ($k=2$)	−0.004	0.008	0.012
PBEh	−0.004	0.008	0.013
SIC-PBEh ($k=0$)	−0.015	0.034	0.048
SIC-PBEh ($k=1$)	−0.011	0.024	0.034
SIC-PBEh ($k=2$)	−0.012	0.015	0.022

V. DISCUSSION

A. Effect of orbital densities on the functional dependence of the SIC results

In our previous studies we found that the Perdew-Zunger SIC works better for LSDA than for other functionals.[9,10] This conclusion seems to hold for the scaled-down correction as well: remarkable improvements are observed for LSDA, whereas the performance of the SIC is less satisfactory for beyond-LSDA functionals.

This observation may be explained as a result of using orbital densities in Eq. (11). Orbital densities often have nodes and minute details, such as the so-called "orthogonalization tails." Thus orbital densities can be much more rapidly varying than normal ground-state densities. Our corrections involve evaluation of the xc energy for an orbital density. LSDA has a limited sensitivity to density variations. Functionals dependent explicitly on the density derivatives (GGA and meta-GGA) are more sensitive to density variations. The reduced gradient $\sim|\nabla\rho|/\rho^{4/3}$ and the reduced Laplacian $\sim\nabla^2\rho/\rho^{5/3}$ diverge at the nodes. Thus, corrections utilizing orbital densities are better suited for LSDA than for higher-level functionals.

The above argument also explains why spherical averaging of orbital densities improves atomic IPs and EAs in the case of SIC-PBE, but not in the case of SIC-LSDA.[10] Spherical averaging of atomic orbitals removes angular nodes.

In Eq. (4) or (11), $E_{\mathrm{xc}}^{\mathrm{DFA}}[\rho_{i\sigma},0]$ is the ground-state exchange-correlation energy for an orbital density $\rho_{i\sigma}(\mathbf{r})=|\phi_{i\sigma}(\mathbf{r})|^2$. In many cases, $\rho_{i\sigma}(\mathbf{r})$ is found from an orbital $\phi_{i\sigma}(\mathbf{r})$ that changes sign or phase and so is not a ground-state wave function. The corresponding ground-state orbital would be $|\phi_{i\sigma}(\mathbf{r})|$, which belongs to a highly singular and rapidly varying external potential $\frac{1}{2}\nabla^2|\phi_{i\sigma}(\mathbf{r})|/|\phi_{i\sigma}(\mathbf{r})|+\text{constant}$, even when $\phi_{i\sigma}(\mathbf{r})$ belongs to a smooth external potential $\frac{1}{2}\nabla^2\phi_{i\sigma}(\mathbf{r})/\phi_{i\sigma}(\mathbf{r})+\text{constant}$. We may expect semilocal approximations to be significantly less accurate for $E_{\mathrm{xc}}[\rho_{i\sigma},0]$ than for $E_{\mathrm{xc}}[\rho_\alpha,\rho_\beta]$, which may cause some accuracy loss in orbital-density-dependent corrections such as Eq. (4) or (11).

B. Formal properties and exact constraints on the parameter *k*

As stated earlier, Eq. (11) with $k\geqslant 0$ is exact for any one-electron density and gives no correction to the exact density functional. For $k=0$, Eq. (11) reduces to the original Perdew-Zunger self-interaction correction,[4] and for $k>0$ the SIC is scaled down in many-electron regions.

The exchange term of Eq. (11) has the proper uniform density scaling[33] and the proper spin scaling[34] when $E_{\mathrm{xc}}^{\mathrm{DFA}}[\rho_\alpha,\rho_\beta]$ does. By design, the self-interaction correction is proportional to $J[\rho_{i\sigma}]+E_{\mathrm{xc}}^{\mathrm{DFA}}[\rho_{i\sigma},0]$, taking advantage of any DFA error cancellation (as in LSDA) between E_x and E_c and also avoiding the use of energy densities for J and $E_{\mathrm{xc}}^{\mathrm{DFA}}$ that are not unique and may not be mutually consistent. If the orbitals $\phi_{i\sigma}(\mathbf{r})$ are localized in regions of space where $\tau_\sigma^W/\tau_\sigma$ does not vanish, then Eq. (11) is size consistent (separable and extensive in the sense of Ref. 35).

In the Perdew-Zunger SIC, there is a formal problem[35] which is not widely appreciated. We do not know if the orbitals that minimize the PZ-SIC ($k=0$) total energy for a uniform density are localized or delocalized.[36–38] (1) If they are localized, then the PZ-SIC, applied to an approximate functional that is exact for the energy of a uniform density, produces an energy that is lower than the exact one. (2) If the SIC orbitals for a uniform density are delocalized, then the PZ-SIC energy of a large finite chunk of uniform density has a "false surface energy" that is correctly proportional to the area of its surface but incorrectly depends upon its shape.

With any $k>0$, the above problems are corrected, since τ^W/τ vanishes for a uniform density. But we still do not know if the orbitals that minimize the SIC ($k>0$) energy for an electron gas of slow or small density variation are localized or delocalized. If they are delocalized, then no further constraint on k is implied. But if they are localized, then k must be an integer $\geqslant 1$ to guarantee the existence of a gradient expansion for $E_{\mathrm{xc}}^{\mathrm{DFA}}$. In particular, $k\geqslant 2$ is needed to preserve all the correct formal properties of LSDA and PBE under self-interaction correction, while $k\geqslant 3$ is needed to preserve all the correct properties of TPSS.

Let us focus specifically upon self-interaction correction of LSDA, for the reasons described in Sec. V A. Consider a uniform electron gas perturbed by a density variation of small amplitude A: $\rho(\mathbf{r})=\text{constant}+Af(\mathbf{r})$. LSDA is known to give a rather good description of the energy variation through order A^2, and indeed the PBE GGA was constructed[20] to preserve this good LSDA behavior. If we want our SIC to do the same even if the SIC orbitals are localized, we must take $k\geqslant 2$ to make $(\tau^W/\tau)^k$ of order A^4 or higher, since $\tau^W\sim|\nabla\rho(\mathbf{r})|^2\sim A^2$. In a sense, SIC-LSDA with $k=2$ is not only a successful approximation, but a particularly well-justified one.

Unfortunately, while increasing k above zero satisfies some additional exact constraints, it violates others. For example, the original Perdew-Zunger SIC ($k=0$) exchange-correlation potential has the correct asymptotic behavior $-1/r$, while the scaled-down SIC has a $-X_{\mathrm{HO}}/r$ behavior, where X_{HO} is the scaling factor of Eq. (5) for the highest occupied (HO) orbital, and X_{HO} is less than one for $k>0$. Our preliminary studies show that $k=0$ may be needed for the highest occupied orbital to provide a good description of charge transfer. Thus, we do not have here an all-purpose self-interaction correction.

VI. CONCLUSIONS

We have introduced a modified self-interaction correction, which is scaled down in many-electron regions. Compared to the original Perdew-Zunger SIC, the new SIC performs much better for thermochemistry and thermochemical kinetics and predicts equilibrium bond lengths much closer to experiment. The scaled-down SIC has one adjustable parameter k. The optimal value of k may differ for different properties and functionals, but its typical suggested values lie between 1/2 and 2. SIC-LSDA with $k=2$ is a particularly successful combination in terms of its performance and its formal properties. It performs significantly better than uncorrected LSDA and somewhat better than uncorrected GGA, and at the same time has almost the status of a nonempirical functional (as explained in Sec. V B).

The new SIC is only marginally more expensive than the PZ-SIC, but unfortunately it inherits all the computational disadvantages of its predecessor. It is not invariant under a unitary transformation of the occupied orbitals, so that the energy minimization is nontrivial. The exchange-correlation energy has to be evaluated at each orbital density, which is one of the major factors that slows down the calculation. Evaluation of SIC requires dense unpruned integration grids since orbital densities are much more rapidly varying than typical ground-state densities. For the same reason, orbital-density-dependent self-interaction corrections work better for LSDA than for higher-level functionals.

Introduction of the scaling factor of Eq. (5) leads to satisfaction of some additional exact constraints. But on the other hand, some other constraints, satisfied by the PZ-SIC, may be lost. More constraints might be preserved in the unitarily invariant SIC of Eq. (22) of Ref. 2 (or in a closer approximation to it), although at an even greater computational cost. The present study makes it likely that the scheme proposed in Ref. 2 will be accurate when applied to LSDA with $k=2$. (Note that $k \geqslant 2$ is needed in this approach to recover the good LSDA energy for a uniform gas perturbed by a density variation of small amplitude.) At any rate, perhaps the most important step towards an all-purpose SIC has been made: we gained a much better understanding of the problems that need to be solved.

We have focused here on self-interaction correction of an existing functional. Alternatively, one can construct a functional that is self-interaction-free from the start (e.g., a hyper-GGA as defined in Ref. 2). However, as we have found here, exactness for all one-electron densities does not guarantee a correct long-range asymptote for the exchange-correlation potential or correct charge transfers.

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APPENDIX: ENERGY DERIVATIVES

The derivative of the total energy with respect to orbital variations under the constraint of orbital orthonormality is

$$\frac{\partial E}{\partial \phi_i(\mathbf{r})} = 2H_i\phi_i(\mathbf{r}) - \sum_j \phi_j(\mathbf{r})(\langle \phi_i|H_j|\phi_j\rangle + \langle \phi_j|H_i|\phi_i\rangle), \tag{A1}$$

where

$$\begin{aligned} H_i = & -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{\mathrm{xc}}^{\mathrm{DFA}}([\rho_\alpha,\rho_\beta],\mathbf{r}) \\ & - X_i^k\left(\int \frac{\rho_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{\mathrm{xc}}^{\mathrm{DFA}}([\rho_i,0],\mathbf{r})\right) \\ & - \left(\frac{\tau^W}{\tau}\right)^k (J[\rho_i] + E_{\mathrm{xc}}^{\mathrm{DFA}}[\rho_i,0]) \\ & - \sum_j \frac{\partial X_j^k}{\partial \rho(\mathbf{r})}(J[\rho_j] + E_{\mathrm{xc}}^{\mathrm{DFA}}[\rho_j,0]). \end{aligned} \tag{A2}$$

The derivatives $\partial X_j^k / \partial \rho(\mathbf{r})$ in Eq. (A2) account for variations in $(\tau^W/\tau)^k$. They are evaluated using the method of Neumann *et al.*,[39] which is typically used for obtaining matrix elements of xc potentials of meta-GGA functionals. The details of the implementation of Eq. (A1) in the Gaussian basis set can be found in Ref. 9.

[1] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[2] J. P. Perdew, A. Ruzsinszky, J. Tao, V. N. Staroverov, G. E. Scuseria, and G. I. Csonka, J. Chem. Phys. **123**, 062201 (2005).
[3] Y. Zhang and W. Yang, J. Chem. Phys. **109**, 2604 (1998).
[4] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[5] S. Goedecker and C. J. Umrigar, Phys. Rev. A **55**, 1765 (1997).
[6] S. Patchkovskii and T. Ziegler, J. Chem. Phys. **116**, 7806 (2002).
[7] J. Gräfenstein, E. Kraka, and D. Cremer, J. Chem. Phys. **120**, 524 (2004).
[8] J. Gräfenstein, E. Kraka, and D. Cremer, Phys. Chem. Chem. Phys. **6**, 1096 (2004).
[9] O. A. Vydrov and G. E. Scuseria, J. Chem. Phys. **121**, 8187 (2004).
[10] O. A. Vydrov and G. E. Scuseria, J. Chem. Phys. **122**, 184107 (2005).
[11] G. I. Csonka and B. G. Johnson, Theor. Chem. Acc. **99**, 158 (1998).
[12] K. Tsemekhman, E. J. Bylaska, E. C. Brown, and H. Jonsson (unpublished).
[13] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Jr., Phys. Rev. Lett. **49**, 1691 (1982).
[14] A. D. Becke, J. Chem. Phys. **109**, 2092 (1998).
[15] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).
[16] J. Jaramillo, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 1068 (2003).
[17] O. A. Vydrov and G. E. Scuseria (unpublished).
[18] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN Development Version, Revision D.02, Gaussian, Inc., Wallingford, CT, 2004.
[19] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[20] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396(E) (1997).
[21] J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).
[22] M. Ernzerhof and G. E. Scuseria, J. Chem. Phys. **110**, 5029 (1999).
[23] C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).
[24] S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. F. Fischer, Phys. Rev. A **47**, 3649 (1993).
[25] See EPAPS Document No. E-JCPSA6-124-307610 for detailed tables. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).
[26] B. J. Lynch and D. G. Truhlar, J. Phys. Chem. A **107**, 8996 (2003); **108**, 1460(E) (2004).
[27] B. J. Lynch, Y. Zhao, and D. G. Truhlar, http://comp.chem.umn.edu/database
[28] G. I. Csonka, A. Ruzsinszky, J. Tao, and J. P. Perdew, Int. J. Quantum Chem. **101**, 506 (2005).
[29] A. D. Boese and J. M. L. Martin, J. Chem. Phys. **121**, 3405 (2004).
[30] Y. Zhao, B. J. Lynch, and D. G. Truhlar, J. Phys. Chem. A **108**, 2715 (2004).
[31] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide, 85th ed. (CRC, Boca Raton, 2004).
[32] A. Ruzsinszky, J. P. Perdew, and G. I. Csonka, J. Phys. Chem. A **109**,

11006 (2005).
[33] M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1983).
[34] G. L. Oliver and J. P. Perdew, Phys. Rev. A **20**, 397 (1979).
[35] J. P. Perdew, Adv. Quantum Chem. **21**, 113 (1990).
[36] M. R. Norman, Phys. Rev. B **28**, 3585 (1983).
[37] J. G. Harrison, Phys. Rev. B **35**, 987 (1987).
[38] M. R. Pederson, R. A. Heaton, and J. G. Harrison, Phys. Rev. B **39**, 1581 (1989).
[39] R. Neumann, R. H. Nobes, and N. C. Handy, Mol. Phys. **87**, 1 (1996).