

Effect of the Perdew–Zunger self-interaction correction on the thermochemical performance of approximate density functionals

Oleg A. Vydrov and Gustavo E. Scuseria

Citation: [The Journal of Chemical Physics](#) **121**, 8187 (2004); doi: 10.1063/1.1794633

View online: <http://dx.doi.org/10.1063/1.1794633>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/121/17?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Self-interaction corrected density functional calculations of molecular Rydberg states](#)

J. Chem. Phys. **139**, 194102 (2013); 10.1063/1.4829539

[The effect of the Perdew-Zunger self-interaction correction to density functionals on the energetics of small molecules](#)

J. Chem. Phys. **137**, 124102 (2012); 10.1063/1.4752229

[Constraining density functional approximations to yield self-interaction free potentials](#)

J. Chem. Phys. **136**, 224109 (2012); 10.1063/1.4728156

[Scaling down the Perdew-Zunger self-interaction correction in many-electron regions](#)

J. Chem. Phys. **124**, 094108 (2006); 10.1063/1.2176608

[Ionization potentials and electron affinities in the Perdew–Zunger self-interaction corrected density-functional theory](#)

J. Chem. Phys. **122**, 184107 (2005); 10.1063/1.1897378



Re-register for Table of Content Alerts

Create a profile.



Sign up today!



Effect of the Perdew–Zunger self-interaction correction on the thermochemical performance of approximate density functionals

Oleg A. Vydrov and Gustavo E. Scuseria

Department of Chemistry, Rice University, Houston, Texas 77005

(Received 7 July 2004; accepted 27 July 2004)

The Perdew–Zunger self-interaction-corrected density functional theory (SIC-DFT) was implemented self-consistently using a quasi-Newton direct minimization method. We calculated SIC-DFT energies for a number of atoms and molecules using various approximate density functionals, including hybrids. Self-interaction errors (SIE) of these functionals were compared and analyzed in terms of contributions from valence and core orbitals. We also calculated enthalpies of formation of the standard G2-1 set of 55 molecules and found that self-interaction-correction (SIC) improves agreement with experiment only for the LSDA functional, while all other functionals show worse performance upon introducing SIC. This is the first systematic study of the effect of SIC on thermochemical properties. We found no direct connection between the magnitude of the SIE contained in a functional and its performance for thermochemistry. Approximate functionals with large self-interaction errors can accurately reproduce enthalpies of formation. Our results do not support the popular belief that a smaller SIE of hybrid functionals is the main reason for their higher accuracy. © 2004 American Institute of Physics. [DOI: 10.1063/1.1794633]

I. INTRODUCTION

In Kohn–Sham density functional theory (DFT)^{1,2} the energy of a many-electron system is expressed as a functional of the electron density,

$$E^{\text{KS}}[\rho_\alpha, \rho_\beta] = T_s[\{\phi_{i\sigma}\}] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + J[\rho] + E_{\text{xc}}[\rho_\alpha, \rho_\beta], \quad (1)$$

where T_s is the kinetic energy of a system of noninteracting electrons

$$T_s[\{\phi_{i\sigma}\}] = \sum_{\sigma=\alpha,\beta} \sum_{i=1}^{N_\sigma} \langle \phi_{i\sigma} | -\frac{1}{2} \nabla^2 | \phi_{i\sigma} \rangle. \quad (2)$$

The second term in Eq. (1) is the interaction between the electron density $\rho(\mathbf{r})$ and the external potential $v(\mathbf{r})$, and J is the Hartree electrostatic self-energy. The total density $\rho(\mathbf{r})$ is the sum of the spin densities $\rho_\alpha(\mathbf{r})$ and $\rho_\beta(\mathbf{r})$, and $\{\phi_{i\sigma}\}$ are the Kohn–Sham orbitals. All parts of the Kohn–Sham energy (1) are known exactly, except for the exchange–correlation (xc) functional E_{xc} , which has to be approximated.

It was noticed already in the early years of quantum mechanics that the Hartree energy

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

does not vanish even for a one-electron system due to the spurious self-interaction (SI) inherent in it.³ In Hartree–Fock theory this does not lead to any problem since all Coulomb self-interaction terms are exactly canceled by the corresponding exchange self-interaction terms. A similar requirement is imposed on the exact exchange–correlation functional

$$E_{\text{xc}}[\rho_i, 0] + J[\rho_i] = 0, \quad (4)$$

where $\rho_i(\mathbf{r})$ is any one-electron density. In approximate exchange–correlation functionals the cancellation is incomplete and the remainder is known as a self-interaction error (SIE). SIE is believed to be the cause of many of the failures of approximate density functionals. More than two decades ago Perdew and Zunger⁴ (PZ) proposed a simple self-interaction-correction (SIC) eliminating the SIE orbital-by-orbital, so that the expression for the total energy becomes

$$E^{\text{PZ}}[\{\rho_{i\sigma}\}] = E^{\text{KS}}[\rho_\alpha, \rho_\beta] + E^{\text{SIC}}[\{\rho_{i\sigma}\}], \quad (5)$$

with

$$E^{\text{SIC}}[\{\rho_{i\sigma}\}] = - \sum_{\sigma=\alpha,\beta} \sum_{i=1}^{N_\sigma} (E_{\text{xc}}[\rho_{i\sigma}, 0] + J[\rho_{i\sigma}]). \quad (6)$$

The summation in Eq. (6) is over all occupied molecular orbitals (MOs) and $\rho_{i\sigma}(\mathbf{r})$ are the orbital densities:

$$\rho_{i\sigma}(\mathbf{r}) = |\phi_{i\sigma}(\mathbf{r})|^2, \quad (7)$$

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

Expression (6) vanishes for the exact exchange–correlation functional and Eq. (5) reduces to the regular Kohn–Sham energy.

Despite its apparent simplicity, the practical implementation of the Perdew–Zunger self-interaction-corrected density functional theory (SIC-DFT) is complicated and that is the reason why it has not been widely used. SIC-DFT does not fit into the standard Kohn–Sham procedure because the SIC-DFT potential is orbital dependent and the energy functional (5) is not invariant under unitary transformations of the orbitals.

Several approximate implementations of the Perdew–Zunger SIC in molecular codes have been reported in recent years. The correction can be applied in a post-SCF manner, subtracting self-interaction terms after a self-consistent Kohn–Sham calculation is done.^{5–7} To maximize the removal of the error, a localization transformation is applied to the orbitals. The simplest self-consistent method is the so-called average-density SIC (ADSIC),^{8,9} based on the original idea of Fermi and Amaldi³ to subtract a fraction $1/N$ from the total density, where N is the total number of electrons. Several groups^{10–14} have reported implementations of SIC-DFT using the Krieger–Li–Iafrate¹⁵ approximation to the optimized effective potential (OEP). The advantage of the ADSIC-based and OEP-based implementations is that they provide SI-corrected orbital energies, which can be directly used for estimating excitation energies and ionization potentials.

A rigorous implementation of SIC-DFT can be done by direct minimization of the energy functional (5) under the constraint of orbital orthonormality

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}. \quad (9)$$

The first self-consistent calculations for molecules were carried out by Pederson, Heaton, and Lin¹⁶ who minimized the SIC-DFT energies of a few homonuclear diatomics. Whitehead followed with some more molecular studies.¹⁷ Goedecker and Umrigar derived the expression for the SIC-DFT gradient under the orthogonality restriction and performed direct minimization calculations for a few atoms and molecules using a plane-wave technique.¹⁸ A self-consistent implementation of SIC-DFT with Gaussian-type orbitals was reported recently.^{19–22} It utilizes a univariate search method similar to that of Seeger and Pople.²³

SIC-DFT has been extensively used in condensed matter calculations. A review of solid state SIC-DFT techniques and studies can be found elsewhere.^{24,25}

The performance of SIC-DFT in comparison to the regular Kohn–Sham DFT is ambivalent. On one hand, a SIC is crucial for proper description of odd electron systems,^{14,21,22} improves activation barriers of chemical reactions,^{5,7,14} and nuclear magnetic resonance chemical shifts.^{12,13} On the other hand, it provides little or no improvement for reaction energies^{14,18,21} and results in too short bond lengths in molecules.^{5,7,18}

II. METHODOLOGY

A. Implementation

In the Perdew–Zunger SIC-DFT, the energy is minimized with respect to orbital variations. The gradient of the energy¹⁸ in the MO basis has the form (with the spin symbols omitted for brevity)

$$\frac{\partial E}{\partial \phi_i(\mathbf{r})} = 2H_i \phi_i(\mathbf{r}) - \sum_k \phi_k(\mathbf{r}) (\langle \phi_i | H_k | \phi_k \rangle + \langle \phi_k | H_i | \phi_i \rangle), \quad (10)$$

where H_i is the orbital-dependent effective Hamiltonian

$$H_i = -\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{xc}[\rho] + \int \frac{\rho_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{xc}[\rho_i]. \quad (11)$$

We will expand MOs $\{\phi_i\}$ as linear combinations of Gaussian basis functions $\{\chi_\mu\}$

$$\phi_i(\mathbf{r}) = \sum_\mu C_{\mu i} \chi_\mu(\mathbf{r}). \quad (12)$$

The gradient (10) can be converted to the new basis by applying the chain rule,

$$\begin{aligned} \frac{\partial E}{\partial C_{\mu i}} &= \int \frac{\partial E}{\partial \phi_i(\mathbf{r})} \chi_\mu(\mathbf{r}) d\mathbf{r} \\ &= 2(\mathbf{H}^i \mathbf{C})_{\mu i} - \sum_k (\mathbf{S} \mathbf{C})_{\mu k} \{ (\mathbf{C}^\dagger \mathbf{H}^k \mathbf{C})_{ik} + (\mathbf{C}^\dagger \mathbf{H}^i \mathbf{C})_{ki} \}, \end{aligned} \quad (13)$$

where $\mathbf{H}_{\mu\nu}^i = \langle \chi_\mu | H_i | \chi_\nu \rangle$ are the matrix elements of the H_i operator (11) and $\mathbf{S}_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$ are the overlap matrix elements.

The SIC-DFT gradient (13) was implemented in a developmental version of the GAUSSIAN program²⁶ and used for the minimization of the energy functional (5) utilizing the Broyden–Fletcher–Goldfarb–Shanno (BFGS) variant of a quasi-Newton method.²⁷ Cubic interpolation was employed as a line search method. After each minimization cycle orbitals were reorthogonalized using Löwdin's procedure:

$$\mathbf{C}' = \mathbf{C}(\mathbf{C}^\dagger \mathbf{S} \mathbf{C})^{-1/2}. \quad (14)$$

In the BFGS Hessian update method, a unit matrix is often used as an initial guess for the Hessian matrix. However, we found that convergence can be accelerated by starting from a diagonal Hessian with the diagonal elements calculated by an approximate formula

$$\begin{aligned} \frac{\partial^2 E}{\partial C_{\mu i}^2} &= 2\mathbf{H}_{\mu\mu}^i - 2(\mathbf{C}^\dagger \mathbf{H}^i \mathbf{C})_{ii} - \sum_k (\mathbf{S} \mathbf{C})_{\mu k} \{ (\mathbf{H}^k \mathbf{C})_{\mu k} \\ &\quad + (\mathbf{H}^i \mathbf{C})_{\mu k} \} (1 + \delta_{ik}), \end{aligned} \quad (15)$$

Equation (15) is obtained from Eq. (13) under the assumption that matrix elements of the H_i operator (11) do not change upon variation of orbital coefficients $C_{\mu i}$.

The time needed for the optimization procedure to converge to a minimum strongly depends on the quality of the initial guess for the orbital coefficients. Applying a localization transformation to the canonical self-consistent Kohn–Sham orbitals provides a good estimate to the self-consistent SIC-DFT orbitals.^{5,14} The Boys localization procedure,²⁸ which minimizes the spatial extension of each orbital, proved to be the most appropriate. However, we found that the Boys method can be unstable for some open-shell systems and molecules containing second row atoms. This problem can be cured by removing a subset of orbitals from the localization set and applying the transformation to the remaining orbitals only. In some particularly difficult cases we resorted to the Pipek–Mezey method,²⁹ which shows no considerable

convergence problems, but provides a somewhat worse guess. The Pipek–Mezey procedure minimizes the number of atoms over which an orbital is extended. Thus it is not suited for localizing MOs located on a single atom such as lone pairs. For multiple bonds, the Pipek–Mezey procedure results in σ - π separation while the Boys method gives a set of equivalent orbitals.

For atoms, the initial guess was prepared by solving the Kohn–Sham equations with the restriction of spherical density and then localizing core and valence orbitals separately.

Self-consistent SIC-DFT orbitals from different parent functionals look similar in the majority of cases. Hence, for a given molecule, orbitals obtained with one functional can be used as a good initial guess in minimization of another SI-corrected functional.

It should be stressed that our implementation works with any functional, including hybrids, whereas most of the previous studies focused on the SI-corrected local spin density approximation (LSDA). There are only a few studies of the SIE in generalized gradient approximation (GGA) functionals.^{5,14,19–22} For hybrid functionals only post-SCF SIC-DFT calculations for the H_2 molecule⁶ and $H_2 + H$ reaction⁷ were reported. No self-consistent SIC-hybrid-DFT calculations have been reported prior to this work.

B. Computational details

We have calculated the Perdew–Zunger SIC-DFT energies for atoms from H to Ar and 55 molecules of the standard thermochemical G2-1 test set.³⁰ Equilibrium B3LYP/6-31G(2df,p) geometries were used for all molecules. We tested a number of DFT functionals representing different groups: SVWN5³¹ (LSDA), PBE³² and BLYP^{33,34} (GGAs), PKZB,³⁵ TPSS^{36,37} and VSXC³⁸ (meta-GGAs), PBE0^{39,40} and B3LYP⁴¹ (hybrid GGAs). SVWN5, PBE, TPSS, and PBE0 are nonempirical functionals and all the rest are semiempirical. The PKZB functional, a precursor of TPSS, was used only in atomic calculations for the sake of comparison with TPSS.

We chose the 6-311+G(3df,2p) basis set as sufficiently large for our purposes. A large unpruned integration grid with 120 radial shells and 770 angular points per shell was used in all calculations. We found that the SIC-DFT energy is more sensitive to the grid size than the regular Kohn–Sham DFT and small grids can even lead to convergence problems. All calculations on open shells are spin unrestricted.

III. RESULTS AND DISCUSSION

A. Magnitude of the SIE

The calculated values of the SIC-DFT energies for individual atoms and molecules as well as the values of E^{SIC} (6) can be found in the Supplementary Information available through the EPAPS depository.⁴²

In order to compare the magnitudes of SIE of different functionals, we computed the mean absolute values of E^{SIC} per electron (Table I). The values are found by, first, dividing the absolute value of E^{SIC} of an atom (molecule) by the number of electrons and, then, averaging among all atoms

TABLE I. Mean absolute Δ and E^{SIC} per electron (a.u.).

Functional	Δ^a	E^{SIC}	$E^{\text{SICb}}_{\text{val}}$
18 Atoms (H–Ar)			
SVWN5	0.0983	0.0992	0.0165
VSXC	0.0259	0.0254	0.0125
B3LYP	0.0112	0.0107	0.0123
TPSS	0.0205	0.0201	0.0116
BLYP	0.0173	0.0167	0.0110
PBE	0.0063	0.0059	0.0102
PBE0	0.0056	0.0053	0.0093
PKZB	0.0098	0.0094	0.0075
55 Molecules (G2-1 set)			
SVWN5	0.0946	0.0957	0.0177
VSXC	0.0257	0.0250	0.0151
B3LYP	0.0117	0.0110	0.0147
TPSS	0.0209	0.0203	0.0147
BLYP	0.0171	0.0161	0.0138
PBE	0.0058	0.0052	0.0119
PBE0	0.0056	0.0052	0.0108

^a $\Delta = \min\{E^{\text{PZJ}}\} - \min\{E^{\text{KS}}\}$.

^bContribution to E^{SIC} from valence orbitals.

(molecules) in the set. The mean absolute E^{SIC} of valence orbitals are shown in Table I separately. For thermochemistry only the valence orbitals are important since core orbitals remain largely unchanged in chemical reactions and contributions of core orbitals mostly cancel out in calculations of any thermochemical property. Indeed, we found that E^{SIC} of the core orbitals of a molecule is almost exactly equal to the sum of the E^{SIC} values of the core orbitals of the composing atoms. This observation is consistent with previous studies.^{11,13} Functionals in Table I are arranged in the order of decreasing average E^{SIC} for the valence orbitals.

Since we directly minimize the energy functional (5), E^{SIC} is not equal to $\Delta = \min\{E^{\text{PZJ}}\} - \min\{E^{\text{KS}}\}$. In fact, Δ can be used as an alternative measure of the SIE. But the difference between Δ and E^{SIC} is fairly small (Table I) and it is more convenient for us to define the SIE as a negative of E^{SIC} since it allows analyzing the breakdown of the SIE into orbital contributions. Total self-interaction errors in atoms are plotted in Figs. 1 and 2 while errors of individual atomic shells are shown in Fig. 3.

LSDA (SVWN5) has a much greater total SIE than any other functional. However, most of the error in LSDA (more than 80%) comes from the core region. The SIE of the valence orbitals is of the same order of magnitude for all functionals. For some of the functionals (PBE, PBE0, B3LYP) the total average E^{SIC} in Table I is smaller than the corresponding value for the valence region. The reason for this is a partial cancellation of the SIE between valence and core regions. For atoms, this effect is illustrated in Fig. 3. Such cancellation of errors reduces the total value of the SIE. But it should be stressed that for the exact xc-functional not only the total error must be zero but also the SIE of every orbital. From Fig. 3 we can tell which regions contribute most of the error in atoms. In LSDA, the first shell (1s) is the major source of SIE. In TPSS, the SIE of the 1s orbitals is close to zero. This is not surprising because TPSS was constructed to

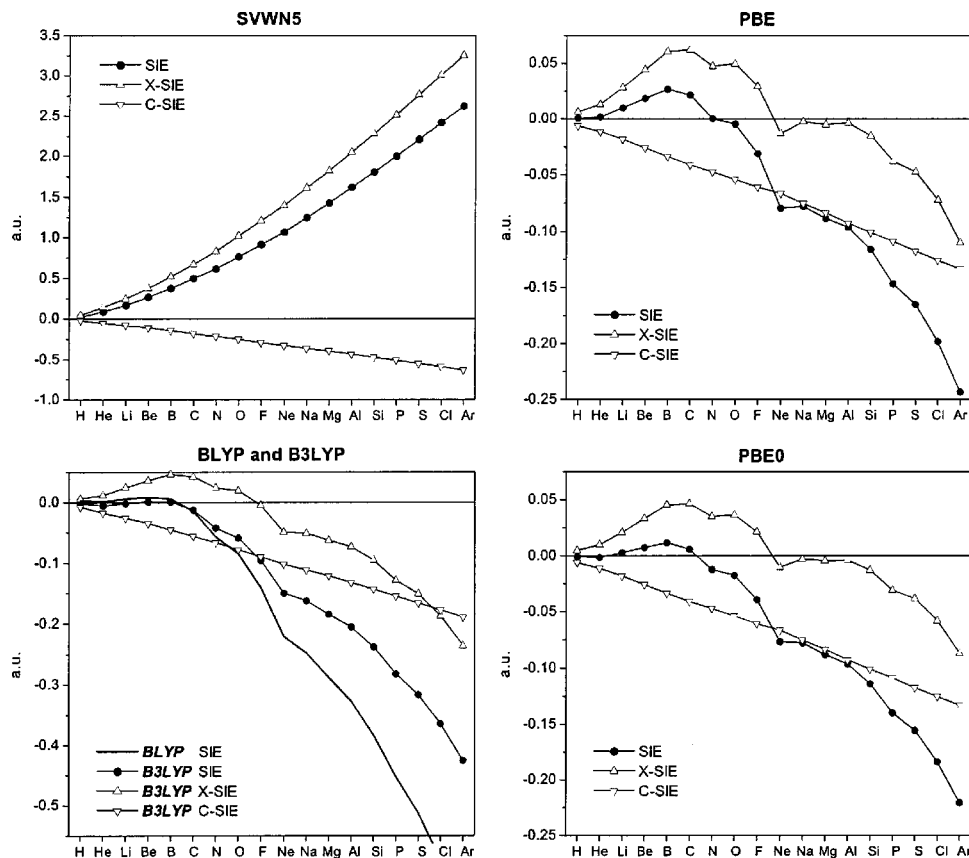


FIG. 1. Self-interaction errors of LSDA, GGA, and hybrid functionals for atoms from H to Ar. The total SIE is broken down into exchange self-interaction error (X-SIE) and correlation self-interaction error (C-SIE).

reproduce the correct energy for the ground state density of the hydrogen atom.³⁶ It is interesting to note that the PKZB functional, which does not satisfy this condition, shows significant SIE in the $1s$ region and at the same time has smaller SIE of valence orbitals than TPSS.

The condition for a functional to be self-interaction-free given by Eq. (4) can be split into two separate conditions for the exchange and correlation components:⁴

$$E_x[\rho_{i\sigma}, 0] + J[\rho_{i\sigma}] = 0, \quad (16)$$

$$E_c[\rho_{i\sigma}, 0] = 0. \quad (17)$$

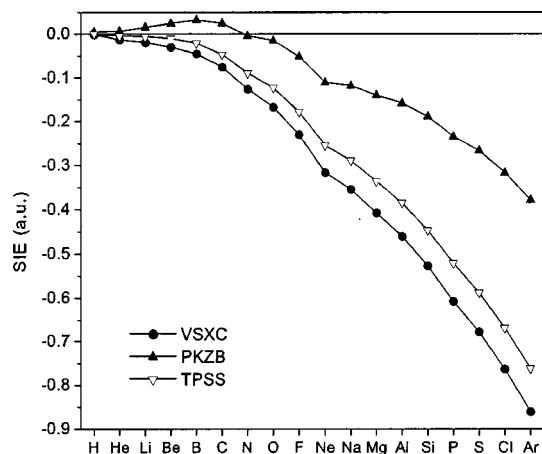


FIG. 2. Self-interaction errors of meta-GGA functionals for atoms from H to Ar.

Equation (17) implies that the correlation energy must be equal to zero for a one-electron density. LYP, VSXC, PKZB, and TPSS correlation functionals satisfy condition (17) by construction and thus they are self-correlation-free. In B3LYP the self-correlation energy is not zero due to the admixture of LSDA correlation. No approximate exchange density functional satisfies Eq. (16) for any one-electron density.

According to Eqs. (16) and (17) we can distinguish two contributions of the SIE, the exchange self-interaction error (X-SIE), defined as the sum of all self-Coulomb and self-exchange terms, and the correlation self-interaction error (C-SIE), which is a sum of all self-correlation terms. Figure 1 shows the breakdown of the total SIE into X-SIE and C-SIE. We see that self-correlation in PBE and PBE0 has the same magnitude, while the error coming from the violation of Eq. (16) is slightly reduced in PBE0 due to the presence of the exact exchange. In B3LYP, the exchange self-interaction error is reduced significantly compared to BLYP, but the LSDA correlation in B3LYP produces a relatively large self-correlation error.

Figure 4 shows X-SIE and C-SIE for individual shells in atoms. In the case of PBE, there is a fortuitous cancellation of X-SIE terms between first and second shells, so that the total X-SIE in PBE is relatively small (Fig. 1).

B. Enthalpies of formation

Using both self-interaction-corrected and uncorrected functionals, we computed the standard enthalpies of forma-

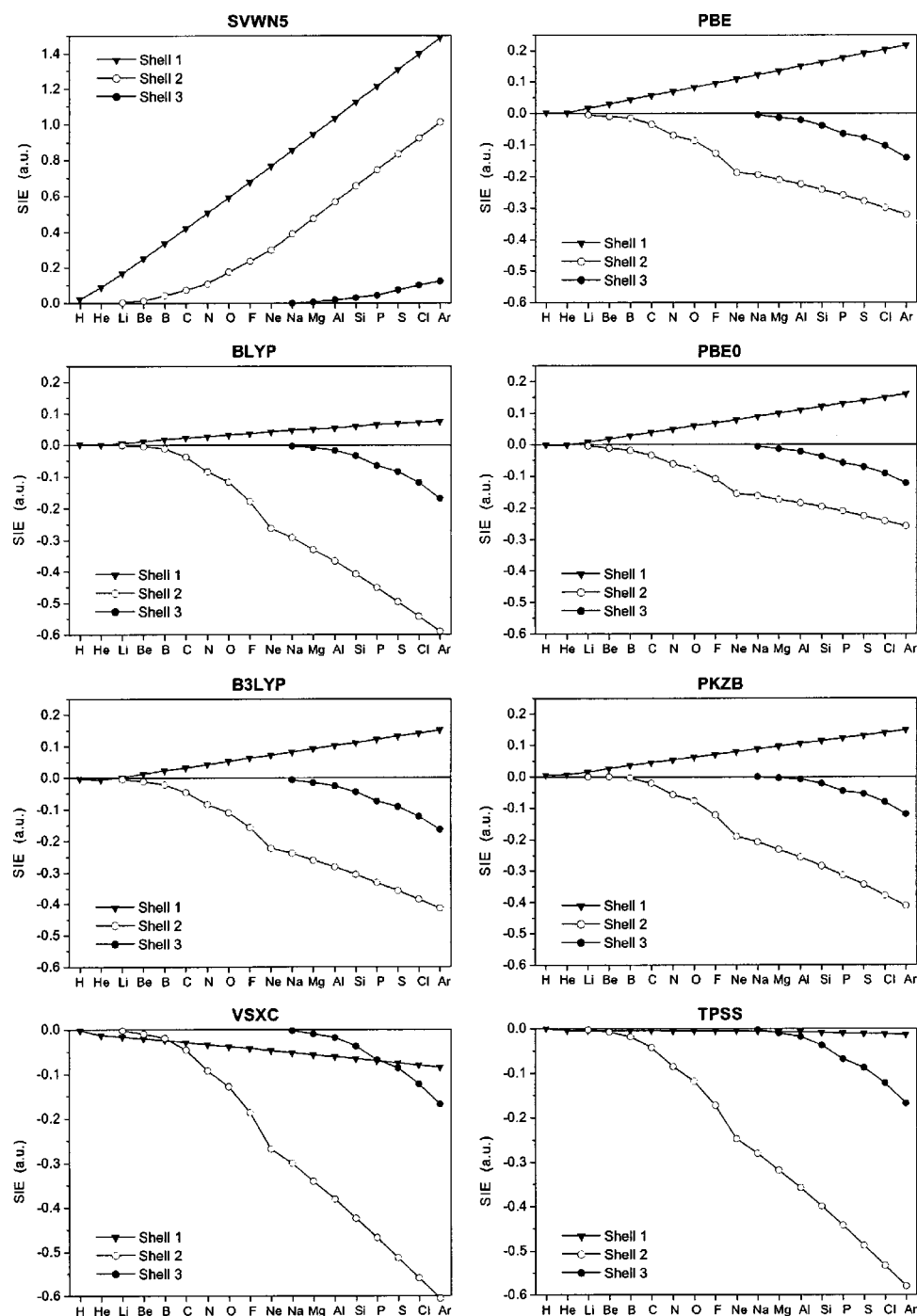


FIG. 3. Contributions to the SIE from individual shells in atoms.

tion for the G2-1 set using methodology described by Curtiss *et al.*³⁰ The deviations from the experimental values for individual molecules can be found in the Supplementary Information.⁴² Table II shows the summary of the deviations. As one can see, the PZ correction improves agreement with experiment only for the LSDA functional, whereas all other functionals show worse performance upon introducing the PZ SIC. This behavior appears reasonable for semiempirical functionals since they are fitted to reproduce experimental data with self-interaction terms included. However, the self-interaction correction leads to a decrease in accuracy for both empirical and nonempirical functionals.

From our results we do not see any correlation between the magnitude of the SIE of a functional and its performance

for the enthalpies of formation. For instance, VSXC has the largest SIE of the three meta-GGA functionals tested (Table I and Fig. 2), yet it outperforms most of the functionals.⁴³ VSXC is a semiempirical functional with as many as 21 empirical parameters fitted to experimental thermochemical data. A large SIE of this functional can be a byproduct of the fitting procedure and SIE may work for a benefit by fortune. This supposition is reinforced by recent studies where SIE was demonstrated to mimic long range (nondynamic) correlation effects.^{19,20}

Similar observations can be made about other functionals. For example, PKZB has a smaller SIE which does not make it a better functional than its successor TPSS.

Another interesting observation is that the thermochemi-

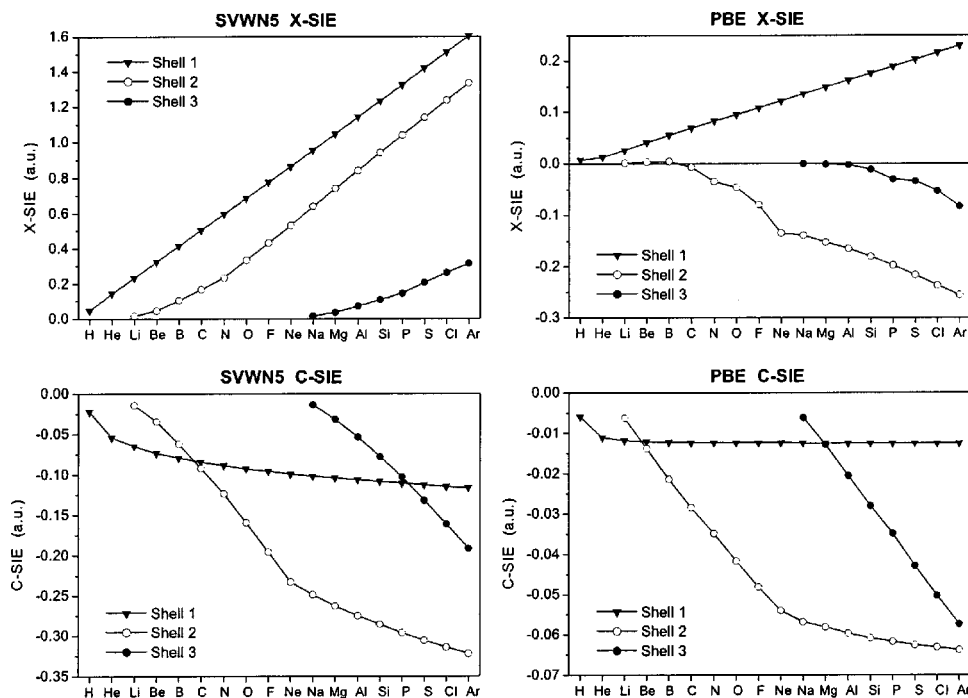


FIG. 4. Exchange self-interaction errors (X -SIE) and correlation self-interaction errors (C -SIE) in terms of contributions from individual shells in atoms.

cal accuracy decreases in the order $PBE0 \rightarrow PBE \rightarrow PZ$ - $PBE \rightarrow PZ$ - $PBE0$. We conclude that the excellent performance of hybrid functionals for thermochemistry is not the result of a smaller SIE but rather of some other factors, e.g., nonlocality of the exact exchange hole. A fraction of the SIE remaining in hybrids is important and its complete removal is by no means beneficial.

IV. CONCLUSIONS

Using a rigorous self-consistent Perdew–Zunger SIC–DFT formalism, we performed a systematic study of self-interaction errors of a number of approximate density functionals and analyzed the components of the error. We found that the SIE of valence orbitals has the same order of mag-

nitude for all functionals. Improvements over LSDA, such as GGA and meta-GGA, do not lead to a considerable reduction of the SIE.

We analyzed the effect of the Perdew–Zunger SIC on the enthalpies of formation and found that SI-corrected functionals are inferior to their uncorrected parent functionals, with the only exception of LSDA.

We also demonstrated that the magnitude of the SIE contained in a functional is not related to its thermochemical performance, so that a smaller SIE does not necessarily mean a better functional for thermochemistry.

Clearly, straightforward removal of the self-interaction terms from an approximate density functional using the Perdew–Zunger formalism⁴ is not a good strategy to improve the functional’s performance, because complete elimi-

TABLE II. Deviations from experiment of standard enthalpies of formation ($\Delta_f H_{298}^\circ$) for the G2-1 test set computed with self-interaction-corrected and self-interaction-uncorrected functionals using the 6-311 + G(3df,2p) basis set. The geometries and zero-point energies were obtained at the B3LYP/6-31G(2df,p) level using a frequency scale factor of 0.9854. All values are in kcal/mol.

Functional	ME	MAE	Max (+)	Max (–)
SVWN5	–36.0	36.1	0.5 (Li ₂)	–86.1 (CO ₂)
PBE	–6.6	8.1	10.7 (Si ₂ H ₆)	–28.9 (CO ₂)
PBE0	1.4	2.9	9.8 (SiO)	–5.9 (BeH)
BLYP	–2.8	4.8	10.7 (Si ₂ H ₆)	–15.4 (O ₂)
B3LYP	–0.4	2.2	7.6 (SO ₂)	–8.0 (BeH)
VSXC	–0.4	2.3	8.0 (N ₂ H ₄)	–7.5 (O ₂)
TPSS	–3.6	4.5	5.6 (SiO)	–18.1 (Si ₂ H ₆)
PZ-SVWN5	–21.5	22.8	8.4 (SiO)	–89.2 (C ₂ H ₆)
PZ-PBE	10.0	12.5	63.6 (CO ₂)	–11.5 (PH ₂)
PZ-PBE0	13.6	14.9	63.5 (CO ₂)	–7.7 (PH ₂)
PZ-BLYP	18.6	21.0	99.7 (CO ₂)	–13.9 (PH ₂)
PZ-B3LYP	15.7	18.7	86.0 (CO ₂)	–13.6 (Si ₂ H ₆)
PZ-VSXC	13.6	16.5	69.4 (CO ₂)	–24.7 (Si ₂ H ₆)
PZ-TPSS	15.0	19.5	83.9 (CO ₂)	–27.9 (Si ₂ H ₆)

nation of the SIE upsets the ongoing balance of error cancellation. It appears that more elaborate ways of constructing SIE-free DFT functionals are needed.⁴⁴ Independent of the present work, it has been argued that the Perdew–Zunger SIC can lose the correct slowly varying density limits of LSDA, GGA, or meta-GGA, and an alternative but untested SIC has been proposed.⁴⁵ This alternative is invariant under unitary transformations of the orbitals. It scales down the SIC in many-electron systems, while apparently solving all formal problems.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (CHE-99-82156) and the Welch Foundation. The authors thank Viktor N. Staroverov for a critical reading of this manuscript. O.V. also wishes to thank Sergey N. Maximoff and Juan E. Peralta for helpful discussions.

- ¹W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- ²R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
- ³E. Fermi and E. Amaldi, Accad. Ital. Rome **6**, 117 (1934).
- ⁴J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- ⁵B. G. Johnson, C. A. Gonzalez, P. M. W. Gill, and J. A. Pople, Chem. Phys. Lett. **221**, 100 (1994).
- ⁶G. I. Csonka, N. A. Nguyen, and I. Kolossvary, J. Comput. Chem. **18**, 1534 (1997).
- ⁷G. I. Csonka and B. G. Johnson, Theor. Chem. Acc. **99**, 158 (1998).
- ⁸C. Legrand, E. Suraud, and P.-G. Reinhard, J. Phys. B **35**, 1115 (2002).
- ⁹I. Ciofini, H. Chermette, and C. Adamo, Chem. Phys. Lett. **380**, 12 (2003).
- ¹⁰J. Garza, J. A. Nichols, and D. A. Dixon, J. Chem. Phys. **112**, 7880 (2000).
- ¹¹J. Garza, R. Vargas, J. A. Nichols, and D. A. Dixon, J. Chem. Phys. **114**, 639 (2001).
- ¹²S. Patchkovskii, J. Autschbach, and T. Ziegler, J. Chem. Phys. **115**, 26 (2001).
- ¹³S. Patchkovskii and T. Ziegler, J. Phys. Chem. A **106**, 1088 (2002).
- ¹⁴S. Patchkovskii and T. Ziegler, J. Chem. Phys. **116**, 7806 (2002).
- ¹⁵J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **45**, 101 (1992); **46**, 5453 (1992); **47**, 165 (1993).
- ¹⁶M. R. Pederson, R. A. Heaton, and C. C. Lin, J. Chem. Phys. **80**, 1972 (1984); **82**, 2688 (1985).
- ¹⁷M. A. Whitehead, in *Recent Advances in Density Functional Methods, Part II*, edited by D. P. Chong (World Scientific, Singapore, 1997).
- ¹⁸S. Goedecker and C. J. Umrigar, Phys. Rev. A **55**, 1765 (1997).
- ¹⁹V. Polo, E. Kraka, and D. Cremer, Mol. Phys. **100**, 1771 (2002).
- ²⁰V. Polo, J. Gräfenstein, E. Kraka, and D. Cremer, Theor. Chem. Acc. **109**, 22 (2003).
- ²¹J. Gräfenstein, E. Kraka, and D. Cremer, J. Chem. Phys. **120**, 524 (2004).
- ²²J. Gräfenstein, E. Kraka, and D. Cremer, Phys. Chem. Chem. Phys. **6**, 1096 (2004).
- ²³R. Seeger and J. A. Pople, J. Chem. Phys. **65**, 265 (1976).
- ²⁴A. Svane, W. M. Temmerman, Z. Szotek, J. Lægsgaard, and H. Winter, Int. J. Quantum Chem. **77**, 799 (2000).
- ²⁵A. Filippetti and N. A. Spaldin, Phys. Rev. B **67**, 125109 (2003).
- ²⁶M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN Development Version, Revision B.07, Gaussian, Inc., Pittsburgh PA, 2003.
- ²⁷W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, 1992).
- ²⁸S. F. Boys, Rev. Mod. Phys. **32**, 296 (1960); J. M. Foster and S. F. Boys, *ibid.* **32**, 300 (1960).
- ²⁹J. Pipek and P. Mezey, J. Chem. Phys. **90**, 4916 (1989).
- ³⁰L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, J. Chem. Phys. **106**, 1063 (1997).
- ³¹S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
- ³²J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396(E) (1997).
- ³³A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
- ³⁴C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988); B. Miehlich, A. Savin, H. Stoll, and H. Preuss, Chem. Phys. Lett. **157**, 200 (1989).
- ³⁵J. P. Perdew, S. Kurth, A. Zupan, and P. Blaha, Phys. Rev. Lett. **82**, 2544 (1999).
- ³⁶J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).
- ³⁷J. P. Perdew, J. Tao, V. N. Staroverov, and G. E. Scuseria, J. Chem. Phys. **120**, 6898 (2004).
- ³⁸T. Van Voorhis and G. E. Scuseria, J. Chem. Phys. **109**, 400 (1998).
- ³⁹M. Ernzerhof and G. E. Scuseria, J. Chem. Phys. **110**, 5029 (1999).
- ⁴⁰C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).
- ⁴¹P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, J. Phys. Chem. **98**, 11623 (1994); see also R. H. Hertwig and W. Koch, Chem. Phys. Lett. **268**, 345 (1997) concerning the parametrization of B3LYP.
- ⁴²See EPAPS Document No. E-JCPSA6-121-305439 for detailed tables. A direct link to this document may be found in the online article's HTML reference section. The document may be also retrieved via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from <ftp.aip.org> in the directory /epaps/. See the EPAPS homepage for more information.
- ⁴³V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, J. Chem. Phys. **119**, 12129 (2003).
- ⁴⁴S. Kümmel and J. P. Perdew, Mol. Phys. **101**, 1363 (2003).
- ⁴⁵J. P. Perdew, A. Ruzsinszky, J. Tao, V. N. Staroverov, G. E. Scuseria, and G. I. Csonka (unpublished).