Density-related properties from self-interaction corrected density functional theory calculations

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Abstract

The Perdew-Zunger self-interaction correction (PZ-SIC) removes unphysical electron selfinteraction from calculations employing standard density functional approximations. Doing so improves many computed properties, bringing them into better agreement with experimental observations or with results from high-level quantum chemistry calculations. However, while PZ-SIC generally corrects in the right direction relative to corresponding reference values, in many cases it over-corrects. For this reason scaled-down versions of PZ-SIC have been proposed and investigated. These approaches have mostly employed exterior scaling in which SIC correction terms are scaled in the same way at every point in space. Recently, a new local, or interior, scaling SIC method was proposed on non-empirical grounds to restore a property of the exact, but unknown, density functional that is broken in PZ-SIC. In this approach, the scaling at each point depends on the character of the charge density at that point. But the local scaling can be done in various ways while still restoring the behavior of the exact functional. In this work, we compare and contrast the performance of various interior scaling approaches for addressing over-corrections of calculated molecular dipole moments and atomic polarizabilities, properties that reflect the nature of the electronic charge density.

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I. INTRODUCTION

Traditional density functional theory (DFT) calculations suffer from self-interaction error (SIE) due to the use of approximate exchange-correlation (XC) energy functionals. In 1981 Perdew and Zunger[1] proposed a scheme to eliminate the unphysical self-interaction. That scheme is exact for a one-electron density, but approximate for a many-electron Since then, the Perdew-Zunger self-interaction correction (PZ-SIC) has been density. implemented and tested with many density functional approximations (DFAs), including local density approximations (LSDA), generalized gradient approximations (GGA), and meta-GGAs (mGGA)[2–12]. The effect of the PZ-SIC have been assessed for many properties, including total energies, reaction barrier heights, orbital energies, atomization energies, magnetic exchange couplings, molecular dipoles, and atomic polarizabilities.[4–7, 13–18]. A general conclusion in many of these studies is that, while PZ-SIC-DFA results improve over those of the bare DFA, PZ-SIC tends to over-correct. For example, Johnson et al.[4] found recently that DFA methods systematically underestimate the dipole moments of ionic molecules. In the corresponding PZ-SIC-DFA calculations, the dipoles agree better with reference values, but they are too large. In response to this tendency to over-correct, approaches that scale down the magnitude of the SIC have been proposed and tested [19–23]. Vydrov et al. [20, 21] proposed to use a different scaling factor for each orbital, while Klüpel et al.[19] used a single or global scaling factor for all orbitals. We refer to both types of approaches as exterior scaling methods, since the scale factor appears "outside" each orbital self-interaction correction.

Non-empirical semi local functionals are constructed to give the exact exchangecorrelation (XC) energy in the limit of slowly varying densities. Remarkably, a recent study by Santra and Perdew[24] revealed that semi local functionals used in conjunction with PZ-SIC violate this basic property. This implies that, while PZ-SIC restores to DFAs the behavior of the exact functional in the limit of a one-electron density, it causes the exact behavior to be lost for a uniform density. This is clearly a problem, since, by construction, global scaling PZ-SIC methods cannot restore both limits exactly with a single scale factor. To address this problem, Zope et al.[25] proposed scaling the self-interaction correction independently at each point in space, with the scaling factor determined by the nature of the local charge density. By using an iso-orbital indicator as the scaling factor, this interior or local scaling SIC approach (LSIC) insures that full PZ-SIC will be applied for a single electron density, while the correction terms are scaled down in many-electron regions and reduced to zero for a uniform density. LSIC-LSDA calculations yield[25] thermochemical properties that are significantly better than those of both LSDA and PZ-SIC-LSDA and are superior to those of the Perdew, Burke, and Ernzerhof (PBE) GGA[26] and nearly as good as those of the strongly constrained and appropriately normed (SCAN) meta-GGA[27] for many equilibrium properties of covalent and ionic bonds. LSIC-LSDA calculations also improve the description of water cluster polarizabilities[28] and the ionization energies of organic molecules.[29] Gauge consistency of energy densities restricts[22] LSIC to the correction of LSDA and disqualifies the similar correction of other standard functionals. For atomization energies involving weak (hydrogen or van der Waals) bonds, LSIC is not recommended,[30] but see Ref. 31 for an alternative.

Given the success of LSIC-LSDA for properties related to total energies, it is of interest to determine how well the method describes properties related to the ground-state charge density. In this work, we used the local scaling SIC approach with several variants of the scaling factor to evaluate the dipole moments of a diverse set of small molecules and the polarizabilities of closed-shell atoms and ions up to Ar. The methods differ in how strongly they scale down the correction in many-electron-like regions of space relative to more oneelectron-like regions. All of the schemes are constructed to yield exact results in the limit of a one-electron density and that of a uniform density. We compare the performance of the methods with each other and with simple global scaling methods. The aim is to gain insight into what features of a local scaling approach are important for making reliable predictions for density-related properties.

II. METHODS AND COMPUTATIONAL DETAILS

A. Global scaling

For global scaling SIC approaches, the total energy can be written as

$$E^{\text{SIC}-\text{DFA}} = E^{\text{DFA}} - \alpha \sum_{i,\sigma} \left(U[\rho_{i,\sigma}] + E_{\text{XC}}^{\text{DFA}}[\rho_{i,\sigma}, 0] \right), \tag{1}$$

where $U[\rho_{i\sigma}]$ is the self Coulomb energy, $E_{\rm XC}^{\rm DFA}[\rho_{i,\sigma}, 0]$ is the self XC energy of the i^{th} orbital in the σ spin channel, and α is the global scaling factor. A value $\alpha = 0.5$ has been found to yield significant improvements to PZ-SIC-PBE calculations.[9, 32] For comparison purposes, in this work we used $\alpha = 0.25$, 0.5 and 0.75, in addition to $\alpha = 0.0$ (uncorrected DFA) and $\alpha = 1.0$ (full PZ-SIC), to systematically explore the effect of moving from no correction to full PZ-SIC following a global scaling scheme.

 $E^{\text{SIC}-\text{DFA}}$ is minimized by finding a set of orbitals (ϕ_i 's) that satisfy

$$(H^{\text{DFA}} + \alpha V_{i,\sigma}^{\text{SIC}}(\vec{r}))\phi_{i,\sigma}(\vec{r}) = \sum_{j} \lambda_{j,i}\phi_{j,\sigma}(\vec{r}).$$
(2)

where H^{DFA} is the standard Kohn-Sham Hamiltonian and the $\lambda_{j,i}$ are Lagrange multipliers. $V_{i,\sigma}^{\text{SIC}}$ is the SIC potential for the i^{th} orbital:

$$V_{i,\sigma}^{\rm SIC}(\vec{r}) = -\left(\int \frac{\rho_{i,\sigma}(\vec{r}')d^3r'}{|\vec{r} - \vec{r}'|} + V_{\rm XC}^{\rm DFA}[\rho_{i,\sigma}, 0]\right),\tag{3}$$

where $V_{\rm XC}^{\rm DFA}$ is the XC potential corresponding to $E_{\rm XC}^{\rm DFA}$.

B. Local Scaling

In the local scaling approach, the SIC energy density is scaled independently at each point in space, depending on the character of the local density. Zope et al.[25] defined the LSIC energy as

$$E^{\text{LSIC}-\text{DFA}} = E^{\text{DFA}} - \sum_{i,\sigma} \left(U^{\text{LSIC}}[\rho_{i,\sigma}] + E^{\text{LSIC}}_{\text{XC}}[\rho_{i,\sigma}, 0] \right), \qquad (4)$$

where

$$U^{\text{LSIC}}[\rho_{i,\sigma}] = \frac{1}{2} \int d^3 r z_{\sigma}(\vec{r}) \rho_{i,\sigma}(\vec{r}) \int d^3 r' \frac{\rho_{i,\sigma}(\vec{r'})}{|\vec{r} - \vec{r'}|}, \qquad (5)$$

is the scaled self-Coulomb energy, and

$$E_{\rm XC}^{\rm LSIC}[\rho_{i,\sigma}, 0] = \int d^3 r z_{\sigma}(\vec{r}) \rho_{i,\sigma}(\vec{r}) \varepsilon_{\rm XC}^{\rm DFA}([\rho_{i,\sigma}, 0], \vec{r})$$
(6)

is the scaled self XC energy.

The scaling factor $z_{\sigma}(\vec{r})$ is an iso-orbital indicator [33] defined as

$$z_{\sigma}(\vec{r}) = \frac{\tau_{\sigma}^{W}(\vec{r})}{\tau_{\sigma}(\vec{r})}, \qquad (7)$$

where

$$\tau_{\sigma}(\vec{r}) = \frac{1}{2} \sum_{i} |\vec{\nabla}\psi_{i,\sigma}(\vec{r})|^2 \tag{8}$$

is the positive definite kinetic energy density, and

$$\tau_{\sigma}^{\mathrm{W}}(\vec{r}) = \frac{|\vec{\nabla}\rho_{\sigma}(\vec{r})|^2}{8\rho_{\sigma}(\vec{r})} \tag{9}$$

is the von Weizäceker kinetic energy density. It can be shown that $0 \leq z_{\sigma}(\vec{r}) \leq 1$, and z_{σ} is zero for a uniform density and exactly one for any single electron density. Thus, the LSIC energy is equal to the full PZ-SIC energy for one-electron densities where PZ-SIC is exact, and equal to the underlying DFA energy for uniform densities where the DFA is exact.

In the original implementation of LSIC, [25] the LSIC energy was computed using the orbital densities obtained from a full PZ-SIC-LSDA calculation. To explore the impact of local scaling on the charge density, we use a simple quasi-self-consistent approach to capture the most important effects. A similar approach was used in Ref. 28. The method is based on the following approximate one-electron equation:

$$\left(H^{\rm DFT} + z_{\sigma}(\vec{r}) V_{i,\sigma}^{\rm SIC}(\vec{r})\right) \phi_{i,\sigma}(\vec{r}) = \sum_{j} \lambda_{j,i} \phi_{j,\sigma}(\vec{r}).$$
(10)

This equation differs from the corresponding fully variational equation in that it neglects the terms related to the variation of $z_{\sigma}(\vec{r})$ with respect to the orbitals. Since the value of $z_{\sigma}(\vec{r})$ depends on the *character* of the density rather than its specific value, we expect the main effect of the local scaling will come from the scaled potential terms included in Eq. 10.

To solve Eq. 10 in practice, we begin by defining $z_{\sigma}(\vec{r})$ using the density obtained from a self-consistent FLO-SIC-DFA calculation. We then keep that $z_{\sigma}(\vec{r})$ fixed and solve Eq. 10 self-consistently for the orbitals $\phi_{i\sigma}$, the corresponding density, and $E^{\text{LSIC-DFT}}$. Then a new $z_{\sigma}(\vec{r})$ is calculated using the updated density. That z_{σ} is then held fixed and Eq. 10 can again be solved self-consistently. This process is schematically shown in Fig. 1. We repeat these steps until $E^{\text{LSIC}-\text{DFT}}$ changes by less than 1×10^{-6} Ha from one selfconsistent solution of Eq. 10 to the next. In a typical case this requires between 4 to 6 cycles.



FIG. 1: Flowchart of a quasi-self consistent LSIC calculation.

In addition to assessing the performance of the original LSIC energy functional, we also explore the effect of replacing $z_{\sigma}(\vec{r})$ by one of several functions $f(z_{\sigma}(\vec{r}))$ These functions were chosen such that f(0) = 0 and f(1) = 1, insuring exact behavior for a uniform density and a one-electron density in all cases. A list of the functions is given in Table I and they are plotted in Fig. 2. The functions clearly differ in how they weight the corrections. For example, in LSIC(a), $f(z_{\sigma}) > z_{\sigma}$ for all $0 < z_{\sigma} < 1$, so that LSIC(a) reduces the SIC less in many-electron regions than the original LSIC or the other LSIC variants shown in Fig. 2. For LSIC and LSIC(b-d), the average of $f(z_{\sigma})$ over all z_{σ} is 0.5, but in LSIC(b-d), $f(z_{\sigma}) \approx 0.5$ over an increasing range of z_{σ} values. LSIC(b) is called LSIC+ in Refs. 30 and 29. Like SCAN, LSIC+ is designed to be exact for all three leading-order terms proportional to $Z^{5/3}$, $Z \ln Z$, and Z for the exchange-correlation energies of neutral atoms of large atomic number Z, while LSIC is only exact for the $Z^{5/3}$ and $Z \ln Z$ terms.

Method	f(z)
LSIC	z
LSIC(a)	$z^{1/3}$
LSIC(b) 0.5 +	$0.5(z - 0.5) + 2(z - 0.5)^3$
LSIC(c)	$0.5 + 4(z - 0.5)^3$
LSIC(d)	$0.5 + 16(z - 0.5)^5$

TABLE I: The functions of the iso-orbital indicator $z_{\sigma}(\vec{r})$ used in the locally scaled self-interaction correction methods studied in this work. LSIC corresponds to the method introduced in Ref. 25. LSIC(b) is called LSIC+ in Ref. 30.



FIG. 2: $f(z_{\sigma})$ vs. the iso-orbital indicator z_{σ} for the different local scaling methods investigated in this work.

The PZ-SIC and LSIC energy functionals are orbital dependent. Thus, in each case minimizing the energy requires finding not only the correct total electron density, but the optimal set of orthonormal orbitals consistent with that density.[2] For all SIC calculations in this study we used the Fermi-Löwdin orbital self interaction correction (FLO-SIC) formalism proposed by Pederson and co-workers[3, 34] to find optimized orbitals. In FLO-SIC, the PZ-SIC energy functional is evaluated using Fermi-Löwdin orbitals (FLOs), which are determined using a set of parameters, N positions in space for N occupied orbitals, known as Fermi-orbital descriptors (FODs). The gradients of the energy with respect to the FODs can be computed[35] and used in a gradient optimization scheme to determine optimal FOD positions. The optimized Fermi-orbital descriptors from the full PZ-SIC calculations are used in the corresponding scaled calculations. All results presented below are taken from calculations using the FLOSIC code.[36] FLOSIC inherits features such as extensive Gaussian-orbital basis sets[37] and a highly accurate numerical integration scheme[38] from its parent program, NRLMOL.[38–40] Here we use the Perdew-Wang exchange-correlation local spin density approximation (LSDA-PW92)[41] in conjunction with PZ-SIC and the various scaled SIC methods.

In this study, we assess the performance of the scaled methods for calculating molecular dipole moments (μ) and atomic polarizabilties. We use a diverse set of 47 molecules employed in the recent work of Johnson *et al.* [4]. The molecules in this set span a range of bonding types and dipole moments. The geometries and reference CCSD(T) dipole values for the molecules are taken from Ref. 42. We compute the dipole $\vec{\mu}$ by integrating over the (quasi-) self consistent density

$$\vec{\mu} = \int d^3 r \rho(\vec{r}) \vec{r}.$$
(11)

This is then converted from atomic units to Debye units, using 1 D = 0.3934 atomic units. To insure the convergence of the dipoles with respect to the basis set, we follow Ref. 4 and add one additional diffuse single Gaussian orbital (SGO) of *s*-, *p*-, and *d*-type to the default FLOSIC basis sets[37]. The exponent G_{i+1} for the additional SGOs is chosen according to an even-tempered scheme: $G_{i+1} = G_i^2/G_{i-1}$. Adding the extra diffuse functions reduces the mean absolute difference between dipole values computed with the PBE functional in the FLOSIC code and corresponding values computed at essentially the complete basis set limit in the reference work of Hait and Head-Gordon[42] from roughly 0.04 D to about 0.01 D.

In the statistical analysis of the relative errors, we use the regularized error (RE)[4, 42]

as the metric for accuracy:

$$RE = \frac{(\mu_{\text{calc.}} - \mu_{\text{ref}})}{\max(1 \text{ D}, \mu_{\text{ref}})} \times 100\%.$$
 (12)

This prevents errors for molecules with small dipole moments from dominating the results. In addition to the full set, we also separate out a subset of 12 ionic molecules with $\mu > 5$ D (LiCH₃, LiBH₄, LiCl, LiCN, LiF, LiH, LiN, NaCl, NaCN, NaF, NaH and NaOH) for analysis. The bonding in the molecules of this ionic subset is more uniform and uncorrected DFAs perform in a more systematic way across the set.

For polarizabilities, we considered the atoms and anions with closed electronic shells from Li to Ar. We compute the polarizability by using the finite field approach

$$\alpha_{ij} = \frac{\mu_i(\delta E_j) - \mu_i(-\delta E_j)}{2\delta E_j} \tag{13}$$

where δE_j is the strength of the uniform external electric field in the Cartesian j direction. We found that a field strength of 0.005 a.u. gives satisfactory results for the numerical derivative. We report the isotropic average values ($\alpha = \frac{1}{3} \sum_i \alpha_{ii}$) of the polarizabilities below. We use the same extended basis sets for the polarizability calculations as used for the molecular dipole calculations.

III. RESULTS AND DISCUSSION

A. Dipole moments

Mean regularized errors (MRE) and mean absolute regularized errors (MARE) of the calculated dipole moments for the 47 molecules from global scaling SIC calculations with the LSDA-PW92 functional are presented in Fig. 3. In all cases, the errors were calculated using CCSD(T) values taken from Ref. 42 as the reference. Results for each individual molecule can be found in the supplemental information. The summary shown in Figure 3 indicates that uncorrected LSDA-PW92 underestimates the dipole moments of the test set on average, while incorporating SIC increases the magnitude of the dipoles relative to the reference values. Full PZ-SIC gives the smallest MRE (-0.2%) for the full set, but the 50% scaling scheme (MRE = -1.8%) performed best in terms of MARE (7.4%). For the subset



FIG. 3: Mean regularized errors (MRE) and mean absolute regularized errors of the calculated dipoles for a 47 molecule test set relative to CCSD(T) reference values using global scaling SIC methods.

of ionic molecules, LSDA underestimates the dipole moments significantly (MRE of -4.8%), while 100% SIC gives dipoles that are somewhat over-corrected, making them larger than the CCSD(T) dipoles (MRE and MARE of 1.4% and 1.6%). 50% SIC gives MRE and MARE between those of LSDA and full PZ-SIC, but 75% scaling gives the best results with a MRE of 0.3% and MARE of 0.8%. These results show that, within a global scaling scheme, a larger scaling factor of the SIC is needed to capture the physically correct charge separation in the more ionic molecules.

The performance of local scaling methods is somewhat mixed. The MRE and MARE for this set of 47 molecules are presented in Fig. 4 along with the corresponding results given by LSDA-PW92, 50% global scaling SIC, full PZ-SIC-LSDA-PW92 and SCAN calculations for comparison. The MRE of the LSIC methods lies between those of LSDA and 100% SIC, as might be expected since the local scaling methods are designed to reduce the effect of the full PZ-SIC. As might be expected from Fig. 2, the MRE for LSIC(a) is closest to that of SIC, and the MRE for LSIC is closest to that of 50% global scaling, while for LSIC(b-d)

the MRE is somewhat smaller in magnitude. In terms of MARE, all LSIC variants perform better than either DFT-LSDA or full PZ-SIC. LSIC and LSIC(b) have the smallest MARE among all the local scaling methods ($\approx 7\%$), which is very similar to the result for 50% SIC. However, none of these methods outperforms the uncorrected SCAN functional (MARE of 5.7%). Interestingly, the MARE for LSIC(b-d) steadily increases, despite the MRE staying approximately the same.

While the average results of the LSIC method and 50% scaling are similar as determined by the MRE and MARE, the details for the individual molecules are different. 50% scaling yields dipoles that are typically close to the mean of the values given by LSDA-PW92 and SIC. Averaged over all molecules, the mean average difference between the 50% dipole and the LSDA-PW92/SIC mean is only 0.05 D. For comparison, the average size of the dipoles in the test set is 3.00 D. For LSIC, the predicted dipoles have a much larger mean average deviation of 0.19 D from the mean of the LSDA and SIC values and in several cases are outside the range set by these values. Thus, the effect of local scaling on the dipole moments is more nuanced than that of global scaling.

For the ionic molecules, the local scaling methods tend to overestimate the dipole moments, with MRE and MARE between 2% and 3%, respectively. A close inspection of the results reveals that they can be divided into two groups, one involving molecules that contain H atoms and one that does not. Detailed results for the individual molecules in these groups are given in the Supplemental Information. The MRE and MARE for the two groups are shown in Table 2 for LSIC and LSIC(a), where they are compared to reference values, and values from LSDA, 50% SIC, and full SIC. LSIC(b-d) results are qualitatively similar to the LSIC results. In both groups of molecules, LSDA underestimates the reference dipole values by about the same amount (MRE of -4.2 and -5.6%, respectively). Similarly, full PZ-SIC overestimates by nearly the same amount (1.5 vs. 1.3%). In clear contrast, the local scaling methods give markedly different results for the two groups. For the molecules without H atoms, LSIC and LSIC(a) perform about as well as PZ-SIC (MRE of 1.4 and 1.5%, respectively). But for the H-containing molecules, LSIC and LSIC(a) have much larger errors (MREs of 5.6 and 3.6%, respectively). For each molecule in this group, the LSIC and LSIC(a) dipoles lie outside the range set by the LSDA and PZ-SIC values.



FIG. 4: Mean regularized error (MRE) and mean absolute regularized error (MARE) of the calculated dipoles for 47 molecules relative to reference CCSD(T) values for the local scaling methods.

System	Ref. LSDA	LSIC	LSIC(a) I	LSIC(b)	LSIC(c)	LSIC(d) 5	0% SIC	SIC	SCAN		
	Ionic molecules without H atoms										
MRE (%)	-4.2	1.4	1.5	0.9	0.4	-0.1	-0.6	1.5	-1.2		
MARE $(\%)$	4.2	1.4	1.5	1.0	0.9	1.1	0.8	1.5	1.2		
	Ionic molecules with H atoms										
MRE (%)	-5.6	5.6	3.6	6.0	5.9	5.4	-1.6	1.3	-0.7		
MARE $(\%)$	5.6	5.6	3.6	6.0	5.9	5.9	1.6	1.7	0.8		
	All ionic molecules										
MRE (%)	-4.8	3.1	2.4	3.0	2.7	2.2	-1.0	1.5	-1.0		
MARE $(\%)$	4.8	3.1	2.4	3.1	3.0	3.1	1.1	1.6	1.1		

TABLE II: Mean regularized error (MRE) and mean absolute regularized error (MARE) of calculated dipoles for the ionic molecules ($\mu > 5.8$ D) in the test set.

To better understand this behavior, it is useful to consider how the values of the

scaling functions vary near the atoms in the H-containing molecules. In Fig. 5 we present $f(z_{\sigma}(\vec{r}))$ for NaH along the interatomic axis for LSIC, LSIC(a), and LSIC(c). $f(z_{\sigma})$ is close to one in a larger volume near the H atom than in the region around the Na atom. The detailed behavior of $f(z_{\sigma})$ can be understood by considering the nature of the charge density in the molecule. Near the H atom, the density is dominated by the H 1s orbital and is thus one-electron like. This is consistent with a value of $z_{\sigma} \sim 1$ in this region and $f(z_{\sigma}) \sim 1$ for all of the local scaling methods. z_{σ} drops to zero at approximately the bond center (~ 2.1 Bohr) where the total density has a local maximum and $f(z_{\sigma})$ goes to zero for each method. In the volume around the Na atom, the average value of $f(z_{\sigma})$ depends on the method. The scaling function is closest to one for LSIC(a). The scaling function is smallest for LSIC(c) over most of the volume near Na. (z_{σ} drops to zero right at the position of the Na and H nuclei. This is an inconsequential artifact that originates in the use of Gaussian-type orbitals, which have zero gradient at the nuclear position.)

The implication of Fig. 5 is that the SIC potentials near the H atom are nearly unscaled, while near the Na atom, they are significantly reduced. Because the SIC potentials are dominated by the self-Coulomb part, they are negative (attractive). Thus, in the local scaling methods, the region near the H atom will be relatively more attractive to electrons than in full PZ-SIC. This affects the dipole moments in the two methods. PZ-SIC gives a dipole of 6.69 D in the negative x-direction for NaH, showing a transfer of electronic charge from Na to H. This is much larger than the value of 5.68 D in LSDA, indicating that SIC helps to stabilize the anionic part of the molecule. In LSIC, the dipole is 7.16 D in the same direction. This shows that there is even more charge transfer towards the H atom in LSIC than in PZ-SIC, consistent with a relatively less attractive SIC potential near the Na atom. For LSIC(a) the dipole is 6.87 D and for LSIC(c), 7.42 D, reflecting less and more relative stabilization of the H site, respectively. It is also interesting to consider the effect of local scaling on diatomic molecules where the H atom loses electronic charge. In HCl, for example, the LSDA dipole is 1.12 D. This is increased to 1.20 D in SIC, reflecting a larger charge transfer from H to Cl, as expected due to the relative stabilization of the anionic side of the molecule by SIC. But the LSIC dipole in this case is only 1.03 D, evidencing a *reduction* in charge transfer from H compared to both LSDA and SIC. In this case, the smaller scaling of the SIC potential around the H atom overrides the tendency of PZ-SIC to

favor greater ionicity. In LSIC(a) the dipole is 1.10 D and in LSIC(c), 1.04 D.



FIG. 5: The interior scaling functions of the iso-orbital indicator $z(\vec{r})$ plotted along the bond direction of NaH for LSIC, LSIC(a) and LSIC(c), respectively. The Na nucleus is located at x=0 and the H nucleus is at x=1.89 Å. The forms of the functions are shown in Table 2. $z(\vec{r})$ falls to 0 at the nuclear positions due to use of atom-centered Gaussian orbital basis sets.

B. Water complexes

Johnson et al. recognized that standard DFAs dramatically overestimate and underestimate the dipole of H₂O-Li and H₂O-F, respectively, and that PZ-SIC largely corrects these errors.[4] This makes these two systems interesting cases in the context of the SIC scaling methods, since the uncorrected DFA dipoles (0% SIC) are far from the reference values, while the SIC values are very close. We present the calculated dipole moments for those two systems using the various scaling methods in Table III. We also include results for H₂O-Al, for which the LSDA dipole (4.19 D) is in reasonable agreement with the reference value (4.36 D). For H₂O-Li and H₂O-F, all of the local scaling methods result in significantly improved dipole moments compared to the LSDA values, i.e. the local scaling results are much closer to the SIC results than the LSDA results. The 50% scaling results, by contrast,

	Ref.	LSDA	LSIC	LSIC(a)	LSIC(b)	50% SIC	SIC	SCAN
H ₂ O-Li	3.62	1.74	3.45	3.35	3.81	2.64	3.42	2.75
H_2O -F	2.19	3.37	2.44	2.22	2.44	2.57	2.18	2.95
H_2O-Al	4.36	4.19	4.42	4.38	4.52	4.32	4.395	4.44

TABLE III: Calculated dipole moments (in D) for three H_2O-X complexes. The 50% scaling method gives dipole values that are near the average of the LSDA and SIC results. The LSIC methods give values that are closer to the SIC results and in better agreement with reference values.

are nearer the mean of the LSDA/SIC results and thus in clearly worse agreement with the reference dipoles. For H_2O -Al, the LSIC and LSIC (b-d) dipoles are somewhat larger than the SIC value and further from the reference. In this instance, the 50% SIC dipole is closer to the SIC value and in reasonable agreement with the reference. Of the local scaling methods, LSIC (a) gives the closest results to the SIC values and also to the reference values.

The H_2O-X complexes are weakly bound systems and it is reasonable to expect that the frontier orbital of the atom is key to determining the properties of each complex. To gain understanding into the relative success of the different methods in describing these complexes, we examine the orbital energies of the highest occupied molecular orbitals (HOMOs) of each constituent. In Table IV we compare the HOMO energies calculated in LSDA, SIC, and the various scaled SIC methods against the experimental ionization potentials (IP) for Li, F, Al, and H₂O. For the exact functional, the negative of the HOMO level equals the IP.[43, 44] In all cases, the magnitude of the LSDA value is significantly smaller than the IP, and the SIC value is somewhat larger. The 50% SIC value is near the LSDA/SIC mean in all cases and smaller than the IP. The LSIC values, on the other hand, are closer to the SIC than the LSDA value and very close to the IP. This better description could account for the relative success of the local scaling methods over 50% SIC for these complexes.

	$\mathrm{IP}_{\mathrm{exp}}$	LSDA	LSIC	50% SIC	SIC
Li	0.198	-0.116	-0.188	-0.159	-0.202
F	0.640	-0.385	-0.645	-0.550	-0.724
Al	0.220	-0.110	-0.223	-0.175	-0.242
$\rm H_2O$	0.464	-0.271	-0.477	-0.403	-0.543

TABLE IV: Comparison of calculated HOMO energy levels (in Hartree) against experimental ionization potentials (IP_{exp}).

C. Molecular dissociation

In approximate DFT, many neutral diatomic molecules dissociate to a minimum energy state with residual charge on the isolated atoms. This undesired effect has been attributed to many-electron self-interaction error. [45]. PZ-SIC typically eliminates this error, giving neutral atoms in the separated atom limit, but scaled-down SIC can fail to do so. An indicator of the error is a non-zero dipole that grows linearly as the atoms are separated. Johnson et al.[4] studied the dipole moment of the HF molecule versus separation and showed that PZ-SIC yields values in good qualitative agreement with results from reference wave function calculations. To investigate the effect of scaling, we repeated these calculations using the LSIC and 50% SIC methods. In Fig. 6 we show the calculated dipole moment versus H-F bond length for LSDA, LSIC, 50% SIC and full SIC, along with reference values obtained from two wave function-based methods, CCSD(2)[46] and CASPT(2)[47]. All methods agree well near the equilibrium bond length of approximately 1 Å and all predict an initial linear increase in the dipole as the bond is stretched beyond that point. The three SIC calculations then predict that a maximum in μ is reached near 1.5 Å, after which the dipole drops gradually to zero, in good qualitative agreement with the reference calculations. The turning points in the LSIC and 50% SIC curves occur at roughly the same bond length, somewhat longer than in full SIC. The value of μ remains significantly larger in 50% SIC than in LSIC at larger separations. All three SIC methods yield zero dipole in the dissociation limit, in agreement with the reference calculations. By contrast, the LSDA dipole grows with the separation of HF, indicating a net charge transfer in the separated atom limit.



FIG. 6: Variation in the calculated dipole moment (μ) (in D) with the separation (in Å) of the atoms in the HF molecule using different methods. The equilibrium HF bond length is near 1.0 Å.

D. Polarizabilities

Table V shows the calculated polarizabilities and the corresponding reference values for spherical neutral atoms and anions from Li to Ar. Results for LSDA, full and 50% SIC and for the various local scaling SIC methods are included. LSDA overestimates (MPE = 6.7%) the polarizabilities for most of the neutral atoms as we found and discussed previously.[5] Full SIC improves the LSDA polarizabilities in all cases, but often overcorrects, leading to underestimated polarizabilities on average (MPE = -2.6%). 50% SIC yields the best MPE among all the methods (0.3%), but is only slightly better than full SIC in terms of absolute errors (MAPE = 5.5 and 5.9% for 50% and 100% SIC, respectively). All the LSIC methods except LSIC(a) significantly overestimate the polarizabilities of the neutral atoms (MPE of ~ 11%). It should be noted that LSIC and LSIC(b-d) perform especially poorly for Li, Be, Na, and Mg, where they overestimate the polarizabilities significantly (from 16 - 20%). For these cases in which the outer electrons are in s-type orbitals, the following comments can be made. First, the polarizability is almost entirely due to shifts in the outer orbital density. Second, for the outer electron, there is nearly no scaling of the SIC potential in

the outer region of the atom, but there is significant scaling down of the SIC potential in the region where the core electron density is significant. This results in the density of the outer electron being reduced in the core region and enhanced in the outer region, leading to a more polarizable outer electron. For the remaining atoms, the local scaling methods still overestimate reference values, but are much closer (from 6.2% to 2.4% from LSIC to LSIC(d)). LSIC(a), which is closest to full PZ-SIC among the local scaling methods, gives the best performance among the local scaling methods and the best MAPE (4.8%) of all methods.

Full SIC underestimates the polarizabilities of the anions significantly (MPE of -21.2%). The local scaling methods increase the calculated polarizabilities and thus correct the full SIC values towards the reference calculations. LSIC yields the best overall results (MPE = 3.6% and MAPE = 8.2%). Like full SIC, LSIC(a) significantly underestimates the polarizabilities on average (MPE = -12.3%). It is clear from these results that local scaling methods do not offer a clear advantage for the calculation of response properties (particularly polarizabilities in this case) for neutral atoms in comparison to the best results of global scaled SIC methods.

For the spherical anions, 100% SIC yields polarizabilities that are too small, corresponding to electrons that are too tightly bound and therefore not sufficiently polarizable (MPE = -21.2%). LSIC(a) also underestimates reference values (MPE = -12.3%). On the other hand, 50% scaling leaves the outer electrons unbound, making the anions unstable in this method, as they are in LSDA. LSIC, LSIC(b), and LSIC(c) yield better mean errors and mean absolute errors for the anion polarizabilities than the other methods.

IV. SUMMARY

In this article we presented molecular dipole moments and atomic polarizabilties calculated using different local scaling approaches in which the self-interaction correction terms employed in PZ-SIC were scaled at each point in space according to the character of the charge density at that point. For comparison, we also included global scaling methods in which the SIC terms in the total energy and in the one-electron Kohn-Sham-like equations were simply reduced to 25%, 50% and 75% of their full PZ-SIC values. The local scaling methods included the LSIC method introduced by Zope et al.[25], as well as several

System	Ref.	LSDA	LSIC	LSIC(a)	LSIC(b)	LSIC(c)	LSIC(d)	50% SIC	SIC
Atoms									
Li	164.19	145.27	181.04	165.03	180.48	180.05	180.30	148.86	151.77
Be	37.79	43.92	47.43	44.91	47.42	47.45	47.57	43.31	42.64
Ν	7.42	8.11	7.91	7.31	7.77	7.64	7.54	7.36	6.80
Ne	2.57	3.37	2.72	2.53	2.69	2.67	2.65	2.65	2.37
Na	162.70	142.64	186.87	166.20	191.88	196.97	202.33	151.30	154.01
Mg	71.53	71.08	82.28	76.05	83.28	84.26	85.36	72.04	71.46
Р	24.50	28.17	27.29	25.59	26.83	26.41	26.11	25.72	24.57
Ar	11.23	11.99	11.36	10.91	11.24	11.17	11.04	10.81	10.67
MPE		6.7	11.3	3.3	11.1	11.0	11.1	0.3	-2.6
MAPE		12.8	11.3	4.8	11.1	11.2	11.6	5.5	5.9
Anions									
Li^-	828.58	-	997.79	919.42	998.73	999.99	1003.22	-	806.75
C^{-}	74.81	-	75.74	55.64	78.94	87.55	84.59	-	45.44
F^-	15.54	-	13.72	11.48	14.37	15.19	15.51	-	10.20
Na ⁻	1106.80	-	1092.67	959.15	1109.04	857.54	1155.34	-	899.30
Si^-	151.76	-	172.34	137.86	173.94	176.43	171.60	-	123.42
Cl ⁻	36.19	-	35.89	32.38	36.27	36.76	36.83	-	29.93
MPE		-	3.6	-12.3	5.6	5.1	8.9	-	-21.2
MAPE		-	8.2	15.9	8.1	13.4	8.9	-	21.8
Overall									
MPE		-	8.0	-3.4	8.7	8.5	10.2	-	-10.9
MAPE		-	10.0	9.6	9.8	12.1	12.7	-	12.7

TABLE V: Calculated polarizabilities of spherical atoms and anions. The reference values for neutral are experimental results[48]. The reference values for anions are from CCSD calculations done with same basis set.

variations of it. All of these local scaling schemes are designed to give exact results in the limits of a single electron density and a uniform density.

Our results show that 50% global scaling gives the best dipole moments on average for our test set of 47 diverse molecules, significantly outperforming 100% SIC in mean absolute regularized error. The locally scaled methods LSIC and LSIC(b) perform essentially as well. Using an ionic subset of the test molecules we found that the LSIC method can give systematic errors in molecules containing H atoms. The SIC potential is largely unscaled in the volume around an H atom in an LSIC calculation, making that region relatively more favorable for electrons than around other atoms. Dipole moments are affected as there is relatively more electron charge transfer to the H atoms than reflected in the corresponding reference dipole values.

Scaling SIC differently in different regions of space proves favorable in weakly bound complexes of a water molecule and Li and F atoms. For these systems full SIC gives an excellent description of the dipoles, while LSDA fails dramatically. The results for the locally scaled methods are similar to the SIC results, while results using 50% SIC global scaling are decidedly worse, essentially just averaging the LSDA and SIC results.

The locally scaled methods perform somewhat worse than the 50% global scaling method in calculating the polarizabilities of neutral spherical atoms. For the atoms with s-type outer electrons, LSIC and its variants overestimate the polarizabilities even more than LSDA does, with the exception of the LSIC(a) variant, which scales down corrections the least of all the locally scaled methods. The LSIC(a) polarizabilities have the smallest mean absolute percentage error of all the methods tested including 50% and 100% SIC. Importantly, and in contrast to 50% global scaling and LSDA, locally scaled methods give bound valence electrons even for atomic anions, and thus can be utilized for the calculation of polarizabilities in anionic systems.

The dramatic improvements in the performance of density functional approximations over the past forty years have been due to constructing functionals that incorporate more and more of the behavior of the exact density functional. Because the local scaling methods are designed to recover a feature of the exact functional that is lost in PZ-SIC, they offer a promising path toward building an improved self-interaction-free method. Our purpose in studying various local scaling corrections here is to better understand how local scaling methods work in a practical setting and not to determine an empirically best scheme for repairing PZ-SIC's tendency to over-correct density-related properties. The results presented show that local scaling has a more subtle effect than global scaling. The 50% SIC method gives results that are typically close to the mean of LSDA/SIC for all properties studied. The local scaling methods are more variable, sometimes giving results close to the LSDA results, in other cases close to the SIC results, and in several cases outside the limits defined by the LSDA and SIC results. The LSIC(a) method, which scales SIC the least of all the local scaling methods tested, gives results that are closest to those of SIC. LSIC and LSIC (b-d) are similar in the sense that the average of the function of the scaling parameter over all values of z_{σ} is 0.5 in all cases. This may be the reason that the results for these methods are generally similar.

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V. DATA AVAILABILITY

The data that supports the findings of this study are available within the article and its supplementary material. The geometries of the molecules studied here and their optimized positions can be found in Ref. 4 and its supplementary material.

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