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Self-interaction-free electric dipole polarizabilities for atoms and their ions using the Fermi-Löwdin self-interaction correction (FLO-SIC)

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Abstract

The static electric dipole polarizability of a system is a measure of the binding of its electrons. In density functional theory (DFT) calculations, this binding is weakened by the presence of unphysical self-interaction in the density functional approximation (DFA), leading to overestimates of polarizabilities. To investigate this systematically we compare polarizabilities for the atoms from H to Ar and their anions and cations calculated in several DFA's and the corresponding self-interaction corrected (SIC) DFAs with experiment and with high-level quantum chemistry reference values. The SIC results are obtained using the Fermi-Löwdin orbital self interaction correction (FLO-SIC) method. Removing self-interaction generally leads to smaller polarizabilities that agree significantly better with reference values. We find that FLO-SIC improves the performance of the local spin density approximation and the generalized gradient approximation (GGA) for polarizabilities to a quality that is comparable to so-called rung 4 functionals, but slightly degrades the performance of the strongly constrained and appropriately normed (SCAN) meta-GGA functional.

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I. INTRODUCTION

One effect of the spurious self-interaction present in density functional approximations (DFAs) of the exchange-correlation energy is that the potential experienced by an electron in a neutral atom decays exponentially at large distances from the nucleus, rather than with the correct $-1/r$ behavior. This leads to weakened binding, especially of the outermost electrons, the effects of which show up in various ways in density functional theory (DFT) calculations. For example, it is well-known that occupied orbital energies are too high in DFT calculations employing semi-local functionals, making them poor predictors of electron removal energies.[1, 2] A related consequence is that DFT calculations predict all atomic anions to be unbound, even in cases where the experimental electron affinity is positive.[1] Removing the self-interaction using the Perdew-Zunger self-interaction correction[1] (PZ-SIC) restores the correct long-range behavior of the potential and leads to physically meaningful orbital energies[2] and bound anions[1].

The static dipole polarizability is another property related to the binding of the electrons and is therefore affected by self-interaction errors (SIEs) in DFT calculations. Early calculations using SIC applied to the local (spin) density approximation (LSDA) found that polarizabilities for closed-shell atoms are reduced by removing self-interaction.[3, 4] Other SIC studies focused on the polarizability of long chain-like molecules[5–7] where again it was found that eliminating SIE reduces DFA polarizabilities and brings them into better agreement with reference values. More recently, SIC polarizabilities were computed to investigate the nature of the bonding in $\mathrm{Na(H_2O)}_n$ complexes.[8]

In this work we return to the question of the effect of SIE on the polarizabilities of atoms and their cations and anions. We are motivated in part by recent efforts devoted to benchmarking the performance of a large number of DFAs for calculating properties of physical and chemical interest, including the polarizability.[9–14] For example, the extensive study of Hait and Head-Gordon[9] investigated the performance of 60 DFAs for predicting the polarizability of a large number of molecules, as well as a number of spherical atoms, comparing the DFA results against reference coupled cluster with single, double, and perturbative triples (CCSD(T)) values at the basis set limit. The results show that the typical performance of a DFA improves with its position on “Jacob’s Ladder” of approximations,[15] with rung 1 functionals (LSDA’s) faring the worst and rung 5 (double hybrid functionals) doing the best. It is interesting to consider how SIC changes the performance of a functional within this ranking scheme.

A second, related motivation is to compare the impact of SIC on the performance of functionals from different "rungs". It is known that SIC can affect the performance of more or less sophisticated functionals differently. For example, restricted to real orbitals, SIC improves the predictions of atomization energies for LSDA, but degrades them for the Perdew, Burke, and Ernzerhof[16] (PBE) generalized gradient approximation (GGA) and the strongly constrained and appropriately normed[17] (SCAN) meta-GGA functional.[18–22] (Using complex orbitals improves the performance of SIC-PBE over PBE,[23, 24] but even with complex orbitals, SIC-SCAN fails to improve uncorrected SCAN for atomization energies.[22]) The GGA and SCAN functionals are constructed to fulfill more of the known constraints satisfied by the exact exchange-correlation functional than LSDA. Adding SIC to these functionals makes them one-electron self-interaction free, a property of the exact functional, but in the process may cause other constraints or norms to be violated.[25] How the corrected functionals perform for computing the polarizability may give additional insight into these problems. Atoms are a good testing ground for exploring the impact of SIC on polarizabilities. Despite their relative simplicity, the calculation of atomic polarizabilities is still challenging for DFAs.[9]

In this work we use the Fermi-Löwdin orbital self-interaction correction (FLO-SIC) method[26–28] to implement SIC.[1] We compute static dipole polarizabilities for all the atoms from H to Ar, and for their cation and anion charge states. We compare results for LSDA (using the parametrization of Perdew and Wang[29]), PBE[16], and SCAN[17], and their corresponding SIC versions against experimental values and reference values taken from high-level wave function-based calculations.[9] In the next section we present methodological details. That is followed by the presentation and discussion of our results. We conclude with a summary of our findings.

II. METHODOLOGY

The PZ-SIC energy functional[1] can be cast in the form

$$E^{\text{PZ-SIC}} = E^{\text{DFT}}[n_\uparrow, n_\downarrow] - E^{\text{SIC}}\,, \tag{1}$$

with

$$E^{\mathrm{SIC}} = \sum_{i;\sigma=\uparrow,\downarrow} \left(E_{\mathrm{xc}}[n_{i\sigma}, 0] + U_{\mathrm{H}}[n_{i\sigma}] \right). \tag{2}$$

Here $U_H[n]$ is the Hartree electrostatic energy for density $n(\mathbf{r})$. Eq. 1 is by construction orbital dependent and thus finding the minimum energy solution for any system requires not only determining the optimal total charge density n_σ, but also the *optimal* choice of the occupied orbitals for evaluating the SIC part of the PZ-SIC functional.[30] Instead of optimizing the energy with respect to *unitary* rotations of the occupied orbitals, Pederson, Ruzsinszky, and Perdew[26] reformulated PZ-SIC such that the SIC energy depends on a set of Fermi-Löwdin orthogonalized orbitals (FLOs). The Fermi-orbitals (FOs)[31, 32] take the form

$$F_{i\sigma}(\mathbf{r}) = \frac{\sum_j^{N_\sigma} \psi^*_{j\sigma}(\mathbf{a}_{i\sigma})\psi_{j\sigma}(\mathbf{r})}{\sqrt{\sum_j^{N_\sigma} |\psi_{j\sigma}(\mathbf{a}_{i\sigma})|^2}}, \tag{3}$$

where N_σ is the number of electrons with spin σ. Each FO, $F_{i\sigma}(\mathbf{r})$, depends on a coordinate in space, $\mathbf{a}_{i\sigma}$, referred to as a Fermi–orbital descriptor (FOD), and the density constructed by any set of orbitals $\psi_{j\sigma}(\mathbf{r})$ that spans the occupied space. Since the localized FOs are normalized but not mutually orthogonal, the Löwdin symmetric orthogonalization procedure[33] is then performed on the FOs to obtain the orthonormal local orbitals (FLOs), $\phi_{i\sigma}(\mathbf{r})$, which are used in the Schrödinger-like PZ–SIC equations, which are solved self-consistently. Complete details of the FLO-SIC methodology and calculations are available elsewhere.[2, 26–28, 34–38].

All the DFT and FLO-SIC-DFT results reported below were obtained using the FLOSIC code[39]. FLOSIC inherits the optimized Gaussian orbtial basis sets[40] and variational numerical integration mesh[41] of its parent NRLMOL code. The SCAN calculations are done using a very fine integration grid that includes roughly three times more points than are needed in LSDA or PBE calculations.

The static dipole polarizability α of a system can be defined as the derivative of its electric dipole μ with respect to an applied uniform electrostatic field, in the zero field limit. We use a finite difference approach to computing the components of polarizability tensor α_{ij}:

$$\alpha_{ij} = \frac{d\mu_i}{dE_j}|_{E=0} = \lim_{\delta E_j \to 0} \frac{\mu_i(+\delta E_j) - \mu_i(-\delta E_j)}{2\delta E_j}. \tag{4}$$

Here μ_i is the i^{th} component of the dipole, computed as an integral over the charge density, and δE_j is the magnitude of a small electric field applied in the j^{th} coordinate direction.

Independent self-consistent (scf) calculations are carried out for each field orientation. In FLO-SIC calculations, both the total charge and the local orbitals must be optimized for every choice of field and we therefore independently optimize the FODs for each. For the neutral atoms, the optimal FODs found previously in zero field[2] are taken as starting points for all field directions. For anion and cation calculations the starting points are the optimal FOD positions of the isoelectronic neutral atoms. In all cases, the starting density for a FLO-SIC calculation is the corresponding zero-field optimized DFT density.

The strength of the applied field is chosen small enough that the zero field limit of the derivative is obtained, but not so small as to cause numerical instabilities. For neutrals and cations, we find that a value of 0.005 atomic units (a.u.) yields converged results. For anions we find that a smaller value of 0.0005 a.u. is required due to the more extensive nature of the orbitals. An scf convergence criterion of 10^{-8} Ha on the total energy is used in all calculations to ensure well converged dipoles.

We also converged the polarizability results with respect to the choice of basis set. The default Gaussian orbital basis sets were optimized for use in DFT calculations[40] and tests comparing standard quantum chemistry basis sets indicate that the NRLMOL basis set roughly corresponds to quadruple zeta quality.[21] The basis for all atoms considered here include s-, p-, and d-type Cartesian functions. The number of exponents used to construct the basis for a given atom was chosen[40] to yield a total energy in zero applied field that is converged to 10^{-6} Ha. Contracted functions are used to represent the occupied orbitals; these are augmented by single Gaussian orbitals.

For accurate cation polarizabilities, we find the default NRLMOL basis sets sufficient to give results converged to better than 1%. For the neutral atoms from C - Ne and Si - Ar we find that we need to include one additional long range Gaussian exponent to the default basis to reach the same level of convergence. For the atoms Li-B and Na-Al, two additional exponents are needed. For the anions, three additional exponents are required to achieve converged results. In all cases, the extra exponents are used to create s, p, and d type single Gaussian orbitals. The added exponents (β) are obtained using the relation $\beta^{N+1} = \frac{\beta^N}{\beta^{N-1}}\beta^N$. This maintains the even-tempered character of the exponents. Given the preceding, the typical longest-ranged Gaussian exponent for cations, neutrals, and anions is 0.2, 0.02, and 0.002, respectively. The long range of the anion basis functions requires that a smaller external electric field be used in the calculations, to achieve convergence. As noted above, a value of 0.0005 a.u. yields consistent results. The integration grid used in the FLOSIC code automatically adjusts to the range of the basis functions to ensure accurate integration in regions far from the nucleus. The grid employed in these calculations generally integrates the total atomic charge to a precision of 10^{-8} e.

We apply fields in the ± x, ± y, and ± z directions to compute each of the diagonal elements of polarizability tensor, α_{ii}. The isotropic average polarizabilities are reported below, defined as $\alpha = \frac{1}{3}\sum_i \alpha_{ii}$. We also computed polarizabilities from finite field coupled-cluster singles and doubles (CCSD) calculations, using the GAUSSIAN software package[42] and an applied field strength of 0.0005 a.u. The CCSD calculations are based on unrestricted Hartree-Fock (HF) reference wave functions. We used the same basis sets in GAUSSIAN as in FLOSIC, in order to promote direct comparisons.

III. RESULTS AND DISCUSSION

A. Neutrals and cations

In Fig. 1 we plot the percent difference between the computed values and the corresponding experimental values ($\frac{\alpha_{calc}-\alpha_{exp}}{\alpha_{exp}} \times 100$) of the polarizabilities versus the atomic number Z for the neutral atoms from H to Ar using LSDA, PBE, SCAN, and FLO-LSDA, FLO-PBE, and FLO-SCAN. A number of observations follow from the figure. First, the results for the uncorrected LSDA, PBE, and SCAN calculations exhibit very similar trends versus Z. All three methods generally overestimate the experimental polarizabilities, except at Li and Na. Overall, the PBE results agree somewhat better with experiment than LSDA, and SCAN somewhat better than PBE. Typical errors for LSDA and PBE lie between 10 and 20%, while errors for SCAN are mostly less than 10%.

FLO-SIC generally reduces the size of the calculated polarizabilities for the neutral atoms for all three functionals, in nearly all cases bringing them into better agreement with experiment. Typical errors are reduced to less than 10% for FLO-LSDA and less than 5% for FLO-PBE and FLO-SCAN. Results for FLO-LSDA, FLO-PBE, and FLO-SCAN also show similar overall trends vs Z, but these are different from the trends for the uncorrected methods. The largest errors occur at Be, O, and F for FLO-LSDA and FLO-SCAN, and Be, O, Na, and Mg for FLO-PBE. FLO-SIC increases the size of the calculated polarizabil-

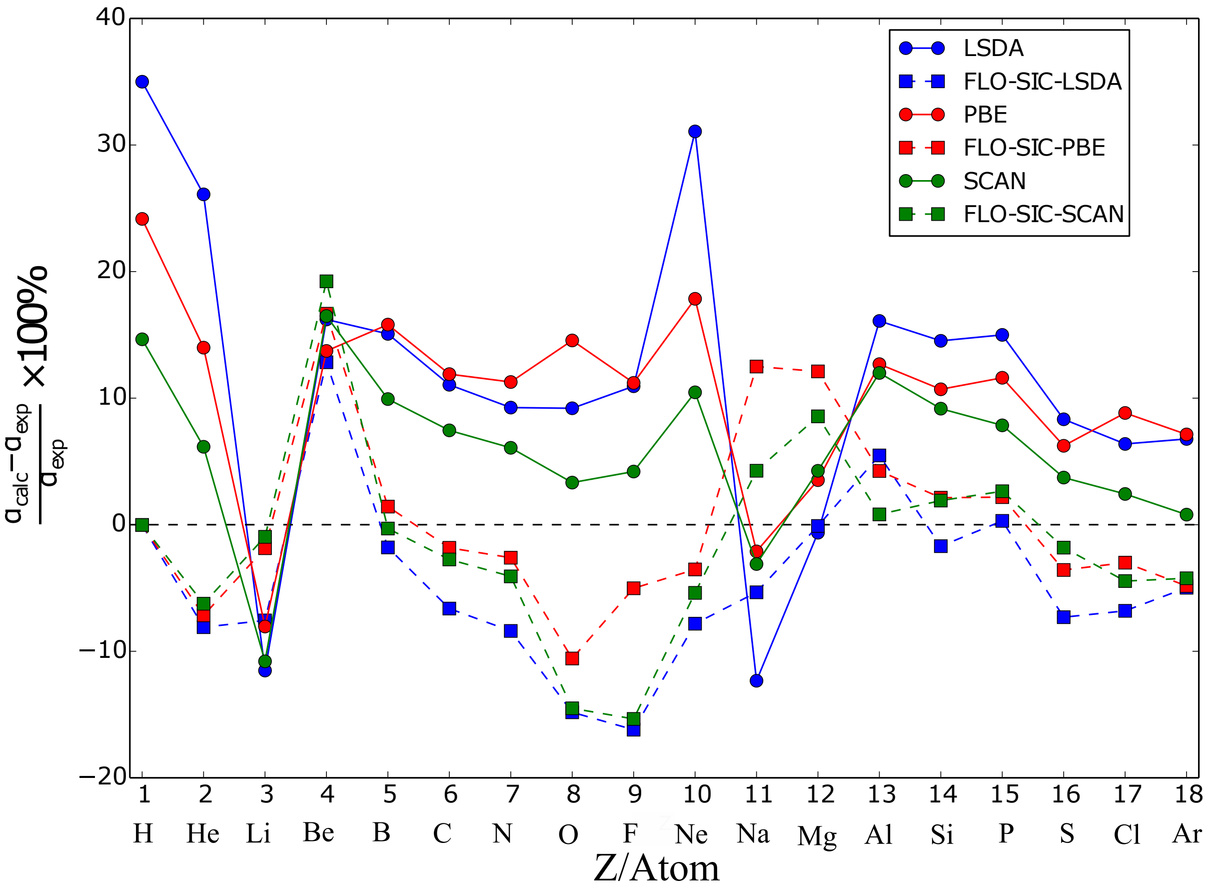

FIG. 1. Percent deviation of calculated polarizabilities from experimental values versus atomic number Z for neutral atoms.

ities for Li and Be and for Na and Mg. For Li, this clearly leads to better agreement with experiment. For Na, FLO-PBE and FLO-SCAN over corrects the DFA polarizabilities to above the experimental values. For Mg, both LSDA and FLO-LSDA results are close to experiment. The PBE and SCAN values are somewhat larger than experiment, and SIC pushes these even higher.

For the cations we use CCSD results as references, since experimental values are not available. The CCSD polarizabilities for the neutral atoms agree very well with experiment, with a mean error of only 1.7% from H to Ar, and a mean absolute error of 2.4%. The only outlier is at Na, where CCSD predicts a polarizability of 187.6 a.u., compared to an experimental value of 162.7. This may be a basis set effect. Hait and Head-Gordon recently obtained[9] a CCSD value for Na of 165.8 a.u. Neglecting this case, we expect that CCSD results provide suitable reference values.

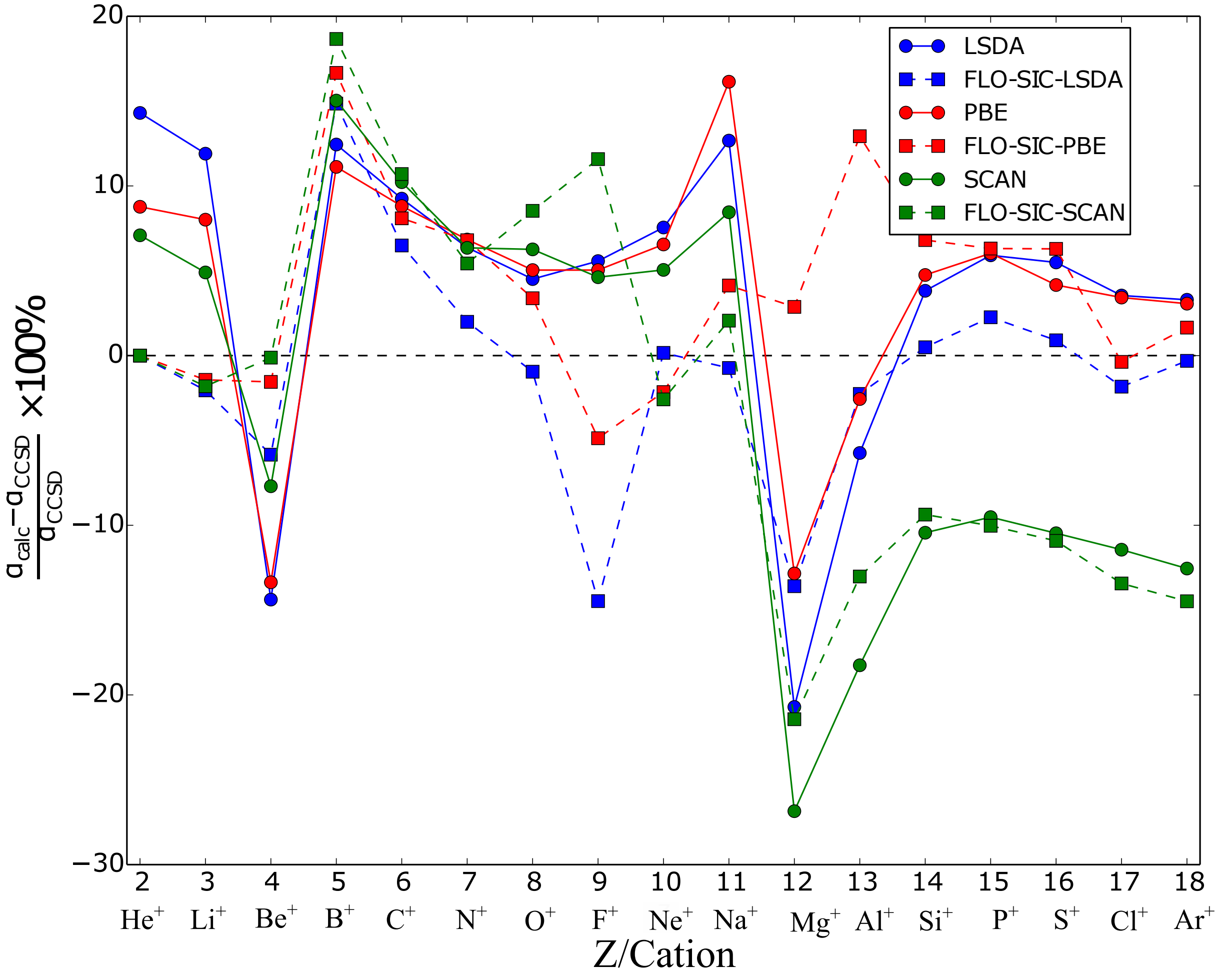

FIG. 2. Percent deviation of calculated polarizabilities from reference CCSD values vs atomic number Z for singly-charged cations.

The calculated LSDA, PBE, and SCAN polarizabilities for the cations again show similar trends versus Z. For He^+ to Na^+ the SCAN polarizabilities are in the best agreement with CCSD on average, but for Mg^+ to Ar^+ the SCAN values are furthest from the reference values. Typical differences lie between 5 and 10% for LSDA and PBE. For SCAN, the typical differences are from 0 to +10% for the lighter cations and from -10% to -20% for the second row. The polarizability of Mg^+ is strongly underestimated by SCAN.

The FLO-SIC corrections for the cations generally reduce the size of the polarizabilities for LSDA and PBE and lead to improved agreement with the reference CCSD values. Typical differences are less than 5% for both methods. FLO-SCAN improves the calculated polarizabilities for about half the cases studied. FLO-SIC increases the polarizabilities at Be^+, B^+, Mg^+, and Al^+, for all three functionals, echoing what occurs for the isolectronic

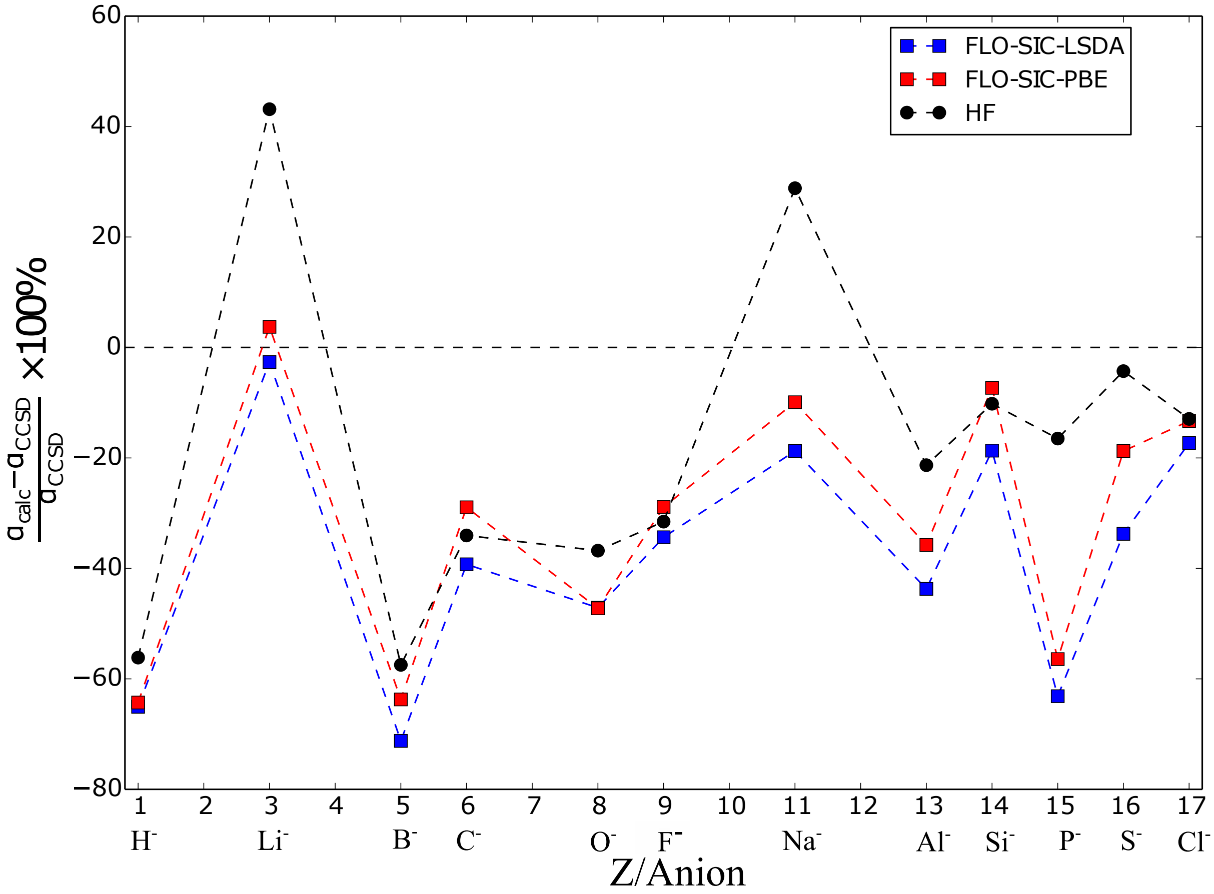

FIG. 3. Percent deviation of calculated polarizabilities from reference CCSD values versus atomic number Z for singly-charged anions.

neutrals. FLO-PBE and FLO-SCAN also increase the calculated polarizability at Si^+ over the uncorrected values. For FLO-SCAN this gives better agreement with the reference value, but for FLO-PBE the agreement becomes worse. The largest errors for FLO-LSDA are at B^+, F^+, and Mg^+, for FLO-PBE at B^+ and Al^+, and for FLO-SCAN at B^+ and Mg^+.

B. Anions

As mentioned in the introduction, standard DFT calculations fail to bind atomic anions due to the presence of electron self-interaction. FLO-SIC removes the self-interaction on an orbital-by-orbital basis and all the anions from H^- to Ar^- that are bound experimentally are also bound in FLO-SIC. In Fig. 3 we present polarizability results for these anions. Shown are the percent differences between FLO-LSDA and FLO-PBE values and corresponding reference CCSD polarizabilities. We also show the percent differences between HF polarizabilities and the CCSD values. The trends versus Z are quite similar for the two FLO-DFA methods. Both underestimate the CCSD values, except at Li^-, where FLO-PBE slightly overestimates the reference. Differences relative to CCSD reference values lie between 0 and -40% in both methods, with outliers at H^-, B^-, and P^-. The FLO-PBE differences are smaller than FLO-LSDA overall. The FLO-DFA results are in better agreement with CCSD than HF for Li^- and Na^-. For those cases, HF significantly overestimates the reference values. For the remaining first row anions the FLO-DFA and HF results are roughly the same in comparison to CCSD, but the FLO-DFA results are generally further from the reference for the second row anions.

TABLE I. Experimental electron affinities, neutral-anion Δ-SCF energies, and absolute value of the highest occupied orbital energies (HOO) for the anions from FLO-LSDA calculations, all in eV.

System	EA_{exp}	Δ-SCF	HOO
H^-	0.75	0.71	1.68
Li^-	0.62	0.55	0.70
B^-	0.28	0.19	1.28
C^-	1.60	1.08	2.42
O^-	1.46	1.06	3.65
F^-	3.40	2.80	5.68
Na^-	0.55	0.53	0.67
Al^-	0.44	0.31	1.01
Si^-	1.38	1.22	1.98
P^-	0.74	0.91	2.17
S^-	2.07	2.06	3.39
Cl^-	3.62	3.46	4.80

The FLO-DFA polarizabilities significantly underestimate CCSD for the anions. This suggests that the electrons are too tightly bound in the FLO-SIC calculations. To investigate the binding of the outer electrons in a different way, we show in Table I the experimental electron affinity for the atom, the total energy difference between the FLO-LSDA calculation for the anion and the neutral charge state (*i.e.* the Δ-SCF value of the electron affinity), and the orbital energy of the highest occupied orbital (HOO) from the FLO-LSDA anion calculations. The magnitude of the HOO orbital energy approximates the energy to remove the electron from the anion, or the electron affinity.

The Δ-SCF values in Table I agree with the experimental electron affinities very well, on average underestimating the experimental values by only about 0.1 eV. The HOO energies, by contrast, overestimate the electron affinities significantly, by roughly 1.1 eV on average. Interestingly, the best agreement(0.1 eV) between the HOO and the electron affinity are for Li^- and Na^-, two cases where the FLO-DFA polarizabilities are relatively close to CCSD. This supports the conclusion that the poor performance of the FLO-DFA methods for the anion polarizabilities is due to overbinding the electrons.

TABLE II. Anion polarizabilities (in atomic units) calculated with various methods. x-only refers to exchange-only versions of the respective density functional approximations.

System	FLO-LSDA X-only	FLO-LSDA	FLO-GGA X-only	FLO-GGA	FLO-SCAN X-only	FLO-SCAN	HF	CCSD
H^-	92.14	73.11	92.22	74.72	92.42	77.66	91.72	209.93
Li^-	1113.03	791.62	1153.34	834.25	1252.69	868.78	1186.05	828.28
F^-	10.98	10.20	12.33	11.05	11.72	10.83	10.64	15.54
Cl^-	32.14	29.93	35.02	31.37	33.35	31.30	31.51	36.19

The HF polarizabilities generally underestimate the reference CCSD values in Fig. 3. This implies that the effect of adding correlation increases the polarizability of the anions, or causes the outer electrons to be less strongly bound. As noted above, exceptions are at Li^- and Na^-, where correlation decreases the HF polarizability. To study the analogous effects in FLO-SIC calculations, we performed exchange-only (x-only) FLO-LSDA, FLO-PBE, and FLO-SCAN calculations for the polarizabilities of H^-, Li^-, F^-, and Cl^-. In x-only calculations, we simply neglect the correlation part of the exchange correlation functional.

The results of the x-only and full exchange-correlation FLO-SIC calculations are shown in Table II, along with the corresponding HF and CCSD values. The FLO-LSDA x-only results are in reasonable agreement with the HF values in all cases. Adding correlation to FLO-DFA x-only calculations decreases the polarizability in all cases, and worsens the agreement with the CCSD reference for all but Li^-, where including correlation in FLO-DFA calculations mirrors the change from HF to CCSD and brings the FLO-DFA results into relatively close agreement with the reference values. A more systematic study of the effect of correlation in these and other FLO-SIC calculations may be of interest for a more detailed understanding of SIC effects and finding improved methods for removing SIE.

C. Discussion

The results presented above show that removing self-interaction error through FLO-SIC calculations generally improves the calculated polarizabilities of the atoms from H to Ar. The Jacob's Ladder scheme[15] of ranking DFAs gives an interesting scale for rating this improvement. In this scheme, rung 1 functionals are LSDA's, rung 2 are GGA's that include both the local spin density and its gradients in the construction of the functional, rung 3 are meta-GGA's that add information related to the local kinetic energy density, rung 4 are hybrid functionals that include some fraction of exact exchange, and rung 5 are those that depend upon unoccupied as well as occupied orbitals, such as double hybrids. In their recent benchmark studies of the performance of density functional methods, Hait and Head-Gordon[9] surveyed roughly 60 DFAs, including multiple representatives of each rung of Jacob's ladder, comparing the computed DFA polarizabilities with reference CCSD(T) results. Their benchmark set included ten spherical atoms (see Table III). The CCSD(T) results for these atoms are in excellent agreement with experimental values, with a mean percentage error of only 0.10%, and thus serve as appropriate references.

In Table III we compare our computed polarizabilities with those of the top-performing DFA of each rung from Ref.[9]. The entries show the mean percentage error (MPE) and mean absolute percentage error (MAPE) compared to CCSD(T) values for the ten spherical atoms. Also shown are the absolute percentage errors for the atoms with the worst agreement for each functional (in parentheses). The Hait and Head-Gordon results indicate that the predicted polarizabilities are more accurate at each successive rung of the ladder, with MAPEs dropping from 14.0% to 2.7% from rung 1 to rung 5, respectively. For rungs 1-4, comparison of the MPE and MAPE values implies that these DFAs generally overestimate

TABLE III. Mean percentage error (MPE), mean absolute percentage error (MAPE), and maximum absolute percentage error (MAXPE) relative to reference CCSD(T) values for the atomic polarizability of ten spherical atoms from H to Ar computed with functionals from the five rungs of Jacob's Ladder (see Ref.[9]) and the DFA and FLO-DFA calculations from this work. The atom corresponding to the MAXPE value is shown in parenthesis for each method.

Method	MPE	MAPE	MAXPE (atom)
Rung 1	10.1	14	35.2 (H)
Rung 2	9.8	13.5	27.2 (Na)
Rung 3	4.2	6.7	14.1 (H)
Rung 4	4.2	5	14.4 (Be)
Rung 5	0.4	2.7	8.6 (Be)
LSDA	11.4	16.4	35.0 (H)
PBE	9.2	11.4	24.2 (H)
SCAN	7.1	7.1	16.5 (Be)
FLO-LSDA	-3.0	5.5	12.4 (Be)
FLO-PBE	2.2	5.8	16.2 (Be)
FLO-SCAN	5.3	8.8	16.5 (Be)

the reference values. Results from our LSDA, PBE, and SCAN calculations are similar to the performance of the rung 1 - 3 functionals, respectively, with MAPEs of 16.4%, 11.4%, and 7.1%. FLO-SIC clearly improves the predictions of LSDA and PBE, reducing the MAPE to 5.5% and 5.8% for FLO-LSDA and FLO-PBE. For SCAN, however, while FLO-SIC reduces the MPE from 7.1 to 5.3%, the MAPE increases slightly, from 7.1% to 8.8%. In the language of Jacob's Ladder, FLO-SIC improves the rung 1 LSDA and rung 2 PBE to roughly the quality of a rung 4 functional, while SCAN is unchanged from rung 3 quality.

We can also consider the worst case for each of the various methods in terms of its perch on Jacob's Ladder. For the rung 1 and 3 functionals, H is the worst case, with errors relative to CCSD(T) values of 35 and 14%, respectively.[9] For rung 2, the worst case is Na, with a 27.2% error, but H is a close second at 24.2%.[9] H is the worst case for our LSDA and PBE calculations, with errors closely matching Hait and Head-Gordon's rung 1 and 2 functionals.

For rungs 4 and 5, which include admixtures of exact exchange that remove some of the SIE, the description of H improves and Be becomes the worst case, with errors of 14.4 and 8.6% respectively. Hait and Head-Gordon[9] concluded that the relatively poor performance of DFAs for Be is due to its multi-reference character and not SIE. For all three FLO-DFA methods, Be is the worst case with errors of 12.2, 16.2, and 16.5% for FLO-LSDA, FLO-PBE, and FLO-SCAN, respectively. These are nearly unchanged from the corresponding LSDA, PBE, and SCAN errors 13.5, 11.1, and 13.8%. The FLO-SIC results thus support the conclusion that the Be error is not due to self-interaction.

The results of Table III indicate that SIC gives the greatest improvement in calculated polarizabilities for LSDA, while it degrades the performance of SCAN slightly. This is reminiscent of the effect of SIC on atomization energies, where SIC improves LSDA, but worsens the already good performance of PBE and SCAN. A discussion of the effect of SIC on atomization energies in terms of noded or lobed orbitals can be found elsewhere.[22]

IV. CONCLUSIONS

Self-interaction error generally results in weaker binding of the electrons in atoms. In this paper we showed the effect this has on the polarizability of the atoms from H to Ar, along with their cations and anions, as calculated in LSDA, PBE, and SCAN. We showed that the polarizabilities for the neutrals and cations are generally overestimated by the uncorrected functionals relative to reference values (experimental values for neutrals and CCSD results for cations and anions) and that the agreement is significantly improved in the corresponding FLO-DFA calculations. For a subset of ten neutral atoms we show that the inclusion of SIC significantly improves the performance of LSDA and PBE compared to accurate CCSD(T) results from mean average percentage errors (MAPE) of 16.4 and 11.4%, respectively to 5.5 and 5.8% for FLO-LSDA and FLO-PBE, effectively moving the performance of these functionals up multiple rungs on the Jacob's Ladder scheme. By contrast, the performance of SCAN is slightly worsened from an MAPE of 7.1% to 8.8% for FLO-SCAN. Although SCAN has the best overall performance of the DFA's studied here, FLO-SCAN has the worst.

For the stable anions, we find that FLO-DFA polarizabilities significantly underestimate CCSD reference values with typical errors around 40%. We investigated the role of correlation for four closed-shell anions, H^-, Li^-,F^-, and Cl^-. Instead of increasing the polarizability, as is typically the case in going from HF to CCSD, adding correlation to exchange-only FLO-DFA calculations results in a decrease, worsening the agreement with the reference value in most cases. Li^- is the exception. In this case, correlation decreases the polarizability in HF as well as FLO-DFA exchange-only calculations, resulting in the best agreement between FLO-SIC and CCSD.

The improved description FLO-SIC gives for the polarizabilities of neutral atoms suggests that similar improvements could be found for molecules and this is worth studying. A somewhat different, but related, effect has to do with the distribution of charge in heteronuclear molecules. A recent study of the performance of DFA's for computing molecular dipoles[43] found that hybrid functionals tend to perform better than corresponding semilocal functionals. This is an indication that self-interaction errors may be affecting the description of dipoles by DFAs. Since self-interaction errors tend to destabilize anions, one might expect that removing those errors with SIC will lead to more stable anions and greater charge transfer in heteronuclear molecules. We are currently studying the impact of FLO-SIC on molecular dipole moments.

V. ACKNOWLEDGMENTS

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