On the question of the total energy in the Fermi-Löwdin orbital self-interaction correction method

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Abstract

The Fermi-Löwdin orbital self-interaction correction (FLOSIC) formalism is a novel method for implementing the Perdew-Zunger self-interaction correction (PZ-SIC) in density functional theory calculations. In this paper we consider how the use of Fermi orbitals affects total energies and other calculated properties compared to a standard approach to PZ-SIC that utilizes the localization equation conditions. We directly compare the results of the two methods using identical basis sets and numerical techniques in calculations for isolated atoms up to Kr and for a large test set of molecules. We find differences in total energies that increase with increasing atomic number and show that these differences can be traced to a less negative SIC

correction for the 1s orbital in FLOSIC. Importantly, energies for highest occupied orbitals and molecular atomization energies are nearly identical in the two methods.

1 Introduction

All approximate semi-local density functionals suffer from an incomplete cancellation of electron self-Coulomb and self-exchange energies, resulting in a residual self-interaction of the electrons. This leads to unphysical self-interaction errors (SIE) that plague density functional theory (DFT) calculations. For example, chemical reaction energy barriers are generally predicted to be too low by semi-local functionals, leading to overestimated reaction rates, while orbital energies are generally too high, producing strongly underestimated electron removal energies. Correcting SIE is an active research area and a variety of approaches are being studied.[1–10]

Perdew and Zunger[11] proposed a pragmatic way to remove electron self-interaction on an orbital-by-orbital basis. Their approach (PZ-SIC) successfully corrects many problems related to SIE, but its traditional implementation leads to an orbital-dependent theory that lacks unitary invariance. Finding the orbitals that minimize the self-interaction corrected total energy ($E^{\text{DFT-SIC}}$) essentially requires finding an optimal unitary transformation from the canonical orbitals that can be thought of conceptually as the Kohn-Sham orbitals from the uncorrected DFT problem. The orbitals stemming from the optimal transformation satisfy a set of $M(M-1)/2$ conditions (for M occupied orbitals) known as the localization equations (LE; see more below).[12]

The Fermi-Löwdin orbital self-interaction correction (FLOSIC) formalism[13] implements PZ-SIC using a Fermi orbital-based approach to finding optimal orbitals. In effect, the method restricts the choice of unitary transformations that can generate optimal orbitals. By doing so, the FLOSIC method ensures size extensivity as well as unitary invariance.[13]

It also reduces the number of conditions that must be satisfied to $3M$. FLOSIC has been shown to successfully mitigate the impact of SIE in a number of applications.[14–18]

Given the different approaches to finding optimal orbitals, it is important to investigate how FLOSIC and traditional PZ-SIC methods (referred to as SIC-LE below) compare in practice. As part of a recent work,[19] we showed that FLOSIC and SIC-LE give similar total energies for isolated atoms up to Ar;[20,21] however, the previous calculations were done using different basis sets and different numerical methods, so the comparisons were not fully quantitative. Furthermore, the previous SIC-LE results did not extend to atoms beyond Ar. This motivated us to make the comparisons more precise by performing both FLOSIC and SIC-LE calculations using identical basis sets and numerical procedures. We also extended the comparison to include all of the third row atoms and a large number of small molecules, as well as to atomization energies and orbital energies.

In the following section we give a brief description of the methodologies we used for the FLOSIC and SIC-LE calculations. We then present results for the atoms from H to Kr and for a subset of the G2 molecule test set.[22] This is followed by a discussion section and our conclusions.

2 Methods

The PZ-SIC total energy is

$$E^{\text{DFT-SIC}} = E^{\text{DFT}} + \sum_i U^{\text{SIC}}[\rho_i], \tag{1}$$

where E^{DFT} is the usual DFT energy functional, ρ_i is the density of a single occupied orbital, and $U^{\mathrm{SIC}}[\rho_i]$ is the correction for the i^{th} orbital

$$U^{\mathrm{SIC}}[\rho_i] = -\frac{1}{2}\int\int \frac{\rho_i(\mathbf{r})\rho_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - U^{\mathrm{xc}}[\rho_i]. \tag{2}$$

Here U^{xc} is the uncorrected exchange-correlation (xc) energy functional. (Spin indices are omitted from these expressions for simplicity.) Kohn-Sham-like equations are derived from $E^{\text{DFT-SIC}}$ in the usual way by requiring the energy to be stationary with respect to variations of the orbitals, resulting in the SIC equations:

$$H_i \left|\phi_i\right\rangle = \sum_j^M \lambda_{ji}^i \left|\phi_j\right\rangle . \tag{3}$$

In Eq.(3) λ_{ji}^i is the matrix of Lagrange multipliers (LM) introduced to ensure that the orbitals are orthonormal. The orbital dependence of the total energy results in orbital dependent effective Hamiltonians:

$$H_i = H^{\mathrm{DFT}} + V^{\mathrm{SIC}}[\rho_i], \tag{4}$$

where H^{DFT} is the uncorrected DFT Hamiltonian and $V^{\mathrm{SIC}}[\rho_i]$ is the SIC potential for the one-electron density ρ_i given by,

$$V^{\mathrm{SIC}}[\rho_i] = -\int \frac{\rho_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' - V^{\mathrm{XC}}[\rho_i], \tag{5}$$

where V^{XC} is the exchange-correlation potential corresponding to U^{XC}. Through U^{SIC}, $E^{\text{DFT-SIC}}$ depends on the individual orbital densities $\rho_i = |\phi_i|^2$ and not just the total density $\rho = \sum_i \rho_i$ as in standard DFT. This implies that for a given density, a specific choice of the orbitals minimizes the total energy. The ϕ_i are commonly referred to as

local orbitals (LO) because of the expectation that localized orbitals will have the largest Coulomb self-energies and therefore the most negative SIC correction, U^{SIC}. We adopt this usage here, but note that the question of the localization of the orbitals in SIC calculations is not trivial.[8] As Pederson et al. showed,[12] the LO that minimize the total energy satisfy additional conditions apart from Eq. (4) known as the LE:

$$\langle\phi_i|H_i - H_j|\phi_j\rangle = \lambda^i_{ji} - \lambda^j_{ij} = 0. \tag{6}$$

Eq. (6) implies that when the total energy is at the variational minimum, the LM matrix is symmetric. We use SIC-LE in the remainder of the paper to refer to PZ-SIC calculations that satisfy both Eq. (4) and (6).

2.1 FLOSIC calculations

The Fermi-Löwdin orbital implementation of SIC (FLOSIC) uses a unitary-invariant procedure to generate the ϕ_i, bypassing the LE. Given a set of M positions in 3D-space known as Fermi orbital descriptors $\mathbf{a}_i$ (FOD), M Fermi orbitals (FO) can be constructed[13] as

$$F_i(\mathbf{r}) = \sum_j^M \frac{\psi_j(\mathbf{a}_i)\psi_j(\mathbf{r})}{\sqrt{\rho(\mathbf{a}_i)}}, \tag{7}$$

where the ψ's represent any set of orbitals that span the occupied orbital space. The FO are normalized, but not mutually orthogonal. Therefore, Löwdin symmetric orthogonalization[23] is applied to yield the local orbitals ϕ_i.

Different FOD positions generally yield different LO. Therefore, minimizing the DFT-SIC total energy in FLOSIC involves two steps, optimizing the occupied orbital space and optimizing the positions of the FODs. The latter can be accomplished by making use of the derivatives of the total energy with respect to the $\mathbf{a}_i$.[24] The negative of these

derivatives can be thought of as forces on the FODs and minimizing the energy can be accomplished by using these forces in a gradient-based algorithm in analogy to molecular geometry optimization. At a minimum of $E^{\text{DFT-SIC}}$ the LO satisfy Eq.(3) self-consistently and the forces on the FODs are zero.

For the FLOSIC calculations reported here, we follow the self-consistency procedure of Yang et al.[25] A brief outline is as follows. First, the current guess of the local orbitals is used to generate the DFT Hamiltonian and SIC potentials, and the matrix elements $\langle\phi_i|H_i|\phi_j\rangle$ are computed. Here the index i extends only over the occupied orbitals, while j extends over both occupied and unoccupied orbitals. The occupied orbitals are then updated via sequential 2×2 unitary rotations with the unoccupied orbitals in order to remove the projection of $H_i\,|\phi_i\rangle$ onto the unoccupied orbitals. The updated occupied orbitals are then used with the FODs to create an updated set of LOs. An updated DFT-SIC energy is evaluated and the next iteration DFT Hamiltonian and SIC potentials are calculated. This process is repeated until the total energy converges (we used a convergence criterion of 1×10^{-8} Ha) and self-consistency is reached. Iteration averaging is applied to the DFT Hamiltonian to hasten convergence. No symmetry considerations were employed in our calculations.

At convergence, the FOD forces are calculated and fed into a conjugate gradient routine that returns an updated set of FOD positions. A new self-consistent calculation is carried out using these FODs, resulting in new FOD forces that are again fed into the conjugate gradient routine, resulting in another update of the FODs. These steps are repeated until the maximum FOD force drops below a tolerance of 10^{-3} Hartree/Bohr. Using this strategy, reaching the tolerance threshold typically requires from tens to hundreds of steps. The convergence behavior depends strongly on the initial FOD positions and the particular system.

We optimized FODs for all atoms from Li to Kr in our earlier work[19] and used these as

starting points to re-converge the atomic calculations with tighter convergence criteria. To create good FOD starting points for molecules, we combined the optimized atomic FOD data with trends found in recent FLOSIC calculations.[14–16,25] In particular, LO associated with single bonds correspond to an FOD in each spin channel lying at the same (or nearly the same) position along the bond axis. For a multiple bond, multiple pairs of up and down spin FODs are positioned around the axis. Starting FODs created following this scheme were used for all molecules.

2.2 SIC-LE calculations

For the SIC-LE calculations, the self-consistency procedure is similar to that used in the FLOSIC calculation, with the following changes. First, after updating the occupied orbitals through rotations with the virtual orbitals, a second operation is used to update the occupied orbitals to symmetrize the LM matrix. The gradient of the total energy $E^{\text{DFT-SIC}}$ with respect to $|\phi_i\rangle$ can be written as

$$|\frac{\partial E^{\text{DFT-SIC}}}{\partial \phi_i}\rangle = \sum_j^M (\lambda_{ji}^i - \lambda_{ij}^j)\,|\phi_j\rangle\,. \tag{8}$$

The occupied orbitals are updated using these gradients in a steepest descent algorithm, taking a small step in the gradient direction at each iteration. It should be emphasized that while some potentially more efficient methods to satisfy the LE have been reported in the literature,[6,26] our procedure is similar to approaches that have been successfully employed by other groups.[21,27] A step size of 0.1 generally led to a self-consistent solution, whereas larger step sizes generally caused the calculation to diverge. To ensure orthogonality, we used Löwdin symmetric orthogonalization of the updated occupied orbitals at every iteration. We used a convergence tolerance of 10^{-9} Ha for the total energy. This corresponded to a root-mean-square (rms) value of the gradient, computed over all orbitals, of less than

10^{-4} Ha. It is clear from Eq. (8) that the LE are satisfied when the gradients vanish. To speed up convergence, the converged FLOSIC LO were used as the initial guesses for all SIC-LE calculations.

We implemented this SIC-LE method in a development version of the FLOSIC code. The key numerical procedures in this code were taken from the earlier NRLMOL code.[28,29] Extensive Gaussian basis sets[30] were used for all atoms and an adjustable integration mesh was used to deliver high accuracy when computing matrix elements and total energies.[28] Identical basis sets and meshes were used to ensure precise comparisons between FLOSIC and SIC-LE results. All calculations used the PW91 local spin density approximation exchange-correlation functional.[31]

3 Results

3.1 Atoms

Calculated values (in Ha) of $E^{\text{DFT-SIC}}$ for the neutral atoms from H to Kr are given in Table 1 for both FLOSIC and SIC-LE. The differences $\Delta E^{\text{DFT-SIC}}$ ($= E^{\text{DFT-SIC}}[\text{SIC-LE}] - E^{\text{DFT-SIC}}[\text{FLOSIC}]$) shown in Table 1 are plotted in Fig.1. For the atoms up to C, the two methods give numerically identical total energies. For the remaining atoms, the SIC-LE total energies are lower than the corresponding FLOSIC energies. For the atoms N-Ar, the difference is at most 0.4 mHa, for S. For the third row atoms the difference grows roughly linearly, reaching a value of approximately 60 mHa for Kr. The difference in off-diagonal LM matrix elements, i.e. $\Delta_{ij} = \lambda_{ij} - \lambda_{ji}$, is an alternative measure of how the FLOSIC and SIC-LE calculations differ. For the SIC-LE calculations, $\Delta_{ij} = 0$ by construction. For atoms up to C, this is also true in FLOSIC. For N-Ar, a typical rms value of Δ_{ij} in the FLOSIC calculations is 1×10^{-3} Ha. For K-Kr, the typical rms values increase to 1×10^{-2} Ha. In all cases, the largest $\Delta\lambda_{ij}$ values correspond to matrix elements involving the 1s

Table 1: FLOSIC and SIC-LE total energies ($E^{\text{DFT-SIC}}$), energy difference ($\Delta E^{\text{DFT-SIC}}$) and highest occupied canonical energies ($-\epsilon_{\text{HOC}}$) for neutral atoms from H to Kr, using the LDA-PW91 density functional.

Atom	$E^{\text{DFT-SIC}}$ (Ha)		$\Delta E^{\text{DFT-SIC}}$ (Ha)	$-\epsilon_{\text{HOC}}$ (eV)	
	FLOSIC	SIC-LE		FLOSIC	SIC-LE
H	-0.499922	-0.499922	0.000000	13.60	13.60
He	-2.919697	-2.919697	0.000000	25.80	25.80
Li	-7.509142	-7.509142	0.000000	5.49	5.49
Be	-14.706650	-14.706650	0.000000	9.09	9.09
B	-24.727041	-24.727041	0.000000	9.38	9.38
C	-37.956704	-37.956704	0.000000	12.36	12.36
N	-54.741062	-54.741184	-0.000122	15.59	15.59
O	-75.284686	-75.284782	-0.000096	16.00	16.01
F	-100.015495	-100.015536	-0.000041	19.70	19.71
Ne	-129.280487	-129.280799	-0.000312	23.73	23.74
Na	-162.672894	-162.673031	-0.000137	5.21	5.21
Mg	-200.548311	-200.548440	-0.000129	7.57	7.57
Al	-242.920315	-242.920494	-0.000178	6.61	6.61
Si	-290.009679	-290.009823	-0.000145	8.70	8.70
P	-341.982417	-341.982569	-0.000152	10.94	10.94
S	-398.928708	-398.929140	-0.000432	11.79	11.80
Cl	-461.058964	-461.059307	-0.000343	14.21	14.19
Ar	-528.537430	-528.537701	-0.000271	16.78	16.79
K	-601.003777	-601.004588	-0.000810	4.31	4.30
Ca	-678.750882	-678.752602	-0.001721	5.96	5.94
Sc	-761.957020	-761.959476	-0.002455	6.26	6.24
Ti	-850.866413	-850.870537	-0.004124	6.48	6.45
V	-945.512879	-945.520083	-0.007204	6.71	6.68
Cr	-1046.122530	-1046.133480	-0.010949	6.63	6.62
Mn	-1152.838303	-1152.850622	-0.012319	7.09	7.06
Fe	-1265.725737	-1265.741199	-0.015462	7.53	7.49
Co	-1385.019698	-1385.037272	-0.017574	7.91	7.86
Ni	-1510.690614	-1510.715435	-0.024821	8.28	8.26
Cu	-1642.968188	-1643.005285	-0.037097	7.30	7.30
Zn	-1782.107182	-1782.140537	-0.033355	8.98	8.98
Ga	-1927.727670	-1927.764106	-0.036437	6.55	6.54
Ge	-2080.027177	-2080.068281	-0.041104	8.35	8.35
As	-2239.100905	-2239.144506	-0.043601	10.18	10.23
Se	-2404.971044	-2405.019632	-0.048588	10.93	10.92
Br	-2577.774230	-2577.827986	-0.053756	12.76	12.84
Kr	-2757.606317	-2757.664131	-0.057814	14.83	14.87

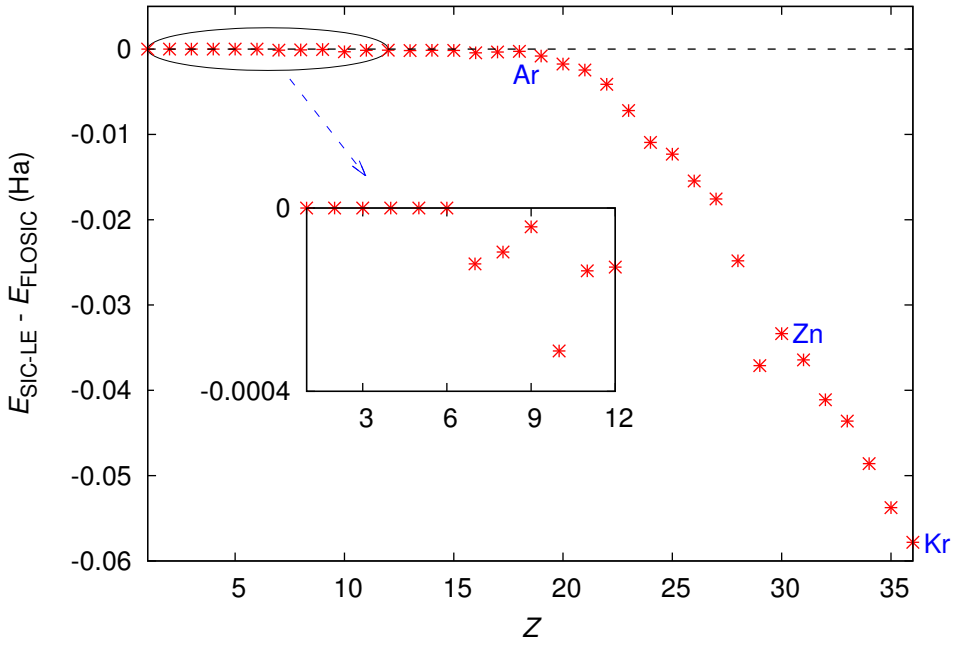


Figure 1: The difference between the SIC-LE and FLOSIC total energies $\Delta E^{\text{DFT-SIC}}$ (= $E^{\text{DFT-SIC}}$[SIC-LE] − $E^{\text{DFT-SIC}}$[FLOSIC]) for the neutral atoms H-Kr. Energies in Hartree (Ha). The inset magnifies the plot for Z = 1 - 12.

orbitals.

The symmetric LM matrix in SIC-LE calculations can be diagonalized to obtain the so-called canonical energies. In FLOSIC, the LM matrix can be symmetrized and then diagonalized to yield approximations of these canonical energies. It has been shown that the FLOSIC highest occupied canonical (HOC) energy agrees well with the observed ionization energy for atoms.[19] This is consistent with a Koopmans-like argument regarding the canonical energies.[12] It should be noted that Vydrov et al.[32,33] have shown that the diagonal elements of the LM matrix in SIC-LE (referred to as orbital energies) correspond to orbital energies in the sense of Janak's theorem.[34]

In Table 1 we list the FLOSIC and SIC-LE HOC energies. In Fig. 2 we present a correlation plot of these values for H-Kr. This figure makes it clear that the HOC energies are very close in the two approaches. The largest difference found is 0.08 eV (Br).

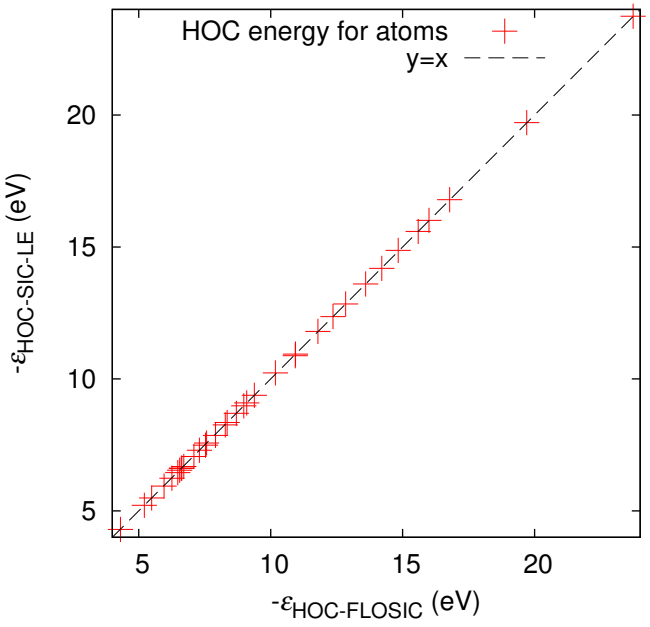


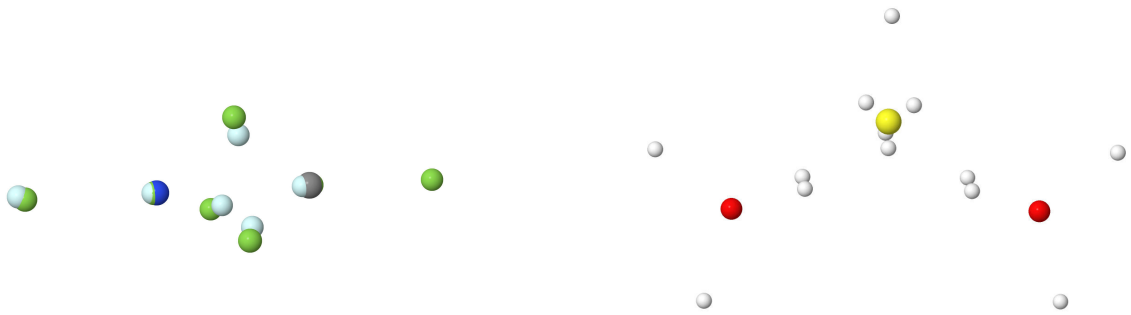
Figure 2: Correlation plot of the highest occupied canonical (HOC) energies for atoms from H to Kr from FLOSIC and SIC-LE calculations. The HOC levels are essentially the same in the two methods.

Comparisons for the other valence orbital energies (i.e. below the HOC) are similarly close.

3.2 Molecules

We compared FLOSIC and SIC-LE total energies for a subset of 30 molecules taken from the G2 test set.[22] For these calculations, we used molecular geometries optimized at the B3LYP/6-31G(2df,p) level of theory.[35] Since the G2 molecules include only atoms lighter than Ar, we also included HBr, LiBr, FBr, and Br_2 in our test set to increase the diversity of our comparisons. For these, we also used optimal B3LYP bond lengths.[35] We created starting FOD positions for all molecules as described in the Methodology section and relaxed these until the FOD forces dropped below the 10^{-3} threshold.

As in previous FLOSIC work,[14–16,18] we found that the optimized FOD positions reflect the nature of the molecular bonds. For example, we find three FODs from each spin channel



(a) CN (b) SO_2

Figure 3: (a): Optimal FODs for the CN radical. The dark blue and gray spheres show the nuclear positions of N and C, respectively. The green and light blue spheres show majority and minority spin FOD positions. (b): Optimal FODs of SO_2. The yellow/red spheres show the nuclear positions of S/O and the white spheres show the FOD positions. For this unpolarized molecule, majority and minority spin FOD positions are the same.

located in the bonding region between carbon and nitrogen in the CN radical (see Fig. 3(a), corresponding to a triple bond. For the unpolarized SO_2 molecule, we find a symmetric FOD arrangement that indicates double bonds between S and both O atoms (See Fig. 3(b) and note that the FOD positions correspond to both majority and minority spin orbitals.).

In Table 2 we compare the FLOSIC and SIC-LE total energies for all molecules in our test set. The energies are identical for molecules with 4 or fewer electrons in each spin channel. For larger molecules involving only atoms smaller than Ar, the total energies are very close, with the SIC-LE total energy lower by at most 2.5 mHa (N_2H_4). The differences are much larger for the molecules containing Br. For example, the total energy for LiBr is 54 mHa lower in SIC-LE than in FLOSIC.

4 Discussion

The steady increase in the difference between SIC-LE and FLOSIC total energies for the third row atoms shown in Fig. 1 is striking. To trace its origin, we first compared the DFT part of the total energy (E^{DFT}) from the SIC-LE and FLOSIC calculations for these

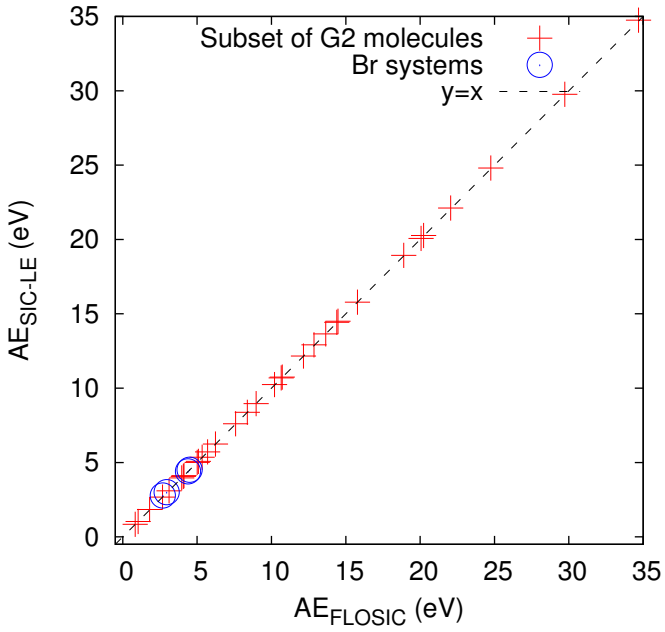


Figure 4: Correlation plot of the atomization energies (AE) calculated with FLOSIC and SIC-LE for the molecules in Table 2.

atoms and found a maximum difference of 3 mHa. Since E^{DFT} depends only on the total electron density, the close comparison implies that the total densities obtained in the two approaches are very similar. It also indicates that the energy differences seen in Fig. 1 stem from the SIC contributions to the energy. We next compared U^{SIC} values on an orbital-by-orbital basis. We found that the differences ($\Delta U^{\mathrm{SIC}}[\rho_i] = U^{\mathrm{SIC}}[\rho_i^{\text{SIC-LE}}] - U^{\mathrm{SIC}}[\rho_i^{\mathrm{FLOSIC}}]$) are largest for the 1s orbitals. In fact, $\Delta U^{\mathrm{SIC}}[\rho_{1s}]$ accounts for at least 79 % of the entire total energy difference for all of the third row atoms. In Table 3 we show $\Delta E^{\mathrm{DFT}} = E^{\mathrm{DFT}}[\rho^{\text{SIC-LE}}] - E^{\mathrm{DFT}}[\rho^{\mathrm{FLOSIC}}]$ and $\Delta U^{\mathrm{SIC}}[\rho_{1s}]$ for the representative cases Cu, Zn, and Kr. The total energy differences for these atoms are shown in Table 1.

It can be shown that the self-Coulomb energy for a hydrogenic 1s orbital scales linearly with the atomic number Z. We find empirically that $U^{\mathrm{SIC}}[\rho_{1s}]$ is also essentially linear

Table 2: Total Energies of Molecules (Ha).

Molecule	E_{FLOSIC}	$E_{\text{SIC-LE}}$	Molecule	E_{FLOSIC}	$E_{\text{SIC-LE}}$
LiH	-8.107571	-8.107571	CH_3OH	-116.150882	-116.153081
BH	-25.372798	-25.372798	OH	-75.968622	-75.968875
BH_2	-26.034890	-26.034890	H_2O	-76.678748	-76.679525
BH_3	-26.728655	-26.728655	NH_3	-56.772928	-56.774015
Li_2	-15.056106	-15.056106	PH_3	-343.928881	-343.929322
CH	-38.607890	-38.607890	N_2H_4	-112.292638	-112.295017
CH_3	-39.993946	-39.994324	F_2	-200.097127	-200.098599
CN	-92.976498	-92.977445	H_2O_2	-152.042028	-152.044090
HCN	-93.726793	-93.728101	Na_2	-325.376591	-325.376917
B_2H_6	-53.546579	-53.547939	H_2S	-400.257931	-400.258188
HF	-100.744434	-100.745039	HCl	-461.745143	-461.745419
LiF	-107.734079	-107.734616	NaCl	-623.881830	-623.882238
CH_4	-40.700345	-40.701423	P_2	-684.160942	-684.161732
C_2H_2	-77.607934	-77.609012	SO_2	-549.889114	-549.891336
C_2H_6	-80.188051	-80.190271	SiH_4	-292.589656	-292.589841
HBr	-2578.439448	-2578.493497	FBr	-2677.897990	-2677.953489
LiBr	-2585.444617	-2585.498476	Br_2	-5155.647399	-5155.757413

Table 3: ΔE^{DFT} and ΔU^{SIC} (in Ha) and the ratio of the latter to $\Delta E^{\text{DFT-SIC}}$, expressed as a percentage (%), for the representative atoms, Cu, Zn, and Kr. See Table 1 for the total energies. See text for additional details.

Atom	ΔE^{DFT}	$\Delta U^{\text{SIC}}[\rho_{1s}]$	$\Delta U^{\text{SIC}}[\rho_{1s}]/\Delta E^{\text{DFT-SIC}}$ (%)
Cu	-0.002	-0.030	79
Zn	-0.002	-0.028	84
Kr	-0.003	-0.051	88

in Z. Attributing the roughly linear increase in the FLOSIC vs SIC-LE energy difference across the third row atoms to $\Delta U^{\rm SIC}[\rho_{1s}]$ therefore can be explained if the ratio between $U^{\rm SIC}[\rho_{1s}^{\rm FLOSIC}]$ and $U^{\rm SIC}[\rho_{1s}^{\rm SIC\text{-}LE}]$ is roughly constant for these atoms. The calculated fractions for Cu (0.989), Zn (0.990), and Kr (0.985) show this to be the case. By contrast, the corresponding fraction for both Ne and Ar is 0.999. In other words, the FLOSIC methodology gives nearly the same result as SIC-LE for the 1s LO for atoms up to Ar, but the constraints involved in constructing LO in FLOSIC begin to impact the optimization of the 1s LO for the third row atoms. In energetic terms, the optimization of the 1s LO in FLOSIC is roughly equally as effective for all 3rd row atoms.

Differences in the 1s LO imply differences in the core and semicore canonical energies between FLOSIC and SIC-LE, since the 1s LO is largely a mixture of core and semicore canonical orbitals. Using Zn as an example, the difference for the semicore 3s and 3p canonical energies is about 14 and 5 mHa, respectively, and 6 and 8 mHa for the 2s and 2p levels. For the 1s core, the difference is about 60 mHa. Note that these differences are a very small fraction of the respective canonical energies. For example, the SIC-LE canonical energy for the Zn 3p level is -3.621 Ha, so that the relative FLOSIC - SIC-LE difference is roughly 0.1 % for this level. As mentioned before, and seen in Fig. 1 for the HOC levels, the valence canonical energies for the 3rd row (and all lighter) atoms are essentially equal. For Zn, the difference for the 4s and 3d canonical eigenvalues in the two methods is 0.2 and 0.6 mHa, respectively.

As noted before, the FLOSIC and SIC-LE total energy differences for molecules mirror those for atoms in that there are significant differences only when the molecules involve heavy atoms. An interesting question is how these differences affect properties such as atomization energies (AE). In Fig. 4 we show a correlation plot of AE computed within FLOSIC and SIC-LE for all the molecules in our test set. Circles indicate the values for the Br-containing molecules. The plot shows that both methods give nearly the same AE

for all the molecules we studied, even those including heavy atoms.

We note that an earlier comparison of the FLOSIC and SIC-LE methods (Table 1 in Ref. 13) gave slightly different AE (about 0.3 eV mean absolute error difference). However, the SIC-LE results quoted in that paper were taken from calculations that employed complex orbitals;[36] this has been shown to give lower SIC-LE energies than calculations restricted to real orbitals.[6] The results in the present work show that FLOSIC and SIC-LE yield virtually identical AE when real orbitals are used in both methods.

The FLOSIC and SIC-LE total energies are *identical* for atoms and molecules with at most 4 electrons in each spin channel. For the ground state spin configurations, this means that atoms up to C have identical energies. Similarly, all the molecules in Table 2 up to CH have fewer than 4 electrons of each spin and identical energies. By contrast, CH_3 has 5 (4) up (down) electrons, and the SIC-LE energy is lower by 0.38 mHa. To test this 4-electron rule further, we re-computed the total energy of the oxygen atom for a zero net spin configuration featuring 4 electrons in both spin channels. We find identical energies of -75.261017 Ha in both methods. In Table 1, the SIC-LE total energy is lower by 0.096 mHa in the 5 up, 3 down ground state spin configuration.

What is the origin of the 4-electron rule? Given the correct total electron density, the variational SIC-LE calculations involve $M(M-1)/2$ conditions that must be satisfied by the M optimal LO of the same spin, whereas FLOSIC imposes only $3M$ conditions. Although the nature of the conditions is different in the two methods, it is reasonable to expect that if $3M \geq M(M-1)/2$, the two methods would produce the same energy. This implies equal energies whenever $M \leq 7$ in both spin channels. But this is clearly violated by our results for the oxygen atom and CH_3 as noted above. A reasonable conclusion is that $3M$ overcounts the effective number of conditions imposed in a FLOSIC calculation. It is easy to see that for $M = 1$, the Fermi orbital construction yields the same result for any choice of FOD position. This suggests that a FLOSIC calculation actually involves

$3(M-1)$ conditions; however, that count implies equal total energies for systems with fewer than 6 electrons in a spin channel, which is still violated. A count of $3(M-2)$ conditions moves the cross-over point to the $M=4$ electrons per spin rule that we see empirically in our results, but we have not found a fundamental way to explain this. We note that uniform rotational and translational symmetry for the FOD positions is broken by the positions of the atomic nuclei, so that these symmetries do not reduce the count of conditions for a FLOSIC calculation in general.

5 Summary

Total energies from FLOSIC and SIC-LE calculations (employing the PW91 LDA functional) were compared for the atoms from H to Kr and for a large test set of molecules. The calculations were performed using identical basis sets and numerical procedures, ensuring precise comparisons. For atoms and molecules with 4 or fewer electrons in each spin channel, the total energies obtained in the two methods are identical. In all remaining cases, the SIC-LE method gives a lower energy. For all the atoms from N to Ar, the total energy difference is less than 1 mHa, but the difference grows roughly linearly across the 3rd row atoms, reaching approximately 60 mHa for Kr. We show that most of the total energy difference for these atoms can be traced to the differences in the self-interaction correction of the 1s orbital. Similarly, for molecules involving light atoms up to Ar, the difference in total energy in the two methods is of the order of 1 mHa, while the differences for molecules involving 3rd row atoms are larger.

The fact that the total energy is higher in general in FLOSIC calculations than in traditional SIC-LE is expected since the Fermi-orbital-based method imposes only $3M$ conditions to optimize the LO compared to the $M(M-1)/2$ conditions used in SIC-LE calculations. Importantly, while the results presented in this paper indicate that the two

approaches yield small total energy differences for atoms and small molecules, quantities corresponding to physical properties like electron removal energies and molecular atomization energies remain essentially the same in both methods.

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