Why the energy is sometimes not enough
A dive into self-interaction corrected density functional theory

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Abstract. In electronic structure methods such as density functional theory (DFT) or closely related methods like self-interaction corrections (SIC), e.g., utilizing Fermi-Löwdin orbitals (FLO) [Schwalbe et al., J. Comput. Chem., vol. 40, 2019], people predominately compute the total energy as the main characteristics to classify a system within a given numerical parameter space - often being a compromise to compute properties for large systems with an acceptable computational effort. But with great power comes great responsibility, and numerical results need to be of high quality, trustworthy, and reproducible. We highlight the importance to analyze central properties beyond the total energy, especially those being characteristics of the density in DFT and SIC [Trepte et al., J. Chem. Phys., vol. 155, 2021], i.e., dipole moments and polarizabilities. The importance of precise numerical procedures is outlined. These back-to-basics concepts may help to understand, classify, and overcome the so-called local minima problem in SIC and cure the intrinsic imbalance of the predictive power of SIC. We also point out the importance of properly chosen initial nuclei arrangements. The relevance of the described physical properties is highlighted, as they play an intrinsic role in closely related research fields such as computational spectroscopy or optics in general.

Keywords: DFT · FLO-SIC · dipole · polarizabilities

1 Introduction/Motivation
Electronic structure methods became more important over the recent years.\textsuperscript{[1][2]} These methods are known from an experimental perspective as a supporter to verify determined trends, to determine properties which are not easily accessible through additional experiments \textsuperscript{[3][6]}, or as a black-tool box to explain experimental observations \textsuperscript{[7][11]}. While not being recognized or accepted by everyone, the role of electronic structure methods has changed significantly over the years. Screening for novel materials utilizing purely theoretical and/or computational
frameworks saves time, work and money. Nowadays, DFT is also used within the field of machine learning (ML) on the one hand to make DFT faster through ML strategies and to speed-up calculations or to find better novel approximations for exchange-correlation functionals.

Density functional theory (DFT) is one of the leading methodologies based on two main pillars, i.e., suitable accuracy and reasonable numerical effort. Certainly, any approximation comes with limitations. Some of the limitations of DFT may at least partially be attributed to the so-called self-interaction error (SIE). In a figurative description, the electrons in DFT can see and feel themselves, which of course is not the case in reality. Based on the efforts of various groups density functional approximations (DFAs) become better in reaching chemical accuracy, as better approximations for the last unknown piece in DFT - the correct universal exchange-correlation functional - are available.

However, they still cannot fully cure the already mentioned SIE. Perdew and Zunger proposed a correction to DFT to encounter the SIE problem. A recent formulation of PZ-SIC utilizing so-called Fermi-Löwdin orbitals (FLO-SIC) showed novel properties such as a sparse description of bonds utilizing Fermi-orbital descriptors (FODs) besides the intrinsic properties of SIC. FODs are variational parameters within FLO-SIC, and can be imagined as semi-classical electron positions. While PZ-SIC perfectly cancels the one-electron SIE, it has a long history of successes and failures. Typically, one is interested in the variational total energy of the system. In SIC, the choice of orbitals is important; it was shown by Lethola et al. that SIC suffers from the local minima problem. Recently, Trepte et al. showed that one can guide and classify local minima in SIC with the help of special sets of FODs that reflect chemical bonding theories of Lewis and Linnett. Trepte et al. proposed to monitor the dipole moment in SIC calculations, as it is one of the most simple descriptor for the electronic density - the key property in any density functional approximation (DFA).

In this work we emphasize the importance of a properly chosen nuclei arrangements as well as a properly investigated numerical parameter space in SIC calculations which respects and reflects not only the total energy of the system but also density-related properties such as electric dipole moments and polarizabilities. Therefore, we propose a classification system of approximations within FLO-SIC with respect to its internal degrees of freedom, i.e., the density matrix (DM) and FODs. In addition, an idea of a classification system for numerical parameter in SIC is proposed. Central aspects are discussed using small illustrative and educationally valuable molecules, as all discussed results should be understandable to everyone, not only to experts. The manuscript is structured as follows. In the first two sections we outline the theoretical background and the computational details, after which we present the major results of this study. In the last section we summarize and conclude our findings.
2 Theoretical background

![Diagram of the self-consistent field (SCF) cycle in DFT.]

For $N$ particles, the Schrödinger equation is a partial differential equation in $3N$ dimensions

$$\hat{H}\Psi = E \Psi \leftrightarrow F^\sigma C^\sigma = SC^\sigma E^\sigma,$$

(1)

where $\hat{H}$ is the Hamiltonian, $\Psi$ is the many-body wavefunction, $E$ is the total energy of the system describing a more abstract equation in the physics world, while $F^\sigma$ is the Fockian, $C^\sigma$ are the molecular coefficients, $S$ is the overlap matrix, and $E^\sigma$ is the eigenvalue matrix for a given spin $\sigma$ describe the same problem in a more explicitly solvable quantum-chemical form [30].

In practice one needs to choose a discretization of the fields, i.e., one needs a basis set to describe wavefunctions and density in DFT calculations (see Fig. 1). In quantum chemistry a typical choice are Gaussian-type orbitals (GTO). Using a GTO representation results in a description of the wavefunction

$$\psi_i^\sigma(r) = \sum_\mu C_{\mu i}^\sigma \phi_\mu(r),$$

(2)

the density matrix

$$P_{\mu \nu}^\sigma = \sum_i f_i^\sigma C_{\mu i}^\sigma C_{\nu i}^\sigma,$$

(3)
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and the total electron density itself

\[ n^\sigma(\mathbf{r}) = \sum_{\mu \nu} P_{\mu \nu}^\sigma \phi_\mu(\mathbf{r}) \]  

(4)

which, in case of spin-polarization, is a sum of the densities of the different spin-channels, e.g., \( \alpha \) and \( \beta \), and can be expressed as

\[ n(\mathbf{r}) = n^\alpha(\mathbf{r}) + n^\beta(\mathbf{r}). \]  

(5)

Here, \( C_{\mu i}^\sigma \) are the orbital coefficients, \( \phi_\mu(\mathbf{r}) \) are the basis functions, \( \sigma \) is the respective spin channel, and \( f_i^\sigma \) are the occupation numbers for \( i \)-th orbital.

Kohn-Sham (KS) [31] DFT is an approximation to solve the Schrödinger equation. The energy of a given system is expressed as a functional of the density

\[ E_{KS}[n^\alpha, n^\beta] = T_s[n^\alpha, n^\beta] + V[n] + J[n] + K_{XC}[n^\alpha, n^\beta], \]  

(6)

where \( T_s[n^\alpha, n^\beta] \) is the kinetic energy of the non-interacting system, \( V[n] \) is the external potential energy, \( J[n] \) is the Coulomb functional, \( K_{XC}[n^\alpha, n^\beta] \) is the exchange-correlation functional, and \( n \) is the electron density of the \( \alpha \) and \( \beta \) spin channel, respectively. In DFT, one needs to use approximations for the tiny fraction of the energy which is not known explicitly, i.e., the exchange-correlation (XC) functional. These approximations lead to artificial interactions of electrons with themselves; this is called self-interaction (SI). For one-electron densities the exchange-correlation energy and the Coloumb energy do not cancel out, resulting in the SI energy

\[ E_{SI}[n^\sigma_i] = K_{XC}[n^\sigma_i, 0] + J[n^\sigma_i]. \]  

(7)

In PZ-SIC, the total \( E_{KS} \) is corrected orbital-by-orbital as

\[ E_{PZ} = E_{KS}[n^\alpha, n^\beta] + E_{SIC} = E_{KS}[n^\alpha, n^\beta] - \sum_\sigma \sum_{i=1}^{N^\sigma} E_{SI}[n^\sigma_i]. \]  

(8)

A novel flavor of PZ-SIC is the Fermi-Löwdin orbital SIC (FLO-SIC) [32–34] utilizing semi-classical electron positions in real-space, i.e., Fermi-orbital descriptors (FODs) \( a_i^\sigma \), to construct the Fermi orbitals (FO) as coefficients

\[ c_{FO}^\sigma = C^\sigma R^\sigma \]  

(9)

using the rotation matrix

\[ R^\sigma_{ji} = \frac{\langle \psi^\sigma_j | a_{i}^\sigma \rangle}{\sqrt{n^\sigma(i^\sigma)}}. \]  

(10)

The respective orthogonalized Fermi-Löwdin orbitals (FLO) are obtained as coefficients via

\[ c^\sigma = c_{FO}^\sigma [T^\sigma(Q^\sigma)^{-1/2}(T^\sigma)^T] \]  

(11)

with \( C^\sigma \) being the molecular orbital coefficient matrix, e.g., from KS-DFT, while \( T^\sigma \) are eigenvectors and \( Q^\sigma \) are eigenvalues of the FO overlap matrix. For a given
molecule, FODs need to be optimized in the employed numerical parameter space using the respective analytical gradients [35], which for brevity are not repeated here. Note that it is not sufficient to optimize FODs using LDA-PW [36] and employ these FODs for more advanced functionals such as PBEsol [37] or r^2SCAN [21] without reoptimizing them. This is rather obvious as even the DFT density can change significantly using different exchange-correlation functionals.

A simple way to analyze and characterize the electronic density can be realized using small disturbances, i.e., applying small external electric fields. The total energy of a system under the influence of an external electrical field $\varepsilon$ can be written as

$$E(\varepsilon) = E_0 + \sum_i \mu_i \varepsilon_i + \sum_{ij} \alpha_{ij} \varepsilon_i \varepsilon_j + O(\varepsilon^3).$$

(12)

In this formulation, $E_0$ refers to a zero-Kelvin ground state energy as typically calculated within KS-DFT $E_{KS}$ (see Eq. (6)) or in PZ-SIC $E_{PZ}$ (see Eq. (8)). From this energy expression we can derive the electric dipole moment as

$$\mu_i = \left( \frac{\partial E(\varepsilon)}{\partial \varepsilon_i} \right)_{\varepsilon_i=0}.$$  

(13)

The electric dipole moment is a measure for the separation of positive and negative electrical charges in a given system. Note, we only discuss the electric dipole moment in this work and refer to it as dipole moment in the following. In short, the dipole moment is a measure for the polarity of a system and tells us about the charge separation in this system.

In addition we can also derive the electric polarizabilities $\alpha_{ij}$ from the above equation as

$$\alpha_{ij} = \left( \frac{\partial E(\varepsilon)}{\partial \varepsilon_i \varepsilon_j} \right)_{\varepsilon_i=\varepsilon_j=0} = \left( \frac{\partial \mu_i(\varepsilon_i)}{\partial \varepsilon_j} \right)_{\varepsilon_i=\varepsilon_j=0}.$$  

(14)

The electric polarizability describes the tendency of a system to acquire an induced dipole moment in the presence of an external electric field. Similar to the dipole moment we will refer to the electric polarizability as polarizability. Both the dipole moments and polarizabilities can be seen as fingerprints of the electron densities, which itself is build up from the underlying orbitals.

As an example, the electron density and the dipole moment of the H_2O molecule is visualized in Fig. 2. Clearly, the dipole moment points from the electron majority towards the electron minority, making it a suitable descriptor for the density. To further simplify the characterization of the density, one can use scalar values. Thus, the vectorial dipole moment $\mu = (\mu_x, \mu_y, \mu_z)$ may be represented as $\mu = |\mu|$. The tensorial polarizability

$$\alpha_{ij} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix}.$$  

(15)
Fig. 2. Illustration of the dipole moment $\mu$ in the H$_2$O molecule using the experimental geometry. Here, $\delta$ indicates partial charges within the molecule. Depending on its definition, $\mu$ points from the electron majority to the electron minority. The visualized density comes from LDA-PW using tier4; see Table 1.

may be represented as $\alpha = \text{Tr}(\alpha_{ij})/3$. Note that Tr refers to the mathematical operations of the trace of a square matrix, which is defined as the sum of the main diagonal elements. We will use this sparse scalar representation of the dipole moment and the polarizability from here on, without introducing separate naming definitions.

While dipole moments and polarizabilities themselves are important for the characterization of systems, they further are fundamental properties in common spectroscopic methods, such as infrared (IR) and Raman spectroscopy. A system is IR-active if there exist a non-zero change of the dipole moment for a certain vibration, and the IR intensity is proportional to

$$I_{\text{IR}} \sim \left(\frac{d\mu}{dQ}\right)^2,$$

(16)

where $Q$ is the normal coordinate of the vibration. A system is RAMAN-active if there exist a non-zero change of the polarizability for a given vibration, and the RAMAN intensity is proportional to

$$I_{\text{RAMAN}} \sim \left(\frac{d\alpha}{dQ}\right)^2.$$

(17)

This further highlights the important of a precise knowledge of dipole moments and polarizabilities. Higher order polarizabilities, i.e., hyper-polarizabilities or shielding constants, are important for other fields like NMR spectroscopy.
3 Computational details

All calculations were performed with the all-electron electronic structure GTO codes PySCF \[42\] and PyFLOSIC2. PyFLOSIC2, available at [https://gitlab.com/opensic/pyflosic2][1], is the successor of PyFLOSIC \[43\] and offers a cleaner and more modular code structure. All essential data presented in the manuscript as well as all scripts used to produce this data are available at [https://gitlab.com/opensic/dippo][2]. All codes use the Libxc \[44\] library, offering access to a vast variety of exchange-correlation functionals. All used codes are Open-Source codes, meaning that they are freely available to everyone. \[45\], \[46\] Open-Source codes enable faster code development, re-usable concepts, and versatile tool-boxes. This is due to the fact that the community acts as a whole and is not competing against each other, as is the case in the old monolith code paradigms, where the same wheel is reinvented over and over again.

The codes are written in Python, where only numerically demanding parts in PySCF are written in C. Its simplicity and elegance, its nice, friendly, and helpful community, as well as various well-maintained libraries are only some reasons why it is very easy for students or non-programmers to start coding with Python. This is not only the case in physics and chemistry, but various scientific- or technology-relevant fields. Thus, even non-trivial tasks are solvable, like writing a DFT code from scratch \[47\] in the limiting time of a master thesis if students are guided and educated with novel strategies \[48\].

For calculations of real- and complex-valued SIC, i.e., RSIC and CSIC \[26\], \[49\], \[50\], we used the ERKALE code \[51\]. The ERKALE code also accesses exchange-correlation functionals through the Libxc library.

Similar to other software projects, we introduce a tier level systems, see Table 1, to set up pre-defined computational parameters going from code debugging to simple test calculations and production quality results. In previous studies \[24\], \[43\] we observed that the pc-n basis sets \[52\]-\[53\] perform well for DFT as well as SIC calculations. Therefore, all tier level use pc-n basis set variants besides tier1. The basis sets can easily be accessed via the Basis Set Exchange project \[54\]. Higher tier levels use increasingly larger basis sets.

A proper numerical quadrature is needed to evaluate exchange-correlation properties in DFT and SIC. For molecules one typically uses quantum-chemical quadratures, which we will simply refer to as grids. A grid consists of a radial and an angular part. The explicit size is given as a tuple; number of radial grids and number of angular points. The PySCF package uses a scalar shorthand notation which defines standard values for quantum chemical grids for each element in the periodic table with increasing accuracy. These shorthand notations are called grid levels and range from 0 to 9. For our tier levels 1 - 3 we use these definitions, as a PySCF user may be familiar with them. However, in SIC one needs significantly finer numerical grids, thus for the higher tier levels we propose other quantum chemical grids. In contrast to the current standards in PySCF, we prune the used grids neither for DFT nor for SIC. This is done as the orbital densities evaluated in SIC are not as smooth as the total density used in DFT, thus one needs a finer resolution to describe all kinds of densi-
ties sufficiently accurate. With higher tier levels the numerical parameters space becomes increasingly more accurate.

**Table 1.** Tier levels (tier), a more systematic way to approach the numerical parameter space in SIC. All tier levels use unpruned grids.

| Tier | Basis | Grid   | Meaning                      |
|------|-------|--------|------------------------------|
| 1    | STO-3G| grid.level=3 | code debugging              |
| 2    | pc-0  | grid.level=3 | exemplary calculation       |
| 3    | pc-1  | grid.level=7 | useful calculation          |
| 4    | pc-2  | (150,1202)  | production quality          |
| 5    | aug-pc2| (200,1454) | high quality                |
| 6    | unc-aug-pc2| (200,1454) | very high quality           |

FLO-SIC has two major degrees of freedom, the DM and the FODs. To handle, analyze and describe these degrees of freedom, we introduce a Flevel system (see Table 2). All FLO-SIC calculations in this work are realized with a two-step FLO-SIC SCF cycle (see Fig. 3). Note that a similar idea exist in literature [55]. However, our realization may differ in various details.

**Table 2.** FLO-SIC levels (Flevel), a systematic classification of FLO-SIC approximations. Here, init stands for the values the calculation is initialized with, whereas opt refers to the fact that these properties are fully optimized. The tag update refers to one property being adjusted with respect to the other property. The meaning is expressed as functional dependencies.

| Flevel | FODs | DM    | Meaning                   |
|--------|------|-------|---------------------------|
| 0      | init | init  | FLO(DM_{init})            |
| 1      | init | update| DM(FOD_{init})            |
| 2      | update| update| DM(FOD(DM_{init}))        |
| 3      | opt  | opt   | SCF(DM_i(FOD_j))         |

In FLO-SIC, the initial DM and initial molecular coefficients are typically the ones from a DFT calculation, but one could use something different, e.g., the respective DM constructed from localized Foster-Boys orbitals [55] or other kinds of calculations, e.g., wavefunction theories. The initial FODs can be generated with various procedures, e.g., PyCOM, fodMC, or other so-called FOD generators [23]. Note that a FOD generator initializes FODs from scratch; tools which only optimize an initial FOD configuration should not be called FOD generator; instead they should be called FOD optimizer. Both PyCOM and fodMC are FOD generators as they fulfill this definition. All initial FOD configurations used in this work were generated using the fodMC.

The first FLO-SIC level, Flevel=0, is designed for problems where one has a DFT calculation and a set of FODs and wants to know how the FLOs would look
Fig. 3. The heart of the FLO-SIC Flevel system - the two-step FLO-SIC SCF cycle. In the outer loop the density matrix is optimized, while in the inner loop the FODs are optimized. The intersection points in the graph show the decisions which are needed to realize/use a certain Flevel, see Table 2. The energy convergence threshold $E_{\text{tol}}$ controls the convergence of the density matrix while $f_{\text{max,tol}}$ controls the convergence of the FODs. The energy is only valid for the used numerical parameter space if both criteria are fulfilled. Obviously, a change in the numerical parameter space requires to restart the procedure.
like in this case. The second level, Flevel=1, can be interpreted as an update of the DM for a fixed set of FODs. Here, the set of FODs can come from one of the FOD generators or from a full FOD optimization (Flevel=3). Using Flevel=1 can be useful to compare different FOD configurations for a given system and compare energy, FOD forces, dipole moment, and spin expectation value to find a proper FOD configuration. For the next level, Flevel=2, the FODs are optimized for the initial DM, after which the DM is updated for those optimized FODs. This can be seen as the first step to a full FLO-SIC calculations, and to approximate how high the computational effort would be for an actual full FLO-SIC calculation (Flevel=3), or how well a set of FODs is converged. The last Flevel is 3, which represent a self-consistent FLO-SIC calculation, thus both degrees of freedom, i.e., DM and FODs, are fully optimized.

Within a full FLO-SIC calculation, i.e., Flevel=3, the FODs are fully optimized in an inner FOD loop for a given DM provided by the outer DM loop. All initial FODs in the inner FOD loop were optimized using the SciPy L-BFGS-B \[57–64\] optimization algorithm with a maximum force component threshold of \(f_{\text{max, tol}} = 2 \cdot 10^{-4} \text{ } E_h/a_0\). All SIC properties are calculated for this DM and the respective optimized FODs. Based on this, the unified Hamiltonian \[43\] is updated which then provides the next DM in the outer DM loop. The two-step procedure is repeated until the FOD forces reach a pre-defined threshold and the DM is not changing anymore, which is measured by an energy threshold. This two-step FLO-SIC SCF cycle is superior to the SCF cycle described in \[43\]. Fully optimized FODs (Flevel=3) should give the same energy, very similar dipole moments, spin expectation values and FOD forces if they are being used in Flevel=1 as initial FODs. Having the possibility to calculate the total energy of the system under the influence of an external electric field allows to study dipole moments using, e.g., a 2-point stencil

\[
\mu_{\text{FD}, i} = \frac{E(+\varepsilon_i) - E(-\varepsilon_i)}{2\varepsilon_i},
\]

(18)

Higher order stencils may improve the accuracy of the numerical results. Otherwise, having the possibility to calculate the electronic density the dipole moment can be calculated

\[
\mu = \sum_A Z_AR_A - \int d^3r \, n(r) \, r,
\]

(19)

where \(Z_A\), \(R_A\), and \(n(r)\) are nuclear charges and positions and the total electron density, respectively. The latter expression is typically implemented in GTO electronic structure codes like PySCF/PyFLOSIC2 and ERKALE. Sometimes it can become useful to verify a certain implementation of Eq. (19) using the finite difference approach of Eq. (18).

With the dipole moment at hand, i.e., Eq. (18) or Eq. (19), one can calculate the directional components of the polarizability tensor as vector components

\[
[a_{\text{FD},ix}, a_{\text{FD},iy}, a_{\text{FD},iz}] = \frac{\mu(+\varepsilon_i) - \mu(-\varepsilon_i)}{2\varepsilon_i},
\]

(20)

which is a row in Eq. (15).
4 Results

4.1 Pandora’s box: The quality of nuclei coordinates matters

To perform electronic structure theory calculations, one needs to have the chemical symbols and the coordinates for all atoms, i.e., the nuclei, of the system; in case of DFT see Fig. 1. While within most theories such a nuclei arrangement can be optimized, it is not uncommon to use a fixed nuclei geometry from a common database to be comparable to other approximations or to simply save computational time, as a full geometry optimization might be computationally very demanding.

For quantum chemical calculations there exist a vast a variety of seemingly promising databases, such as CCCBDB [65], ChemSpider [66], PubChem [67], and many more. However, one needs to be aware that the quality of the nuclei arrangements in these databases may vary [68]. While CCCBDB offers access to experimental geometries, the ones in PubChem provides nuclei arrangements calculated using the MMFF94s [69] force field. For other databases such as ChemSpider it is even not that trivial to find which quality the nuclei arrangements have.

The main messages and key results will be discussed based on the small, educational systems H$_2$O, CH$_2$O, and CH$_3$NO$_2$. We summarized some essential molecular information for those molecules in Table 3, including reference values for dipole moments and polarizabilities.

Table 3. Molecular information for H$_2$O, CH$_2$O, and CH$_3$NO$_2$ with number of atoms, electrons, $\alpha$ and $\beta$ electrons $N_{\text{nuc}}, N_{\text{elec}}, N_\alpha$ and $N_\beta$. References for the dipole moments [70] and polarizabilities [65] are provided.

| System       | $N_{\text{nuc}}$ | $N_{\text{elec}}$ | $N_\alpha$ | $N_\beta$ | $\mu_{\text{REF}}$ [D] | $\alpha_{\text{REF}}$ [$\text{a}_0^9$] |
|--------------|-----------------|------------------|-------------|----------|-------------------------|-----------------------------|
| water H$_2$O | 3               | 10               | 5           | 5        | 1.85                    | 10.13                       |
| formaldehyde CH$_2$O | 4        | 16               | 8           | 8        | 2.33                    | 18.69                       |
| nitromethane CH$_3$NO$_2$ | 7        | 32               | 16          | 16       | 3.46                    | 32.39                       |

The question of the quality of the nuclear arrangements might be important for other fields as well, e.g., machine learning [71] when an observable is learned for low quality nuclei arrangement, while one might have expected the geometry to be an experimental one. For SIC calculations, the quality of the nuclei arrangement is of great importance, as the electronic geometry and the corresponding density is very sensitive to the nuclei arrangement. However, full geometry optimization require very high computational effort.

We show that the effect of different nuclei arrangements on density fingerprints, i.e., dipole moments and polarizabilities, is significant. Even at the DFT level the results for various chemical databases show significant differences (see Fig. 4).

For the used test systems CCCBDB provides the best nuclei arrangements; the dipole moments and polarizabilities are close to the values obtain from nuclei
Fig. 4. Effect of nuclei arrangements on dipole moments and polarizabilities calculated using LDA-PW DFT and several tier level. Geometries are taken from common chemical databases. In addition, an optimized geometry was used (started from CCCBDB geometry, using ERKALE with tier4). Reference values are provided in Table 3.

arrangements that are fully optimized with DFT. For all investigated properties for the tested molecules it is obvious that the basis set effect is significant, and only the highest tier level provide reasonable results. The nuclei arrangements from PubChem and ChemSpider should be used with care. With respect to the computational effort we find that tier5 gives reliable results with respect to larger tier levels, see Fig. 4. For all performed calculations, the finite difference approximation agrees well with the analytical values. The mean error for the dipole moments is 0.00 D, while the respective insignificant mean errors for the polarizabilities are given in Table 4. Accordingly, the chosen value of $10^{-7}$ a.u. for the magnitude of $\varepsilon$ for the 2-point finite difference approximation delivers excellent numerical results for dipole moments and polarizabilities. Having examined the dependence on the nuclei degrees of freedom, in Section 4.2 we investigate electronic degrees of freedom in FLO-SIC, i.e., DM and FODs.

Table 4. Mean error of polarizabilities in $\alpha_0^a$ comparing analytical $\alpha$ and finite difference $\alpha_{FD}$. The magnitude of $\varepsilon$ was chosen to be $10^{-7}$ a.u. for the 2-point finite difference approximation.

| Database  | tier1 | tier2 | tier3 | tier4 | tier5 | tier6 |
|-----------|-------|-------|-------|-------|-------|-------|
| CCCBDB    | +0.02 | ±0.00 | −0.01 | −0.02 | −0.01 | −0.01 |
| ChemSpider | ±0.00 | ±0.00 | −0.01 | −0.02 | ±0.00 | ±0.00 |
| PubChem   | +0.05 | +0.01 | ±0.00 | −0.01 | +0.02 | +0.03 |
| DFTopt    | ±0.00 | +0.01 | −0.01 | −0.02 | −0.03 | −0.01 |
4.2 The sword of Damocles: Curse and blessing of approximations

Approximations are often needed and can be useful to enable the treatment or computation of a specific property at a certain theory level. However, each approximation needs to be investigated before usage to explore the limits of its predictive power.

Effect of FLO-SIC approximations In FLO-SIC it is rather trivial to make various approximations, consciously or unconsciously. A common approximation is to use fixed FODs which are not optimized for the numerical parameter space of the respective calculation. In this section we will use our proposed Flevel system to show the predictive power as well as the limitations of such approximations in FLO-SIC.

![Fig. 5. Displaying both nuclei and initial FODs based on Lewis theory for H$_2$O and CH$_2$O. The picture is generated with the PyFLOSIC2 graphical user interface (GUI). Note, only H$_2$O and CH$_2$O are shown as they have only one trivial initial FOD configuration, whereas CH$_3$NO$_2$ is more complex and will discussed later; see Fig. 8.](image_url)

We start the discussion for H$_2$O and CH$_2$O which have trivial bonding situations, see Fig. 5. For both molecules, trivial bonding situation refers to the fact that they are described with exactly one Lewis structure. Examining different Flevel for water and formaldehyde (see Fig. 6), it can be seen that there is a significant change in the total energy as well as in the SIC energy going from DFT to the simplest FLO-SIC approximation, i.e., Flevel=0. Thus, going from the delocalized KS orbitals to more localized FLOs leads to a decrease in energy. However, as the density is not changing for Flevel=0, also the fingerprint of density, i.e., the dipole moment is not changing. Another large change in energy occurs between Flevel=1 and Flevel=2; this highlights the importance of optimizing the FODs. Further, the SIC energy decreases with increasing Flevel. This showcases the increasing accuracy in terms of SIC for the Flevel system; the more you optimize, the better your description of SIC. As proposed by some of
monitoring the dipole moment is important to classify and analyze different SIC solutions. To get a computationally efficient first idea about how SIC influences the density, and with that the respective dipole moment, $F_{\text{level}}=2$ can be used. In addition, $F_{\text{level}}=2$ can be used to approximate the magnitude of the SIC energy.

Although the trends for the different $F_{\text{level}}$ are consistent for different tier level, the absolute values of the studied properties change with increasing basis set size. Clearly, the energy appears to converge faster than the dipole moment. While it is necessary to converge the energy it is not sufficient if one is interested in density-related properties, i.e., dipole moments or polarizabilities.

From the timings one sees the trade-off of using a higher $F_{\text{level}}$; the timings increase, and using the full FOD optimization typically takes longer than any other $F_{\text{level}}$. As such, the $F_{\text{level}}$ system can determine the best trade-off between accuracy and computational time for the system and objective one wants to study.

However, global statements and generalization of trends are only valid for full FLO-SIC calculations, i.e., $F_{\text{level}}=3$, in combination with a sufficient tier level, i.e., tier5. The global trends whether DFT or SIC underestimate or overestimate the experimental value depend significantly on the used tier level. Also, the relative trends between both methods show a similar effect. For the systems investigated in this work the lowest tier significantly underestimates the dipole, while increasing the tier level typically increases the dipole with respect to tier1, reaching convergence at larger tier levels. The converged dipole moments are usually slightly smaller than the tier2 value. This is noteworthy given that tier2 uses a double-$\zeta$ basis set quality which is not untypical for SIC calculations.

![Fig. 6. FLO-SIC $F_{\text{level}}$ vs. tier levels for the LDA-PW exchange-correlation functional in (a) for H$_2$O and (b) for CH$_2$O. The individual subplots in (a) and (b) visualize the total energy and the respective SIC energy, Eq. (8), the dipole moment, Eq. (19), and the real time. In all plots the x-axis represents different approximations ranging from worst to best SIC description. The colors represent the different tier levels.](image-url)
Effect of exchange-correlation functional For analyzing trends, as done here for \( \text{H}_2\text{O} \) and \( \text{CH}_2\text{O} \) as they have trivial and reproducible FOD configurations, LDA-PW already describes dipole moments qualitatively correctly for DFT and SIC with respect to other higher rung exchange-correlation functionals, see Fig. 7. Note that for \( \text{CH}_3\text{NO}_2 \) this comparison was not carried out as it is not trivial, given that various FOD arrangements are possible, which can converge to different final FOD solutions, see Fig. 8.

**Fig. 7.** Effect of the exchange-correlation functionals on the dipole moments in (a) for \( \text{H}_2\text{O} \) and (b) for \( \text{CH}_2\text{O} \), comparing LDA-PW, PBEsol and \( r^2\text{SCAN} \). Using tier5 for both DFT and FLO-SIC, while Flevel=3 was employed for the FLO-SIC values.

Effect of different SIC methods The numerical parameter space is properly chosen and represented by tier5, given that there is no significant difference between FLO-SIC and RSIC values, see Table 5. This is noteworthy as the results are calculated with different electronic structure codes.

**Table 5.** Comparison of \( \mu \) in D using tier5 and the LDA-PW functional, using the experimental geometries. DFT values are obtained from \texttt{PySCF}, FLO-SIC values are obtained from \texttt{PyFLOSIC2}, and RSIC and CSIC values come from \texttt{ERKALE}.

| Molecule | \( \mu_{\text{DFT}} \) | \( \mu_{\text{FLO-SIC}} \) | \( \mu_{\text{RSIC}} \) | \( \mu_{\text{CSIC}} \) |
|----------|------------------------|------------------------|------------------------|------------------------|
| \text{H}_2\text{O} | 1.86 | 1.99 | 1.99 | 2.06 |
| \text{CH}_2\text{O} | 2.28 | 2.72 | 2.72 | 2.75 |
| \text{CH}_3\text{NO}_2 | 3.50 | 3.68 | 3.71 | 3.91 |

Effect of different initial FODs For \( \text{H}_2\text{O} \) and \( \text{CH}_2\text{O} \) one might unconsciously place the FODs correctly, as those molecules only have one trivial Lewis structure. On the other hand, for \( \text{CH}_3\text{NO}_2 \) it is possible to find several possible
chemical bonding arrangements, especially for the -NO$_2$ group. This leads to various different initial FOD configuration for this molecule.

We investigated bonding motifs given by Lewis theory of bonding, where one has one double N=O and one single N-O bond in the -NO$_2$ group. Clearly, there exist two identical Lewis configuration where the double and single bond are exchanged with each other. Those Lewis configuration have N-O bond orders of BO$_{N,O} = \{2,1\} = \{1,2\}$. In LDQ theory one would place 2 electrons of one spin channel and 1 electron of the other spin channel between N and O, leading to N-O bond orders of BO$_{N,O} = \{1.5,1.5\}$. Changing the N-O bonds will affect the local chemical environment, i.e., the core and lone electrons of the respective N and O atoms. Besides those FOD configuration which follow chemical bond theories also other FOD configuration can be used, e.g., one where we construct an over-binding N atom placing two N-O double bonds in the molecule. We denote such FOD configurations as other.

We investigated the effect of these different FODs for CH$_3$NO$_2$, see Fig. 8. FODs based on LDQ deliver the lowest energy. An initial LDQ configuration as well as an initial Lewis configuration converges to a final FOD arrangement resembling an LDQ FOD configuration. Interestingly, the over-binding N, i.e., other initial FODs stay in the initialized configuration, but the final energy is higher than the LDQ FODs final energy. The initial FOD configurations calculated using Flevel=1 already show significantly different dipole moments, where only the LDQ value is close to the experimental value. Thus, LDQ not only gives the lowest energy but also the best SIC dipole moment for CH$_3$NO$_2$. We want to highlight that if one calculates the center of mass (COM) for the optimal RSIC localized orbitals using ERKALE, they also reflect the LDQ chemical bonding motif, see the RSIC box in Fig. 8.

Fig. 8. Various FOD configurations for CH$_3$NO$_2$. Other represents a structure with two N-O double bonds. Any other tested structure converges into the LDQ solution. Optimized configurations correspond to tier5 and Flevel=3. In addition, the RSIC centroids are shown in the light green box as comparison to the final LDQ FODs.
5 Summary and Conclusion

In the first sections, see Sections 1 and 2, we presented an overview for DFT and FLO-SIC, where we centered the discussion on properties being useful as fingerprints of the density, i.e., dipole moments or polarizabilities. We highlighted the importance of the awareness of the quality of nuclei coordinates, i.e., the effect of experimental or computed nuclei coordinates as starting points in DFT calculations in Section 4.1 for fingerprints of the density. This is essential as SIC calculations start from DFT calculations. Thus, SIC is influenced by this effect as well. If there are no further constraints given, we recommend the usage of experimental or DFT optimized nuclei arrangements for SIC calculations.

As shown in Section 4.2 and already stated in earlier works in the field [24, 43, 49], SIC needs finer numerical quadrature meshes and also bigger basis sets in comparison to respective DFT calculations. Global comparisons between the predictive power of SIC in comparison to the underlying DFT are only meaningful using very accurate numerical parameter spaces. Therefore, we propose a tier level system to systematically approach the numerical parameter space in FLO-SIC. When computational time matters, the simplest approximation for exchange-correlation functionals, i.e., a local density approximation like LDA-PW, provides reasonable trends, e.g., for dipole moments in SIC. If computational time is not limited we recommend to use another higher rung functional like PBEsol or r\textsuperscript{2}SCAN to verify and further analyze determined trends.

For molecules with non-trivial bonding situations, e.g., where one can draw more than one trivial Lewis bonding configuration, as shown in this work for nitromethane in the last part of Section 4.2 it is highly recommended to use various initial FOD configurations following chemical bonding theories, i.e., Lewis and Linnett, to reasonably sample the FOD configuration space and determine the most reasonable FOD configuration. For trivial bonding situations Lewis and Linnett may describe the same chemical bonding configuration, whereas for non-trivial bonding situations LDQ FODs are often superior to Lewis FODs in FLO-SIC.

Any approximation which enables the calculation of bigger systems in FLO-SIC with proper numerical effort needs to be carefully tested and verified; numerical results can change significantly such that even trends are not presented correctly. In this work we proposed the Flevel system to systematically classify approximations in the FLO-SIC theory. A typical global trend for the direct comparison of DFT and SIC is that the numerical results, i.e., dipole moments, significantly depend on the used numerical parameter space and can clearly change using better numerical parameters, i.e., climbing up the proposed tier level ladder. Further, in FLO-SIC the initial set of FODs can significantly change dipole moments as well. Another observation is that the total energy and the SIC energy appear to converge faster than density-related properties. While it is necessary to converge the energy it is not sufficient for the study of density-related properties, i.e., dipole moments or polarizabilities.

We want to emphasize the importance of Open-Science and Open-Source developments, as this work would not be possible without them.
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