Koopmans’ condition in self-interaction corrected density functional theory

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We investigate from a practitioner’s point of view the computation of the ionization potential (IP) within density functional theory (DFT). DFT with (semi-)local energy-density functionals is plagued by a self-interaction error which hampers the computation of IP from the single-particle energy of the highest occupied molecular orbital (HOMO). The problem may be cured by a self interaction correction (SIC) for which there exist various approximate treatments. We compare the performance of the SIC proposed by Perdew and Zunger with the very simple average-density SIC (ADSIC) for a large variety of atoms and molecules up to larger systems as carbon rings and chains. Both approaches to SIC provide a large improvement to the quality of the IP if calculated from the HOMO level. The surprising result is that the simple ADSIC performs even better than the original Perdew-Zunger SIC (PZSIC) in the majority of the studied cases.

I. INTRODUCTION

Density Functional Theory (DFT) [1–3] has become a standard theoretical tool for the investigation of electronic properties in many physical and chemical systems. It provides fairly reliable results with moderate computational effort. Practical implementations of DFT employ simple and robust approximations for the exchange and correlation functional. The simplest one is the Local Density Approximation (LDA), which has been proven very useful in calculations of electronic structure and dynamics. Typical applications are reaching from first principle calculations on the electronic ground state and molecular geometries [4], over dynamic studies of near equilibrium situations (e.g. optical response, direct one-photon processes) to highly non-linear dynamical scenarios [5–7]. However, LDA is plagued by a self-interaction error [8]: The Kohn-Sham (KS) mean field is computed from the total density which includes all occupied single-particle states, including the state on which the LDA field actually acts. Locality of the exchange functional leads to a wrong asymptotic KS field. This is still a great hindrance in many applications, for instance a possibly large underestimation of IP and the absence of Rydberg or excitation series in the static KS spectrum [9–10], the polarizability in chain molecules [11–12] or the spectral and fundamental gap in solids [13–14]. Another challenging application is the description of molecules or clusters deposited on surfaces [15–16]. In dynamic scenarios, the self-interaction error also dramatically affects ionization dynamics, especially close to thresholds, e.g., in a time-dependent DFT model of electron emission [17–19].

In practice, the wrong asymptotics of the KS field stems from an incomplete cancellation of the self-interaction error between the Hartree potential and the approximate exchange and correlation field. Such a spurious self-interaction is avoided by a complicated non-locality in exact KS-DFT [20–22]. For the total energy, the requirement for non-locality can be incorporated into gradients of density leading to the generalized gradient approximation (GGA) [23–25]. This approximation indeed served to lift DFT to a quantitative level in molecular physics and chemistry problems, but is insufficient to restore proper asymptotics of the mean field.

Although there are approaches to improve the asymptotic KS potential [26] those are often too demanding for practical calculations, in particular in the time-domain. The aforementioned examples show that there is still a need for robust and practical approaches to improve on the asymptotic KS potential, such as self-interaction correction (SIC).

The original proposal for a SIC [8] by Perdew and Zunger (PZ) has been developed at various levels of refinements and proved to be useful over the years, in particular for structure calculations in atomic, molecular, cluster and solid state physics, see e.g. [28–35]. This original PZSIC scheme, however, leads to an orbital-dependent mean field which causes several formal and technical difficulties [29–32, 33–35, 36]. There are attempts to circumvent the orbital dependence by treating SIC with optimized effective potentials (OEP) [37], for a review see [38]. However the resulting formalism is, again, quite involved and usually treated approximately [39]. A very robust and simple SIC is the average density SIC (ADSIC) which was proposed already very early [40], taken up in [41], and has been used since in many applications to cluster structure and dynamics in all regimes.

ADSIC takes the total density divided by the electron number as a reference for the single electron density in each state. Non-locality is incorporated in the scheme by the global density integral providing the total particle number. However the ADSIC functional, unlike the PZSIC one, is a functional of the total density and thus, the subsequent mean field is not orbital dependent anymore. Having the correct total charge, ADSIC provides the proper asymptotics for the mean field. It is argued
that the approximation by one and the same (average) single-particle density for each state is only applicable in simple metals where all electronic states cover the same region of space, that is, in the case of a cluster, the whole cluster itself [41, 42]. Later studies revealed that ADSIC is also an efficient correction scheme for non-metallic systems with delocalized electrons, such as organic molecules [43, 44].

The aim of this paper is to investigate the performance of ADSIC in direct comparison to PZSIC for a large variety of atoms and molecules in their ground state. The sample covers systems of different binding types, and not only metallic ones. We will compare ADSIC with a mere DFT treatment using (semi-)local functionals and with PZSIC, also occasionally with Hartree-Fock. The comparison focuses on the proper description of the IP. We start from atoms as elementary building blocks of any molecule, proceed to a large variety of molecules from simple dimers to more complex organic structures, and finally discuss carbon rings and chains with a systematic variation of sizes. Such a strategy allows us to cover various binding types but also various geometries and even dimensionality.

II. IONIZATION POTENTIAL

A. Definitions

The key quantity of this survey is the ionization energy $I$, commonly called ionization potential (IP). The IP of a $N$ electron system is given by the energy difference

\[ I \equiv I_\Delta = E(N-1) - E(N) . \]  

(1)

The energies $E(p)$ correspond to ground-state configurations of a $p$ particle system in a given external potential, typically the Coulomb potential created by the nuclear charges. Both energies, $E(N)$ as well as $E(N-1)$, are fundamental observables in ground-state DFT and so is its difference, the IP. DFT should thus allow one to calculate the IP of electronic systems. A distinction has to be made here. The definition of an IP is unique in atoms. In molecules, however, we distinguish vertical and horizontal IP. The vertical one considers the energy difference from the removal of one electron for frozen atomic positions. This typically corresponds to photon induced fast emission processes. The horizontal IP is built from the difference of fully relaxed molecular configurations. It accounts for the energy change on a long time scale on which all molecular relaxation processes are finalized. We will consider throughout this paper the vertical IP which accounts for fast electronic processes and which is closely related to the properties of the electronic ground state of the mother system, in particular to the highest occupied molecular orbital (HOMO).

In the exact electronic ground state, the asymptotic decrease of the ground state density $n$ is related to the IP by

\[ n(r) |_{r \to \infty} \sim \exp \left( -2\sqrt{2I} |r| \right) . \]  

(2)

In an exact KS-DFT, the asymptotic decay of the total density is defined merely by the highest occupied KS orbital, i.e., the HOMO [4]. In combination with the proper asymptotic behavior of the KS potential ($v_\text{KS}(r) \to 0$), the ionization energy can thus be related to the single-particle energy of the HOMO:

\[ I \equiv I_\epsilon = -\varepsilon_{\text{HOMO}} . \]  

(3)

For an exact exchange-correlation functional, both definitions of the ionization energy, i.e., Eqs. (1) and (3), coincide, i.e. they obey $I_\Delta = -\varepsilon_{\text{HOMO}}$. The identification of the negative HOMO energy with the IP was referred to as Koopmans’ theorem [45] long before the fundamental concepts where extended rigorously to the framework of DFT [46, 47]. For approximate energy functionals Koopmans’ condition does not necessarily hold [2] and the deviation from the ideal behavior can be used to define the Non-Koopmans (NK) energy

\[ \Delta E_{\text{NK}} = I_\epsilon - I_\Delta . \]  

(4)

A value $\Delta E_{\text{NK}} = 0$ signals that Koopmans’ theorem is fulfilled. In such a situation, the properties of the HOMO level are closely related to ionization and electron emission. We know that LDA produces rather large violations of Koopmans’ theorem and thus exhibits sizable $\Delta E_{\text{NK}}$. SIC should reduce that, and the amount of reduction is one measure of the efficiency of the actual SIC scheme.

It is also interesting to compare the performance of a calculation with respect to data. Thus we consider in addition to the NK energy the bare error in the IP relative to experiments or other reference data. As we have two definitions of the IP, there are two bare errors in an approximate theory:

\[ \Delta I_\epsilon = I_\epsilon - I_{\text{ref}} , \quad \Delta I_\Delta = I_\Delta - I_{\text{ref}} . \]  

(5)

An experimental reference energy may be hampered by uncertainties, as ionic relaxation throughout the ionization process can lead to situations which lie between the idealized vertical IP (for very fast ionization) and horizontal one (for very slow ionization). Here only vertical IP in the ground-state geometry is considered. Reliable atomic coordinates for small molecules are given by the MP2 optimized structures as provided in the G2 dataset [48]. G2 theoretical and experimental energies may differ by several tens to hundreds of meV [49]. This error can be considered negligible on the scale of the expected errors, stemming from the approximate nature of the used exchange-correlation functionals and the use of pseudo-potentials [50]. Experimental data for vertical IP therefore appear as a safe choice of reference [51].

In contrast to the errors in the IP [5], the NK energy does not require any reference data that may be hampered by experimental uncertainties. It therefore provides a rather rigorous criterion for the quality of energy functional approximations.
B. Impact of a proper description of IP

The two definitions \( I \) and \( \eta \) for the IP are equally justified in an exact calculation. However, for (semi-)local functionals (as in LDA and GGA), it is usually found that only the energy difference \( I \) can be used to extract a good estimate for the IP. The estimate \( \eta \) from the single-particle spectrum requires the proper \( 1/r \)-asymptotics of the exchange-correlation potential (for neutral systems). This is not provided in calculations based on typical semi-local functionals.

While energy differences often allow reliable estimates already with semi-local functionals, they require two calculations, which is more involved than a straightforward extraction from the HOMO level. This alone would not be a priori a major hindrance. But there are many situations where the extraction via energy difference is not an option: In periodic calculations (e.g., on surfaces), a rigorous calculation of the IP (called work function in this case) from an energy difference is hard to achieve because one cannot easily model a single excess charge in a periodic setup. The same situation applies for calculation of band-gaps in solids. In dynamical situations, as described by time-dependent DFT, an accurate modeling of the ionization process requires an accurate static single-particle spectrum. As the propagation of the single-particle states is driven by the time-dependent KS Hamiltonian, the energy differences in its spectrum and a proper position of the IP is more essential than the total energy. Ionization properties are also mostly defined by the HOMO level which thus has to be correctly described.

A way to illustrate the self-interaction error is to consider the energy \( E(\nu) \) as a function of a fractional particle number \( \nu \). The ionization process goes along \( \nu = N \rightarrow N - 1 \). An exact functional produces a linear behavior \( 20 \), as:

\[
E(\nu) = (1-x)E(N) + xE(N-1), \quad x = N - \nu \in [0,1]. \quad (6)
\]

A similar linear behavior is also observed for ionization from an anion to the neutral system \( (N+1 \rightarrow N) \). This exact \( E(\nu) \) is shown as (red) solid line in Figure 1. The remarkable feature is a discontinuous derivative, that is a kink, at \( \nu = N \). Semi-local functionals deal with smooth functions (no kinks, no discontinuities) and produce smooth trends as shown in the (green) dotted line. The definition \( \eta \) of the IP through the HOMO energy coincides with the slope of the total energy for fractional particle numbers at \( \nu \gtrsim N \):

\[
I_\varepsilon = - \frac{dE}{d\nu} \bigg|_{\nu \gtrsim N} \quad (7)
\]

as indicated in the figure. The linear trend of the exact energy naturally guarantees \( I_\varepsilon = I_\Delta \), while the convex curve from LDA necessarily implies \( I_\varepsilon < I_\Delta \).

The (blue) dashed line in Figure 1 finally shows results from exact exchange in Hartree-Fock (HF). Full HF is free from self-interaction error. Thus it qualitatively yields the correct result, namely the kink at \( \nu = N \). It however differs from the linear trend in between the integer particle numbers. This leads to an overestimation of the IP from the HOMO, \( I_\varepsilon > I_\Delta \). We will address this question in the last example of carbon chains, see Figure 8.

III. VARIOUS SCHEMES FOR A SIC

As SIC is rather an ad-hoc measure to cure the self-interaction problem, various recipes and approximations are used, depending on the field of application. In this section, we briefly summarize the PZSIC and ADSIC which we will use later on in the extensive comparison of results.

A. Perdew-Zunger SIC

As already mentioned in the introduction, a very popular approach to the definition of a one-particle self-interaction error and a corresponding correction was presented by Perdew and Zunger \[8\]. The self-interaction error is given by accumulating the contributions from the individual orbital densities \( n_i(r) = |\varphi_i(r)|^2 \) for a set of single-particle states \( \varphi^N = (\varphi_1, \ldots, \varphi_N) \). It reads

\[
E_{SI}[\varphi^N] = \sum_{i=1}^{N} (E_{H}[n_i] + E_{xc}[n_i]) \quad (8a)
\]
where \( E_H \) is the Coulomb Hartree energy and \( E_{xc} \) the density functional for exchange and correlations. Note that this is not a functional of density alone. In fact, \( E_{SI}[\varphi^N] \) depends on the detailed orbitals. The PZSIC is defined by subtracting the self-interaction error from the original functional, i.e.,

\[
E_{PZSIC}[\varphi^N] = E_H[n] + E_{xc}[n] - E_{SI}[\varphi^N],
\]

where \( n = \sum_{i=1}^N n_i \) is the total electronic density.

The mean-field equations are derived in straightforward manner by variation of the SIC energy \( E_{PZSIC} \) with respect to the occupied single-particle orbitals \( \varphi_i \). It turns out that mean-field Hamiltonian depends explicitly on the particular single-particle state on which it acts. This emerges because the PZSIC energy functional is not invariant under unitary transformations amongst the occupied states. There are several ways to deal with such a state-dependent Hamiltonian \([28-31]\). A particularly efficient way is to use two different sets of single-particle states which are connected by a unitary transformation amongst occupied states. That is actually the solution scheme which we are using, for details see \([52]\). In this approach, the HOMO level is defined as usual, in the basis-set which diagonalizes the Hamiltonian matrix.

### B. Average Density SIC

The average density SIC (ADSIC) starts from the SIC energy \([83]\) and simplifies it by assuming that indistinguishable electrons are represented by equal single-particle densities. In such an extreme simplification, one expresses them as the one-particle fraction of the total spin-density \( n_i(r) = n_{\sigma}(r)/N_{\sigma}, \) where \( \sigma \) is the spin of state \( i \) and \( N_{\sigma} \), the number of particles with spin \( \sigma \). In such a scheme, the standard PZSIC functional is represented by the ADSIC functional:

\[
E_{ADSIC}[n_\uparrow, n_\downarrow] = E_H[n] + E_{xc}[n] - \sum_{\sigma=\{\uparrow, \downarrow\}} N_{\sigma} (E_H[n_{\sigma}] + E_{xc}[n_{\sigma}]),
\]

where \( n = n_\uparrow + n_\downarrow \). This is a spin-density functional and can be treated in the same manner as any LDA or GGA scheme. This makes it extremely simple and efficient to use in atomic and molecular systems. However, the ADSIC functional contains a cumbersome non-locality as it explicitly depends on the particle number \( N_{\sigma} = \int d^3r n_{\sigma}(r) \). This inhibits an application in periodic systems, where \( N_{\sigma} \) is infinite.

### IV. RESULTS

#### A. Numerical scheme and pseudo-potentials

The calculations use a representation of the single-particle wave functions on a coordinate-space grid with a spacing of 0.2 Å. Densities and fields where represented on a refined grid of 0.1 Å to account for the higher Fourier components in products of single-particle states. The core electrons are handled within the frozen-core approximation by a real-space implementation of the projector augmented wave (PAW) method \([53]\) using a development version of GPAW \([54]\). The projectors and partial waves of the PAW method are taken as provided within the GPAW repositories for bare LDA exchange and correlation, i.e. without accounting for a SIC.

This corresponds to use pseudo-potentials developed for LDA applications in the context of PZSIC or ADSIC without readjustment of the pseudo-potential parameters. This minor inconsistency is acceptable in various applications of SIC \([32, 55, 56]\). Here such an improvement is avoided in favor of using a unique set of pseudo-potentials for all energy functionals.

For the following survey, we show results from LDA using the PW92 parameterization \([57]\). For most of the examples below, we have also performed GGA calculations with the PW91 functional \([24]\). Even if the GGA slightly improves the overall quality of the IP, in particular if calculated from energy differences, with very few exceptions, the effect of the gradient dependence is less than 0.5 eV. Thus it neither affects the overall magnitude of errors or change the general trends that are discussed in the following sections. We therefore focus on the LDA part in this survey.

#### B. Atoms

The first step is to investigate the performance of both SIC approaches for atoms. The latter ones are the basic building blocks of molecules and solids. Thus they must be correctly described before we can proceed to more complex scenarios. The electronic structure of atoms incorporates single-electron states with similar shape but different spatial extensions. Thus atoms are a critical test case for SIC which is known to strongly depend on the level of localization.

Figure 2 shows the IP as such for neutral atoms from hydrogen \((Z=1)\) to argon \((Z=18)\). All methods yield very similar IP if it is evaluated as \( I_\Delta \), i.e. as the energy difference \([1]\). Results differ more for \( I_\varepsilon \) computed from the HOMO according to Eq. (3). Here, the bare \((semi-)local energy functionals underestimate the ionization energy of by 30-40%. The defect is well known and can be traced back to the wrong asymptotic behavior of the exchange-correlation potential for \( |r| \to \infty \) \([8]\). Obviously, both SIC approaches cure the problem and yield excellent agreement with experimental data. ADSIC is slightly superior in case of open shell atoms, while PZSIC slightly overestimates the IP. Accounting for GGA (not shown here) has an insignificant effect for both \( I_\Delta \) as well as \( I_\varepsilon \). The results do not sufficiently differ to justify a separate plot.

Figure 3 shows the same data of figure 2 but in terms
of errors with respect to experimental data and of the NK energy. This reveals some differences between PZSIC and ADSIC where, somewhat surprisingly, the technically much simpler ADSIC visibly yields smaller NK energies and errors $\Delta I_e$.

At this point, it is worth recalling that the ADSIC scheme can be derived as an approximation to PZSIC, assuming a most delocalized representation of the single-particle densities. In ADSIC, orbitals are extending over the whole atom in stark contrast to the localized orbitals that are commonly found in PZSIC calculations. It thus appears that a significant higher level of delocalization is actually desirable, which confirms previous concerns that PZSIC orbitals are too localized.

### C. Simple Molecules

As a next step, we consider simple molecules, as many dimers, and a few more complex ones. The selection has been adapted from [51]. It covers systems which do not have the problem of spatial symmetry breaking by an unrestricted mean-field calculation. Reference data was taken from [51].

Figure 4 shows the IP for a chosen set of molecules. At first glance, the results resemble those for atoms in Figure 2. The $I_\Delta$ provides reasonable results for all methods while $I_\varepsilon$ shows dramatic differences between LDA and the SIC models. However, taking a closer look, we also see that results for ADSIC and PZSIC show larger differ-
ences than in the case of atoms. Somewhat surprisingly, ADSIC comes again much closer to experimental data than PZSIC.

Figure 5 shows the data from the previous figure in terms of energy differences, the errors $\Delta I$ as compared to reference data and the NK energy. The results confirm the impressions indicated in the comparison of the IP as such: The $\Delta I$ shows significant differences between PZSIC and ADSIC since the latter one generally performs better.

One may argue that comparison with reference data is also influenced by other details of the calculations or the choice of the reference data. The NK energy (lowest panel) is free of these uncertainties. ADSIC clearly delivers the smallest NK energies. This was seen already for atoms. But here in the case of molecules the effect is even more pronounced as PZSIC shows larger deviations.

D. Systematic sets of molecules

In this section, we look at a systematic variation of molecules around basic carbohydrates. The first family $(\text{CH}_x)$ represents a variation of the number of C-H bonds. The second family changes the character (single, double, triple bonds) in $\text{C}_x \text{H}_y$. The third family is similar to the first one but replacing carbon by a heavier element (silicon) with the same number of valence electrons, while the fourth series replaces the carbon atom by nitrogen (which has a different valence). In the final series one of the single bonded hydrogen atoms in $\text{CH}_x$ is substituted by a different group. The last element of the third and fourth series are not strictly within the systematics.

We have seen in the previous systems that energy differences are showing more details than the energies as such. We thus proceed here immediately to energy differences which are compiled in Figure 6. The results are very similar to the previous case of simple molecules, see Figure 5. Some of the deviations are however larger than in the previous case. This indicates that these complex molecules are more critical test cases. Even in this more demanding scenario, we find again that ADSIC performs superior with respect to the deviation from reference data and even more so for the NK energies.

Thus we find that the ADSIC which assumes orbital densities that are delocalized over the whole molecule yields a systematic improvement over PZSIC. This is
somewhat surprising in view of the deficits of ADSIC, in particular as its inability to describe dissociation and the lack of size consistence are directly attributed to a too high level of delocalization.

For infinite matter, ADSIC is not applicable due to the explicit dependence on the particle number. Already for larger systems, the explicit dependence on the total particle number quickly renders the SIC contribution to the energy functional an inefficient approach to cure problems of the LDA. The observation that delocalization on the length-scale of small molecules is in fact favorable for the quality of the NK energy and IP calls for more systematic investigations.

E. Carbon rings and chains

The self-interaction error on the IP for the Coulomb Hartree term is typically of order of \( e^2/R \) where \( R \) is the radius of the system. The error for the exchange-correlation potential can be estimated within ADSIC as \( v_{\text{xc}}[n/N] \). Both shrink with increasing system size. In order to explore the evolution of the self-interaction errors with increasing size, we consider carbon rings and chains. For the latter ones, we only consider odd numbers of atoms because only these have stable electronic configurations for spin saturated ground states. The carbon atoms have more or less constant bond length. This means that increasing the number of carbon atoms induces a (linear) growth of the geometrical extension, either of the chain or the ring.

The upper two panels of Figure 7 show the IP for carbon rings as a function of the number of atoms. Comparing ADSIC and LDA, we see again the equally good performance for \( I_\Delta \), and the large self-interaction error in \( I_e \) for LDA while ADSIC behaves very well. The reference data, here calculated LDA values \( I_\Delta \), show a pronounced step structure due to the successive filling of the electronic shells. Large \( I \) indicate particularly stable electronic structures, i.e., shell closures. The sudden reductions shows that a new, and less bound, electronic shell has to be opened to place the given number of electrons. LDA and ADSIC reproduce the shell effect. On first glance, the PZSIC results are quite surprising since they deviate even qualitatively from the other results, as they show less pronounced shell effects, at least with increasing chain length.

It shall be noted, that missing points also indicate that reliable minimization of the PZSIC energy becomes challenging for anionic configurations, where various local minima exist. The local minima correspond to different, almost energetically equivalent, configurations with different levels of delocalization of the excess electron in the spin-majority channel. The effect is worse for mid-shell systems but less problematic for closed shell configurations. No such problem exists for ADSIC due to the absence of the orbital-dependence.

The lowest panel of Figure 7 shows the NK energies.

The \( \Delta E_{\text{NK}} \) from LDA starts large but shrinks with increasing size as one could have expected. The ADSIC result is small throughout, but has a slight tendency to increase with size, and of course, never becoming larger than the error from LDA. However, the \( \Delta E_{\text{NK}} \) from PZSIC is generally large and even grows with system size. This finding is rather cumbersome, as it confirms that the difference between the behavior of LDA and ADSIC on the one hand, and PZSIC on the other hand, actually stems from misconceptions in the PZSIC partially compensated in the approximate ADSIC.

The significant and positive NK energy indicates that strong correlation effects, which are underestimated in semi-local exchange and correlation, are overestimated by the PZSIC. The screening of such strong correlation effects has to be reintroduced in the self-interaction corrected approach, e.g., by the assumption of more delocalized states, as in case of the ADSIC.

The convergence of ADSIC and LDA yet illustrates the
collapse of ADSIC as a working SIC scheme for extended systems, where $N \gg 1$, contrary to the case of small $N$ where the NK energy is still improved significantly. The almost constant but finite NK energy indicates that, although ADSIC is not capable of a complete curing of the non-linear dependence of the LDA energy functional for fractional occupation, it at least provides a scheme that yields similar magnitudes of errors for compact systems and extended ones, whenever LDA is by itself considered a reasonable approximation there.

Figure 8 shows IP and $\Delta E_{NK}$ for carbon chains. In this case, we added also results from a pure Hartree-Fock (HF) calculation. PZSIC looks more agreeable here than for rings. Starting out perfect for the smallest chain $C_3$, the NK energy jumps already for $C_5$ and continues to grow further. This sounds, at first glance, very surprising as HF is free of any self-interaction error. However, removal of one electron causes polarization effects on the mean field of the remaining electrons. These may be small in compact molecules. But polarizability grows huge particularly in chains. The missing correlations from polarization effects are the source of the increasing NK error with HF. This can also be seen from the IP as such. The HF result deviates much from the others for $I_\Delta$ (middle panel), while it nicely stays in between for $I_\varepsilon$. The missing polarization effects explain the mismatch for HF. The fact that the DFT based methods perform better indicate that some polarization effects are properly modeled in DFT, although it is also known that DFT underestimated the polarizability in some chain molecules [58].

**F. Discussion**

To summarize the results presented in the above figures, we have computed average errors for each group of system considered, atoms, simple molecules, and families of systematically varied molecules. Thereby, we distinguish between mean error, mean absolute error and the error fluctuations defined as

$$\text{ME}(\Delta O) = \frac{1}{N_{\text{ samp}}} \sum_i \Delta O_i,$$

$$\text{MAE}(\Delta O) = \frac{1}{N_{\text{ samp}}} \sum_i |\Delta O_i|,$$

$$\sigma(\Delta O) = \frac{1}{N_{\text{ samp}}} \sum_i |\Delta O_i - \text{ME}(\Delta O)|,$$

where $O$ is one of the considered observables, that is $I_\Delta$, $I_\varepsilon$, or $E_{NK}$. The index $i$ runs over the $N_{\text{ samp}}$ samples in a given group, and $\Delta O_i = O_i - O_i^{(\text{ref})}$ stands for the observables deviation from the reference data $O_i^{(\text{ref})}$. The resulting averages for each group are listed in Table I. Computation of IP as $I_\Delta$, i.e. from energy differences, is always a safe procedure yielding reliable results already with LDA. Computation as $I_\varepsilon$ via the HOMO is possible with good accuracy in both SIC models. The great surprise is that the very simplistic ADSIC approach performs very well for the $I_\varepsilon$, typically even better than PZSIC. The same conclusion is deduced from the non-Koopmans energy $\Delta E_{NK}$. This was already seen from the above figures and is corroborated in Table I on a quantitative level.

The excellent performance of ADSIC from compact systems both in terms of accuracy and the small violation of Koopmans’ condition is remarkable. Still, one should keep in mind the known deficiencies of the approach. Most notably is the violation of size consistency which becomes apparent in the dissociation of a molecule. Consider a dimer with total electron number $N$ which dissociates into one part containing $N_1$ electrons and another one with $N_2$ electrons. The ADSIC for the compound involves, of course, the total electron number $N$. But note that we have considered rather short chains. There are again large differences between PZSIC and ADSIC. This time, however, they are distributed almost symmetrically around zero error (see lowest panel). No clear preference can be deduced in this example.
Since we follow the dissociation path continuously, we necessarily have to keep using \( N \) in the correction. After all, we end up with two isolated atoms which would be treated by one common correction still regulated by the total \( N \). This is, of course, wrong as we know that each single atom has to be separately corrected with its own \( N_i \). The case is even worse in violent dynamics leading to multi-fragmentation. The problem could already have been spotted from the fact that the dependence on \( N = \int d^3 r n(r) \) implies a non-locality which becomes increasingly itching if \( n(r) \) ceases to be compact, but is rather distributed over several regions of space.

Fully accomplished dissociation and multi-fragmentation are, of course, extreme limits. The defects of ADSIC in this respect tend to show up earlier, for example, in the Born-Oppenheimer energies along the dissociation path. Thus one should not use ADSIC for computing large-amplitude molecular vibrations without careful checking its range of validity for the given application. Problems may also show up in molecules which combine very different length scales as, e.g., in NaH\(_2\)O where the Na atom adds a rather dilute electron distribution to the otherwise compact H\(_2\)O. In spite of the encouraging results presented above, one should check the NK energy \( \Delta E_{NK} \) for each new application again.

These known shortcomings should not hinder us to appreciate the good performance attained by ADSIC in structural and low energy dynamical situations. As illustrated all along the present work, ADSIC provides a remarkably robustness in terms of Koopmans’ violation. This implies, in particular, that it can be safely used in the perturbative dynamical regime where only a tiny fraction of an electron is emitted.

|          | \( I_\Delta \) ME | \( I_\Delta \) MAE | \( I \) ME | \( I \) MAE | \( E_{NK} \) ME | \( E_{NK} \) MAE |
|----------|-------------------|-------------------|-----------|-----------|----------------|----------------|
| atoms    |                   |                   |           |           |                 |                 |
| LDA      | 0.2               | 0.3               | -5.0      | 5.0       | 1.5            | -5.1            | 5.1            |
| PZSIC    | 0.3               | 0.3               | 0.7       | 0.8       | 0.7            | 0.4             | 0.5            |
| ADSIC    | 0.4               | 0.5               | 0.2       | 0.4       | 0.4            | -0.3            | 0.4            |
| small molecules |            |                   |           |           |                 |                 |                 |
| LDA      | 0.3               | 0.4               | -4.6      | 4.6       | 0.7            | -4.9            | 4.9            |
| PZSIC    | 0.5               | 0.6               | 1.4       | 1.5       | 0.9            | 0.9             | 0.7            |
| ADSIC    | 0.6               | 0.7               | 0.4       | 0.6       | 0.6            | -0.2            | 0.4            |
| systematic mol. |             |                   |           |           |                 |                 |                 |
| LDA      | 0.3               | 0.4               | -4.1      | 4.1       | 0.5            | -4.3            | 4.3            |
| PZSIC    | 0.5               | 0.6               | 1.4       | 1.4       | 0.7            | 0.9             | 0.9            |
| ADSIC    | 0.5               | 0.6               | 0.1       | 0.5       | 0.5            | -0.5            | 0.5            |

TABLE I. Mean error (ME), mean absolute error (MAE) and error fluctuations \( \sigma \) as defined in eqs. (10) for IP as well as NK energy for the data sets shown in figures 3, 5 and 6. Redundant data in \( \sigma \) is only considered once in the averages.

V. SUMMARY AND CONCLUSIONS

We have compared the performance of two different approaches to self-interaction correction regarding calculated ionization potentials and violation of Koopmans’ theorem. We have focused the discussions on two SIC procedures: the original Perdew-Zunger approach (PZSIC) and the average density version thereof (ADSIC). A wide range of electronic systems has been considered ranging from atoms and simple molecules up to subsystems of moderate size molecules, in particular carbon systems. The overall survey is thus quite general, so that the conclusions attained have a safe ground, beyond any specific effect.

We find in all examples considered here that ADSIC provides more reliable estimates of IP and a smaller violation of Koopmans’ theorem. This is a welcome result in view of the remarkable simplicity (and correlatively low computational price) of ADSIC.

We have also explored a known collapse of the ADSIC approach for extended systems. It was shown that PZSIC also fails to cure flaws of LDA in this regime. An optimistic interpretation of the data obtained on the example of carbon chains allows to conclude that an efficient orbital-density dependent SIC should provide weak localization of the single-electron states over several atoms. Such a weak localization is in line with the excellent performance of bare ADSIC in case of the smaller molecules studied here.

Whereas the results of this survey question the quality of PZSIC as a benchmark approach to a SIC, they simultaneously encourage the educated use of the much simpler ADSIC approach. However, as also noted, ADSIC certainly does not provide the ultimate SIC scheme as it fails by construction, for example in the modeling of dissociation processes or strong ionization. The limits of ADSIC with respect to dissociation or molecular structural rearrangement need to be explored further. Still it remains a viable and robust option for many dynamical situations, especially in the case of perturbative ionization, where the ionization potential, precisely the negative HOMO level, plays a central role. This implies that ADSIC remains the favorably self-interaction correction in the calculation of reliable photo-electron spectra and angular distributions of emitted electrons, which represent an ever-growing issue in the dynamics of irradiated clusters and molecules.

Future work should also aim at investigating to which extent the level of localization can be controlled within the PZSIC scheme by modifying the functional form, e.g., within the framework of GGA-SIC or by implying alternative localization criteria during the optimization of internal degrees of freedom, i.e., the unitary transformation amongst the single-particle states.
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