Non-Koopmans Corrections in Density-functional Theory: Self-interaction Revisited

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In effective single-electron theories, self-interaction manifests itself through the unphysical dependence of the energy of an electronic state as a function of its occupation, which results in important deviations from the ideal Koopmans trend and strongly affects the accuracy of electronic-structure predictions. Here, we study the non-Koopmans behavior of local and semilocal density-functional theory (DFT) total energy methods as a means to quantify and to correct self-interaction errors. We introduce a non-Koopmans self-interaction correction that generalizes the Perdew-Zunger scheme, and demonstrate its considerably improved performance in correcting the deficiencies of DFT approximations for self-interaction problems of fundamental and practical relevance.

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Because density-functional theory (DFT) accounts for correlated electron interactions via an explicit functional $E_{xc}$ of the total density $\rho$, it provides a computational scheme that is far more predictive and practical than the Hartree-Fock (HF) method for determining the Born-Oppenheimer energy of quantum systems [1]. In spite of the proven accuracy of local and semilocal DFT total energy calculations, it has long been recognized that the eigenvalues $\epsilon_{i\alpha}$ of the Kohn-Sham Hamiltonian, which are defined in the strictest sense as the Lagrange multipliers associated to the orthonormality constraint in the self-consistent energy minimization, have limited physical relevance [2]. Indeed, due to the fact that Koopmans’ theorem does not hold for approximate DFT functionals, the Kohn-Sham single-electron energies are not related to any physical ionization process, at variance with their HF counterparts that can be directly identified as the opposite electron removal energies $-\Delta E_{i\alpha}^{(0)}$ of the unrelaxed electronic system (i.e., without self-consistent modification of the electronic wavefunctions). Following the seminal work of Perdew and Zunger [3], one can accurately quantify Kohn-Sham deviations from the ideal Koopmans behavior by defining non-Koopmans energy contributions $\Pi_{i\alpha} = \epsilon_{i\alpha} + \Delta E_{i\alpha}^{(0)}$ (this heuristic definition will be made explicit later in the course of our discussion).

As pointed out by Perdew and Zunger, for any self-interaction-free single-electron theory, the Koopmans condition

$$\Pi_{i\alpha} = 0$$  \hspace{1cm} (1)

is rigorously satisfied (in particular, the HF functional verifies $\Pi_{i\alpha}^{HF}=0$ precisely because of the cancelation of the Hartree and exchange self-energy terms) [3]. This non-self-interaction criterion establishes a central and exact correspondence between the non-Koopmans behavior of a given energy functional and self-interaction errors, which favor electronic delocalization and considerably affect the accuracy of local and semilocal Kohn-Sham calculations. Indeed, self-interaction is responsible for well-known quantitative and qualitative failures of conventional DFT functionals in describing important phenomena, such as electron transfer [4], electronic transport [5], and electrical polarization in extended systems [6].

In this work, we examine the cancelation of the non-Koopmans terms $\Pi_{i\alpha}$ that results from the Perdew-Zunger self-interaction correction (PZ-SIC) and show that the non-self-interaction condition (Eq. 1) is satisfied to second order in the single-electron densities. In order to achieve a higher level of accuracy, we introduce an alternative non-Koopmans self-interaction correction (NK-SIC). We validate our method by studying the dissociation of $\text{H}_2^+$ and $\text{H}_2$ molecules, and compare its performance to that of the original PZ-SIC approach in describing the longitudinal electrical response of dimerized hydrogens.
hydrogen chains, a complex self-interaction problem that has received much attention for its fundamental relevance in molecular optoelectronics.\[4\]

As a prelude to studying self-interaction in many-electron systems, we analyze the non-Koopmans behavior of the local spin density (LSD) functional in the simplest case of the \( \text{H} \rightarrow \text{H}^+ \) ionization (Fig. 1). The dependencies of the relaxed energy \( E_{\text{LSD}} \) and unrelaxed energy \( E_{\text{LSD},(0)} \) as a function of the fractional occupation of the LSD 1s state are depicted and compared to HF in Fig. 1 (in these calculations, we use the standard generalization of the HF theory to fractional occupations). The derivatives of the LSD energies, which correspond to the relaxed and unrelaxed single-electron energies \( e_{\text{LSD}} \) and \( e_{\text{LSD},(0)} \) (Janak’s theorem), are also shown. Since, for this one-electron system, the relaxation contribution \( \Pi_{\text{LSD}} = E_{\text{LSD}} - E_{\text{LSD},(0)} \) vanishes at \( f = 0 \) and \( f = 1 \), the ionization energy \( \Delta E_{\text{LSD}} = E_{\text{LSD}}(0) - E_{\text{LSD}}(1) \) is exactly equal to its unrelaxed counterpart \( \Delta E_{\text{LSD},(0)} \). Note however that the small relaxation energy \( \Pi_{\text{LSD}} \) remains strictly negative in the transition state region at variance with HF, for which no relaxation occurs. Although LSD predicts the energy of the hydrogen atom to be -0.94 Ry in agreement with the exact HF result of -1 Ry, the LSD energy departs significantly from the linear Koopmans behavior due to unphysical self-interaction: the slopes \( e_{\text{LSD}} \) and \( e_{\text{LSD},(0)} \) are largely underestimated close to \( f = 0 \), reflecting the predominance of the negative \( O(f^{4/3}) \) exchange-correlation contribution, while they are overestimated around \( f = 1 \) due to the positive \( O(f^2) \) Hartree term. Despite these notable non-Koopmans deviations, we observe that the LSD energies approach the expected Koopmans behavior at \( f = 0 \) (i.e., \( e_{\text{LSD},(0)} \approx e_{\text{LSD}} \rightarrow e_{\text{HF}} = -1 \) Ry). As an important consequence, the non-Koopmans contribution to the unrelaxed ionization energy must be defined by reference to the single-electron energy of the empty state: \( \Pi = e(0)(0) + \Delta E(0) \). Extending these observations to many-electron systems with fractional occupations and making use of Slater’s theorem [3], the non-Koopmans self-interaction energies can be rewritten as

\[
\Pi_{iα} = e_{iα}(0)f_{iα} + \Delta E_{iα} = \int_0^{f_{iα}} dλ \left( e_{iα}(0)(0) - e_{iα}(λ) \right),
\]

where \( e_{iα}(λ) \) denotes the effective energy of the orbital \( ψ_{iα} \) with occupation \( λ \) in the unrelaxed transition state. Note that in the absence of self-interaction, the unrelaxed single-electron energies satisfy \( d\epsilon_{iα}(λ)/dλ = 0 \) (by definition) and Eq. 1 is verified.

We are now in a position to evaluate the non-Koopmans energy cancelation resulting from PZ-SIC, which consists of subtracting single-electron Hartree and exchange-correlation contributions to the Kohn-Sham functional \( E^{\text{KS}} \). Explicitly, the Perdew-Zunger functional and orbital-dependent Hamiltonian are defined as

\[
\begin{align*}
E^{\text{PZ}} & = E^{\text{KS}} - \sum_{iα} E^\text{H}[ρ_{iα}] + E^{\text{xc}}[ρ_{iα}] \\
\hat{H}^{\text{PZ}} & = \hat{H}^{\text{KS}} - v_{\text{H}}[ρ_{iα}] - v_{\text{xc},α}[ρ_{iα}],
\end{align*}
\]

where \( ρ_{iα} = f_{iα}|ψ_{iα}|^2 \) denotes single-electron densities, \( v_{\text{H}} = \delta E_H/δρ \) is the electrostatic Hartree potential, and \( v_{\text{xc},α} = δ E^{\text{xc}}/δρ_{iα} \) stands for the exchange-correction potential. Rewriting the non-Koopmans energies (Eq. 2) in terms of the corrected Hamiltonian (Eq. 3) and expanding each energy contribution in terms of the variables \( ρ_{iα} \) at the self-interaction-free empty-state density \( \overline{ρ}_{iα} = (ρ_{iα} - ρ_{iα}, r_α) \) (with \( r_α \) opposite to \( α \)), we obtain:

\[
\Pi_{iα}^{\text{PZ}} = \int_0^{f_{iα}} dλ|ψ_{iα}⟩ \left( \hat{H}^{\text{PZ}}(0) - \hat{H}^{\text{PZ}}(λ) \right) |ψ_{iα}⟩ \propto \sum_{j≠i} \int f_{\text{xc},α,β}(r_α, r_β) \rho_{jα}r_{iα}\rho_{iα}dr_1dr_2dr_3dr_4,
\]

where \( f_{\text{xc}}(r_α) \) denotes the nth-order functional derivative of \( E^{\text{xc}}[ρ] \). As a result, PZ-SIC cancels self-interaction contributions up to the second order in the single-electron densities, which considerably ameliorates the precision of calculated ionization energies and related properties [4-11] but tends to sensibly overestimate self-interaction errors for many-electron systems [12-13, 14].

A more accurate self-interaction cancelation can be obtained by modifying the expression of the corrective terms in Eq. 3. In fact, due to the direct correspondence between non-Koopmans contributions and self-interaction errors, it is legitimate to identify the orbital self-interaction correction as the single-electron non-Koopmans energy \( \Pi^{\text{NK}}_{iα} \). The resulting NK-SIC energy reads \( E^{\text{NK}} = E^{\text{KS}} + \sum_{iα} E^{\text{NK}}_{iα} \) and variation with respect to the single-electron density \( ρ_{iα} \) yields the orbital-dependent Hamiltonian

\[
\hat{H}^{\text{NK}}_{iα} = \hat{H}^{\text{KS}} - v_{\text{H}}[ρ_{iα}] + v_{\text{xc},α}[ρ_{iα}] - v_{\text{xc},α}[ρ_{iα}] + w_{x_{c,iα}},
\]

where \( v \) is the external potential and \( w_{x_{c,iα}} \) is defined as

\[
\begin{align*}
w_{x_{c,iα}}(r) = \sum_{jβ≠iα} v_{x_{c,α}}(ρ_{jβ}) \rho_{jβ}(r) - v_{x_{c,α}}(ρ_{iα}) \rho_{iα}(r) + \int dr' f_{\text{xc},α,β}(r, r') ρ_{jβ}(r').
\end{align*}
\]

Substituting Eqs. 6 and 7 in the expression of the non-Koopmans energies (Eq. 2), we obtain the following estimate for the self-interaction contributions:

\[
\Pi_{iα}^{\text{NK}} \propto \int f_{\text{xc},α,β}(r_α, r_β, r_1, r_2, r_3, r_4) \rho_{jβ}(r_1) ρ_{iα}(r_2) ρ_{iα}(r_1) dr_1dr_2dr_3dr_4
\]

(note that only the term \( w_{x_{c,iα}} \) contributes to self-interaction). Consequently, our modification of the PZ-SIC functional brings about an additional factor of precision in the cancelation of spurious electronic interactions.
The improved accuracy of the NK-SIC scheme in comparison to PZ-SIC will be shown below.

At this point, one may observe that an exact cancelation of the non-Koopmans self-interaction contributions is obtained by defining the orbital-dependent Hamiltonian as \( \hat{h}_{i\alpha} = -\frac{1}{2} \nabla^2 + v + v_{\text{xc},n}[\rho_{i\alpha}] + v_{\text{xc},\alpha}[\rho_{\alpha\beta}] = -\frac{1}{2} \nabla^2 + v_{\text{xc},n}[\rho_{i\alpha}] \). Nevertheless, such a scheme does not derive from the minimization of any physical energy, as this would lead to the following variational inconsistency: \( \frac{\partial^2 E}{\partial \rho_{i\alpha} \partial \rho_{j\beta}} \neq \frac{\partial^2 E}{\partial \rho_{i\alpha} \partial \rho_{j\beta}} = \frac{\partial^2 E}{\partial \rho_{i\alpha} \partial \rho_{j\beta}}. \) The NK-SIC Hamiltonian (Eq. 4), which includes the additional term \( w_{\text{xc},i\alpha} = O(\sum_j \beta \rho_{i\alpha} || \rho_{j\beta} ||) \) for variationality, provides a close physical approximation to this exact correction.

The implementation of the NK-SIC method requires computing the kernel of the local or semilocal exchange-correlation energy \( f_{\text{xc}}^{(2)} \). This calculation is performed using the scheme proposed by Dal Corso and de Gironcoli in the context of phonon-dispersion computations [17]. Moreover, the determination of the NK-SIC terms necessitates calculating the Hartree self-interaction energy \( E_H[\rho_{i\alpha}] \) and potential \( v_H[\rho_{i\alpha}] \), which entails treating a system with a net electrical charge. To eliminate periodic-image errors in the plane-wave evaluation of \( E_H[\rho_{i\alpha}] \) and \( v_H[\rho_{i\alpha}] \), we employ countercharge correction methods [16]. Since the determination of \( f_{\text{xc}}^{(2)} \) and the periodic-image corrections are relatively inexpensive, the computational burden of NK-SIC computations is comparable to that of conventional PZ-SIC calculations.

We first study the dissociation of the \( H_2^+ \) molecular ion. The LSD and NK-SIC(LSD) energies are compared to the exact Born–Oppenheimer potential energy curve in Fig. 2 We observe that the LSD energies of this one-electron system are largely overestimated by as much as 0.1 Ry in the vicinity of the equilibrium bond length due to self-interaction errors, at variance with the NK-SIC energies, which are in close concordance with the exact results. Moreover, in the infinite separation limit, the NK-SIC electronic ground state is correctly predicted to be degenerate (with an energy of \(-1\) Ry) with respect to the effective occupations \( n_1 \) and \( n_2 = 1 - n_1 \) of the two hydrogen sites, at variance with LSD, which yields a nondegenerate and delocalized split-electron state \( (n_1 = n_2 = 1/2) \) of lower energy.

As a second self-interaction paradigm, we examine the dissociation of \( H_2 \) in the uncorrelated limit. The dependencies of the unrestricted Hartree-Fock (UHF), uncorrelated NK-SIC(LSD), and uncorrelated LSD Born–Oppenheimer energies as a function of the intramolecular distance are depicted in Fig. 3. Similarly to the \( H_2^+ \) case, we observe that LSD overestimates the total energy of the system, in contrast to NK-SIC, which brings the potential energy curve in close accordance with the self-interaction-free result. Furthermore, the analysis of the spin occupations \( n_{i\alpha} \) of the hydrogen sites at large atomic separation reveals that both the NK-SIC and LSD methods predict a two-fold degenerate ground state, in which each electron is localized at one site \( (n_{1\uparrow} = n_{2\downarrow} = 1 \) or \( n_{1\downarrow} = n_{2\uparrow} = 1 ) \). However, this transition occurs for distinct reasons in the two cases: while electronic localization is driven by the reduction of the interelectronic Hartree energy for NK-SIC, it is the enhancement of unphysical self-exchange that leads to localization for LSD. This fact explains salient differences in the asymptotic behaviors of the LSD and NK-SIC energies.

Having validated the NK-SIC method for archetypical one- and two-electron problems (for which PZ-SIC would also be exact), we turn to the difficult case of the electrical response of extended hydrogen chains, which are frequently employed as model systems in molecular optoelectronics and represent a critical test in assessing the predictive performance of electronic-structure methods [17]. We consider a linear chain geometry characterized...
by alternating H–H distances of 2 and 3 bohr, as reported in the literature [20]. The LSD and NK-SIC longitudinal polarizabilities $\alpha_N$ of the hydrogen chain as a function of the number of H$_2$ units are compared with HF, fourth-order Møller-Plesset perturbation theory (MP4), coupled cluster [CCSD(T)], and PZ-SIC predictions in Table I. We observe that the computed polarizabilities follow an increasing and progressively linear trend as a function of the number of hydrogen dimers. In spite of these similarities, we note that LSD dramatically overestimates the electrical response of the system. The Perdew-Zunger correction sensibly improves the accuracy of LSD results, reducing the mean absolute error from $\Delta \alpha_{\text{LSD}} = 39.9$ to $\Delta \alpha_{\text{PZ}} = 13.9$ a.u. relative to CCSD(T) polarizabilities (which we choose as our standard of accuracy). Despite this notable amelioration, the performance of the PZ-SIC scheme remains inferior to that of self-interaction-free HF ($\Delta \alpha\text{HF} = 8.0$ a.u.). This should be contrasted to NK-SIC predictions, which are found to be much more accurate than their HF counterparts with a precision comparable to semi-empirical downscaling procedures.

As a final note, it is important to mention that several successful refinements of the PZ-SIC method have been proposed in the literature [12, 13]. One limitation of such approaches is that they require to scale down the Hartree self-energy although this corrective term is in principle exact (as a result of the linearity of $\psi[H][\rho]$). The NK-SIC method represents a parameter-free alternative to semi-empirical downscaling procedures.

In conclusion, we have revisited self-interaction in light of the Koopmans condition (Eq. 1) and introduced a non-Koopmans correction (NK-SIC), which provides a more accurate cancelation of self-interaction contributions in comparison to PZ-SIC. In order to validate the NK-SIC method, we have studied the dissociation of H$_2^+$ and H$_2$, finding excellent agreement with exact and self-interaction-free calculations. Finally, we have demonstrated the much improved performance of the NK-SIC scheme in describing the electrical response of hydrogen chains, which represents a stringent and technologically relevant benchmark for electronic-structure methods.

The computations in this work have been performed using the Quantum-Espresso package [19]. The authors acknowledge support from the Grant in Aid for Research, Artistry and Scholarship of the Graduate School of the University of Minnesota. Helpful suggestions and comments from Stefano de Gironcoli, Éric Cancès, Nicolas Poilvert, and Andrea Floris are gratefully acknowledged.

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**Table I: Longitudinal polarizability $\alpha_N$ (in a.u.) of the hydrogen chain as a function of the number of dimers $N$. The mean absolute deviations $\Delta \alpha$ from CCSD(T) results are also reported.**

| method              | $\alpha_2$ | $\alpha_3$ | $\alpha_4$ | $\alpha_6$ | $\Delta \alpha$ |
|---------------------|------------|------------|------------|------------|-----------------|
| CCSD(T)$^a$         | 29.0       | 50.9       | 74.4       | 124.0      | —               |
| MP4$^b$             | 29.5       | 51.6       | 75.9       | 126.9      | 1.4             |
| NK-SIC(LSD)         | 30.9       | 49.0       | 71.3       | 122.3      | 2.1             |
| HF$^a$              | 32.2       | 56.6       | 83.0       | 138.6      | 8.0             |
| PZ-SIC(LSD)$^a$     | 33.0       | 59.7       | 89.1       | 152.0      | 13.9            |
| LSD$^c$             | 37.6       | 72.9       | 115.3      | 212.1      | 39.9            |

$^a$Ref. [17], $^b$Ref. [18], $^c$Ref. [8].

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[20] We employ a norm-conserving hydrogen pseudopotential with an energy cutoff of 25 Ry for the plane-wave expansion of the electronic wavefunctions. The NK-SIC problem is solved using a preconditioned conjugate-gradient band-by-band method [1]. The longitudinal electrical polarizability $\alpha$ is evaluated by finite difference from the dipole moment computed at an electric field of 0.005 a.u., starting from zero electric field. Using the above method and calculation parameters, the polarizability of an isolated hydrogen atom is verified to be within less than half a percent of the exact value ($\alpha(H) = 4.5$ a.u.).