Two Avenues to Self-Interaction Correction within Kohn-Sham Theory: Unitary Invariance is the Shortcut

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Abstract

The most widely-used density functionals for the exchange-correlation energy are inexact for one-electron systems. Their self-interaction errors can be severe in some applications. The problem is not only to correct the self-interaction error, but to do so in a way that will not violate size-consistency and will not go outside the standard Kohn-Sham density functional theory. The solution via the optimized effective potential (OEP) method will be discussed, first for the Perdew-Zunger self-interaction correction (whose performance for molecules is briefly summarized) and then for the more modern self-interaction corrections based upon unitarily-invariant indicators of iso-orbital regions. For the latter approaches, the OEP construction is greatly simplified. The kinetic-energy-based iso-orbital indicator $\frac{r_W^W(r)}{r_\sigma(r)}$ will be discussed and plotted, along with an alternative exchange-based indicator.

1 Introduction

Paradoxically, some of the most widely-used and reliable theoretical approaches to many-electron systems, including the local spin density [1] (LSD) and generalized gradient [2] (GGA) approximations, are not exact for one-electron systems. The error they make in these systems is called the self-interaction error. An early self-interaction correction [3, 4] (SIC) to LSD led to dramatic successes and failures, and has been largely bypassed by the development of GGA, which provides a more uniform improvement over LSD and has an easier Kohn-Sham theory implementation. Since the time finally seems ripe for the development of reliable self-interaction-free approximations, this article will discuss some of the possibilities for self-interaction correction within Kohn-Sham density functional theory [1].
In Kohn-Sham theory, the many-electron ground-state spin densities \( n_{\uparrow}(r) \) and \( n_{\downarrow}(r) \) and energy \( E \) are predicted by self-consistent solution of the one-electron equations

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + v_s^\sigma (r) \right] \varphi_{\alpha\sigma}(r) = \varepsilon_{\alpha\sigma} \varphi_{\alpha\sigma}(r),
\]

\[ n_\sigma(r) = \sum_\alpha |\varphi_{\alpha\sigma}|^2 \Theta(\mu - \varepsilon_{\alpha\sigma}) \tag{2} \]

where the spin-dependent effective potential is

\[
v_{\sigma}^s (r) = \rho_{\sigma} (r) + e^2 \int d^3 r' \frac{n(r')}{|r - r'|} + v_{xc}^\sigma (r). \tag{3}\]

In Eq. (3), \( v_\sigma (r) \) is the external potential created by the nuclei and external scalar fields, \( n = n_{\uparrow} + n_{\downarrow} \) is the total electron density, and

\[
v_{xc}^\sigma (r) = \frac{\delta E_{xc}[n_{\uparrow}, n_{\downarrow}]}{\delta n_\sigma(r)} \tag{4}\]

is the exchange-correlation potential. \( \mu \) is the Fermi level, and \( \Theta(x) \) is the step function (\( \Theta = 1 \) for \( x > 0 \) and \( \Theta = 0 \) for \( x < 0 \)). The energy is

\[
E = T_s[n_{\uparrow}, n_{\downarrow}] + \sum_\sigma \int d^3 r n_\sigma(r) v_\sigma(r) + \frac{e^2}{2} \int d^3 r \int d^3 r' \frac{n(r)n(r')}{|r - r'|} + E_{xc}[n_{\uparrow}, n_{\downarrow}]. \tag{5}\]

The non-interacting kinetic energy is

\[
T_s[n_{\uparrow}, n_{\downarrow}] = \sum_\sigma \int d^3 r t_\sigma(r) = \sum_\sigma \int d^3 r \tau_\sigma(r), \tag{6}\]

where

\[
t_\sigma(r) = \sum_\alpha \varphi^*_{\alpha\sigma}(r) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \varphi_{\alpha\sigma}(r) \Theta(\mu - \varepsilon_{\alpha\sigma}), \tag{7}\]

\[
\tau_\sigma(r) = \sum_\alpha \frac{\hbar^2}{2m} |\nabla \varphi_{\alpha\sigma}(r)|^2 \Theta(\mu - \varepsilon_{\alpha\sigma})
= t_\sigma(r) + \frac{\hbar^2}{4m} \nabla^2 n_\sigma(r). \tag{8}\]

Since the Kohn-Sham orbitals \( \varphi_{\alpha\sigma}(r) \) are functionals [1] of the spin densities \( n_{\uparrow} \) and \( n_{\downarrow} \), so is \( T_s \).

While the equations of the previous paragraph are exact in principle, in practice \( E_{xc}[n_{\uparrow}, n_{\downarrow}] = E_x[n_{\uparrow}, n_{\downarrow}] + E_c[n_{\uparrow}, n_{\downarrow}] \) must be approximated. In the local spin density approximation [1],

\[
E_{xc}^{\text{LSD}}[n_{\uparrow}, n_{\downarrow}] = \int d^3 r n_\sigma \epsilon_{xc}^{\text{unif}}(n_{\uparrow}, n_{\downarrow}), \tag{9}\]

where \( \epsilon_{xc}^{\text{unif}} \) is the known exchange-correlation energy of an electron gas with uniform spin densities \( n_{\uparrow}, n_{\downarrow} \). In the generalized gradient approximation [2],

\[
E_{xc}^{\text{GGA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3 r n_\sigma \epsilon_{xc}^{\text{GGA}}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}). \tag{10}\]
These approximations are exact for a uniform density and accurate for a slowly-varying \( n(\mathbf{r}) \), but are not exact for one electron densities.

One-electron densities are fully spin-polarized (e.g., \( n_\uparrow = n \) and \( n_\downarrow = 0 \)). In a one electron system, the exchange energy must cancel the Hartree electrostatic energy:

\[
E_x[n_\uparrow,0] = -\frac{e^2}{2} \int d^3r \frac{n_\uparrow(\mathbf{r})n_\uparrow(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (N = N_\uparrow = 1)
\]

and the correlation energy must vanish:

\[
E_c[n_\uparrow,0] = 0 \quad (N = N_\uparrow = 1).
\]

To satisfy Eqs. (11) and (12), Perdew and Zunger [3] proposed a self-interaction correction to LSD:

\[
E_{xc}^{\text{SIC}} = E_{xc}^{\text{LSD}}[n_\uparrow, n_\downarrow] - \sum_{\alpha\sigma} \left\{ \frac{e^2}{2} \int d^3r \int d^3r' \frac{n_{\alpha\sigma}(\mathbf{r})n_{\alpha\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}^{\text{LSD}}[n_{\alpha\sigma}, 0] \right\},
\]

\[
v_{xc}^{\alpha\sigma}(\mathbf{r}) = v_{xc}^{\text{LSD},\sigma}(n_\uparrow, n_\downarrow; \mathbf{r}) - \frac{e^2}{2} \int d^3r' \frac{n_{\alpha\sigma}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} - v_{xc}^{\text{LSD},\uparrow}(n_{\alpha\sigma}, 0; \mathbf{r}),
\]

where

\[
n_{\alpha\sigma}(\mathbf{r}) = |\varphi_{i\sigma}(\mathbf{r})|^2 \Theta(\mu - \varepsilon_{\alpha\sigma})
\]

is an orbital density. The potential (14) has the correct asymptotic behavior

\[
v_{xc}^{\sigma}(\mathbf{r}) \rightarrow \frac{e^2}{r} \quad \text{as} \quad r \rightarrow \infty
\]

as one moves away from any compact system, while \( v_{xc}^{\text{LSD},\sigma}(\mathbf{r}) \) tends to zero exponentially in this limit. Unlike LSD, the SIC exchange-correlation energy displays [4] a derivative discontinuity very much like that of the exact \( E_{xc}[n_\uparrow, n_\downarrow] \).

There is no unique way to make a self-interaction correction, and alternatives to Eqs. (13) – (15) have been proposed [5, 6, 7, 8, 9]. But Eqs. (13) – (15) have been widely tested for atoms [3, 10, 11, 12, 13], atomic ions [14], molecules [15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25] and solids [26, 27] (see earlier references in Ref. [19]). SIC is exact for one-electron systems, and usually accurate for strongly localized electrons. For covalent molecules near equilibrium, it has been argued [23, 24, 25] that the self-interaction error in LSD and GGA exchange [28] is needed to mimic the effect of static correlation on the electron density.

In applications to molecules, the performance of SIC is somewhat mixed. Total energies are better than in LSD, and the highest occupied orbital energy is much closer to minus the ionization potential than in LSD [16, 18]. The localized SIC valence orbitals correspond to the localized bonds and lone pairs of chemical intuition [18]. SIC significantly improves the energy barriers to chemical reactions [17, 22], but net reaction energies are less strongly improved relative to LSD.
Many nuclear magnetic resonance properties of molecules are improved by SIC [21]. There are relatively few studies of atomization energies in SIC, but there seems to be an improvement over LSD for the cases studied: $\text{Li}_2$ [16], $\text{O}_2$ [21], and $\text{N}_2$ [24]. The most disappointing results are the SIC bondlengths, which are shorter than the experimental ones by $\approx 0.07$ bohr on average [18], while the LSD bond lengths are much more realistic.

2 Perdew-Zunger SIC within Kohn-Sham Theory

The SIC of Eqs. (13) – (15) goes outside the Kohn-Sham scheme by introducing an orbital-dependent effective potential $v_s^\sigma(\mathbf{r})$. As a result, the self-consistent SIC orbitals are not Kohn-Sham orbitals, and are not even strictly orthogonal unless off-diagonal Lagrange multipliers are introduced. The SIC orbitals tend to localize around atomic centers, while the Kohn-Sham orbitals are delocalized canonical or molecular orbitals. The SIC orbitals can be found, even for molecules, by directly minimizing Eq. (13) under the constraint of orbital orthogonality [15, 16, 23, 24, 25].

Although not a Kohn-Sham theory, the Perdew-Zunger SIC belongs [3] to a wider class of density functional theories. At least to the extent that the SIC orbitals are localized, it is also a size-consistent theory [4], i.e., one which works consistently well for small or large systems.

But there are clearly computational and conceptual advantages to Kohn-Sham theory, not only for the ground state but also for time-dependent processes and excitations. To bring SIC under the umbrella of Kohn-Sham theory, one must construct a common effective potential for all the occupied orbitals of spin $\sigma$. Especially in the context of time-dependent DFT, different procedures emphasizing computational simplicity have been suggested to construct a common local potential [29, 30, 31], and the influence of the self-interaction correction on optical properties of atoms [30], the molecule $\text{N}_2$ [32] and clusters [29, 33] has been discussed. A rigorous way of constructing a common potential is given by the optimized effective potential (OEP) method [34, 35, 36]. For any orbital functional $E[\{\varphi_\alpha\sigma\}]$, the OEP method delivers a Kohn-Sham potential and a set of Kohn-Sham orbitals which minimize that functional. When the orbital functional is Hartree-Fock, there is no problem, but when it is SIC (Eq. (13)) the resulting scheme is not size-consistent: Applied to one atom, where all the Kohn-Sham orbitals are localized, this scheme will deliver a properly self-interaction-corrected energy. But, applied to a periodic lattice of atoms separated by large lattice constants, where all the Kohn-Sham orbitals are delocalized, this scheme will produce no self-interaction correction to the energy of an atom, since the sum in Eq. (13) will then vanish on a per-atom basis [3]. The considerations put forward in Refs. [3, 4] suggest that this is true for all Perdew-Zunger-like SIC schemes that directly use the Kohn-Sham orbitals. Therefore, such schemes would be good for atoms, but would degrade for molecules or clusters as the number of
atoms increased.

A clue to the solution of this problem was given in the work of Pederson, Heaton and Lin [16], who introduced two sets of occupied orthonormal orbitals related by unitary transformation: the localized SIC orbitals, and the delocalized canonical orbitals. Garza, Nichols and Dixon [20] proposed that the canonical orbitals could be Kohn-Sham orbitals belonging to an optimized effective potential \( v_{\sigma}(r) \) constructed from the localized orbitals. In their work, and in that of Patchovski and Ziegler [21, 22], the Krieger-Li-Iafrate approximation [37] to OEP is used, as is a standard (non-optimal) localizing transformation.

As an exactification of this approach, the correct Kohn-Sham version of Perdew-Zunger SIC would be conceptually this: Start with a given external potential \( v_{\sigma}(r) \) and electron number \( N \). Form a trial effective potential \( v_{\sigma}^{\tau}(r) \), and solve Eq. (1) to find the corresponding occupied Kohn-Sham orbitals. Then find the unitary transformation to localized orbitals that minimizes Eq. (13). Finally, choose the effective potential that delivers the lowest minimum of Eq. (13).

### 3 Unitarily Invariant Iso-Orbital Indicators

The prescription outlined above for the implementation of the Perdew-Zunger self-interaction correction to LSD (or GGA) within Kohn-Sham theory was greatly complicated by the fact that the self-interaction correction was not invariant under a unitary transformation of the occupied orbitals. This section will discuss self-interaction corrections that are unitarily invariant, and thus can be implemented within Kohn-Sham theory by a direct application of the OEP method [34, 35, 36] to the Kohn-Sham orbitals. This subject is timely because of the recent appearance of accurate and efficient solutions [35, 36] to the OEP problem.

A Slater determinant of occupied orbitals of a given spin \( \sigma \) is invariant under unitary transformation of those orbitals, and so is any quantity that can be constructed from the Slater determinant, such as the spin density of Eq. (2) or the kinetic energy densities of Eqs. (7) and (8). The one-electron density matrix

\[
\rho_{\sigma}(r, r') = \sum_{\alpha} \varphi_{\alpha \sigma}^{*}(r) \varphi_{\alpha \sigma}(r') \Theta(\mu - \varepsilon_{\alpha \sigma}) \tag{17}
\]

is also invariant. (The step function must of course be re-interpreted as a restriction to the occupied orbital space.) The exact exchange energy

\[
E_{x} = -\frac{e^{2}}{2} \sum_{\sigma} \int d^{3}r \int d^{3}r' \frac{\rho_{\sigma}^{2}(r, r')}{|r' - r|} \tag{18}
\]

is clearly invariant, as is the the local exchange energy per electron \( e_{x}(r) \):

\[
e_{x}(r) = -\frac{e^{2}}{2} \sum_{\sigma} \int d^{3}r' \frac{\rho_{\sigma}^{2}(r, r')}{n(r)|r' - r|} \tag{19}
\]
On the “Jacob’s Ladder” \[38\] of density functional approximations, full freedom from self-interaction error is achieved only at the hyper-GGA level, which employs full exact exchange and a highly nonlocal functional of the occupied orbitals for correlation. A somewhat different way to eliminate the self-interaction error is via a local hybrid functional \[39\]. But in either case one needs an iso-orbital indicator to identify regions of space in which the electron density is dominated by a single orbital shape. The iso-orbital regions where \(n_{\uparrow}n_{\downarrow} = 0\) are one-electron regions in which the correlation energy per electron \(e_c(r)\) can and should be zeroed out by a self-correlation-free density functional.

The exact exchange energy of Eq. (18) is self-interaction free, since for a one-electron \((N = N_\sigma = 1)\) ground-state \(\rho_\sigma(r, r') = n^{1/2}_\sigma(r)n^{1/2}_\sigma(r')\). Thus

\[
y_\sigma(r, r') = \frac{n^{1/2}_\sigma(r)n^{1/2}_\sigma(r')}{\rho_\sigma(r, r')} \tag{20}
\]

is an iso-orbital indicator which equals unity when both \(r\) and \(r'\) are in an iso-orbital region. However, as \(r' \to r\), \(y_\sigma(r, r')\) tends to 1 in any region, iso-orbital or not. This problem does not arise for

\[
x_\sigma(r) = \lim_{r' \to r} \frac{\nabla_r \cdot \nabla_{r'} n^{1/2}_\sigma(r)n^{1/2}_\sigma(r')}{\nabla_r \cdot \nabla_{r'} \rho_\sigma(r, r')} = \frac{\tau^W_\sigma(r)}{\tau_\sigma(r)} \tag{21}
\]

Eq. (21) provides a point-by-point iso-orbital indicator which equals unity in any iso-orbital region and is otherwise bounded between 0 and 1 \[40\]. In Eq. (21), \(\tau_\sigma(r)\) is the kinetic energy density of Eq. (8), and

\[
\tau^W_\sigma(r) = \frac{\hbar^2}{8m} \left| \nabla n_\sigma(r) \right|^2 \tag{22}
\]

is the von Weizsäcker or bosonic kinetic energy density. For a uniform density, \(x_\sigma(r)\) vanishes everywhere.

\(x_\sigma(r)\) of Eq. (21) is clearly invariant under unitary transformation of the occupied orbitals. The idea of using the condition \(\tau_\sigma(r) = \tau^W_\sigma(r)\) to identify an iso-orbital region and zero out the self-correlation goes back to Colle and Salvetti \[41\], but in density functional theory to Becke \[42\] and Dobson \[43\]. \(x_\sigma(r)\) is an ingredient of self-correlation free meta-GGA’s including those of Refs. \[44\] and \[45\], and of local hybrids \[39\] and hyper-GGA’s \[38\].

Fig. 1 shows \(x_\sigma(r)\) of Eq. (21), plotted as a function of the distance from the center of two spherical densities, the Ne atom and a jellium cluster with 34 electrons having the average valence electron density of Na \((r_s = [3/(4\pi n)]^{1/3} = 3.93 \text{ bohr})\). \(x_\sigma(r)\) correctly identifies the density tails as iso-orbital. In the Ne atom, the 1s core is also found to be nearly iso-orbital. The interior of the jellium cluster, however, is found to be a region of strong orbital overlap, as expected. The densities and orbitals have been evaluated by solving \[34, 36\] the OEP problem for exact exchange.
While $x_\sigma(r)$ of Eq. (21) seems to be a satisfactory iso-orbital indicator, it does display an order-of-limits problem [45]: Define $\alpha = (\tau - \tau^W)/\tau_0$, where $\tau_0 = \frac{3\hbar^2}{10m}(3\pi^2)^{2/3}n^{5/3}$, and $p = \frac{3}{5}(\tau^W/\tau) = |\nabla n|^2/[4(3\pi^2)^{2/3}n^{5/3}]$. Then, for $n_\uparrow = n_\downarrow$,

$$x = \frac{\tau^W}{\tau} = \frac{1}{1 + \frac{3\alpha}{5p}},$$  

$$\lim_{p \to 0} \lim_{\alpha \to 0} x = 1 \quad \text{but} \quad \lim_{\alpha \to 0} \lim_{p \to 0} x = 0.$$  

This problem shows up in nearly-iso-orbital ($\alpha \to 0$) regions where the gradient of the density approaches zero ($p \to 0$), and thus perhaps at covalent bond centers.

Because of the order-of-limits problem of $\tau^W/\tau$, it may be worthwhile to consider alternative iso-orbital indicators. For example, the exact exchange potential $v_x(r)$ and the exact exchange energy per electron $e_x(r)$ (Eq. (19)) of a spin-unpolarized system are related in the iso-orbital limit

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
N & ratio & N & ratio \\
\hline
2 & 1.000 & 40 & 0.547 \\
8 & 0.834 & 58 & 0.528 \\
18 & 0.679 & 92 & 0.528 \\
20 & 0.640 & 106 & 0.390 \\
34 & 0.571 & 138 & 0.442 \\
\hline
\end{tabular}
\caption{The ratio of Eq. (28) for closed-shell jellium spheres of increasing electron number N.}
\end{table}
Figure 2: The exchange-based iso-orbital indicator $\tilde{x} = \frac{3}{2} \left( \frac{v_x(r)}{e_x(r)} - \frac{4}{3} \right)$ of Eq. (27), for the same densities as in Fig. (1).

by

$$\frac{v_x(r)}{e_x(r)} = 2 \quad (N = 2), \quad (25)$$

and in the uniform-density limit by

$$\frac{v_x(r)}{e_x(r)} = \frac{4}{3} \quad \text{(uniform density).} \quad (26)$$

One might define

$$\tilde{x}(r) = \frac{3}{2} \left( \frac{v_x(r)}{e_x(r)} - \frac{4}{3} \right) \quad (27)$$

as an alternative iso-orbital indicator, which varies from 1 in the iso-orbital limit to 0 in the uniform limit. Table 1 shows that

$$\frac{3}{2} \left[ \int d^3r n(r) v_x(r) - \frac{4}{3} \right] \quad (28)$$

varies almost smoothly from 1 for the $N = 2$ jellium cluster to 0.4 for the largest cluster studied here. Fig. 2 however shows that $\tilde{x}(r)$ of Eq. (27) can be negative, fails to recognize the 1s core of the Ne atom as a strongly iso-orbital region, and fails to recognize the interior of the jellium cluster as a region of strongly overlapped orbitals.

Thus it seems that $x_\sigma(r)$ of Eq. (21) is the preferred iso-orbital indicator. Note that Eq. (22) assumes that the orbitals can be chosen to be real. If the state of interest has a nonzero current density

$$j_\sigma(r) = \text{Re} \frac{\hbar}{m} \sum_\alpha \varphi_{\alpha\sigma}^*(r) \frac{1}{i} \nabla \varphi_{\alpha\sigma}(r), \quad (29)$$

then [43, 46]

$$r_{\text{W}}^\sigma(r) = \frac{\hbar^2}{8m} \frac{\left| \nabla n_\sigma(r) \right|^2}{n_\sigma(r)} + \frac{m \left| j_\sigma(r) \right|^2}{2n_\sigma(r)} \quad (30)$$
To ensure that $x_\sigma$ equals one for a one-electron density and zero for a uniform density (with or without a uniform current), the best choice may be $x_\sigma = \tau_W^\sigma / \tilde{\tau}_\sigma$ where $\tau_W^\sigma = \tau_\sigma^W - m |j_\sigma|^2/(2n_\sigma)$ and $\tilde{\tau}_\sigma = \tau_\sigma - m |j_\sigma|^2/(2n_\sigma)$. In this way, the self-correlation error can be corrected even in a general excited state.

4 Conclusions

For many standard applications of ground-state density functional theory, the self-interaction errors of modern GGA’s and meta-GGA’s are relatively benign. There are a few striking exceptions to this rule, such as the binding properties of diatomic molecules with an odd number of valence electrons [19, 47] and the static (hyper-) polarizabilities of long-chain molecules [48]. For applications involving time-dependent and excited-state Kohn-Sham density functional theory [32, 49], the self-interaction errors can be severe.

While the Perdew-Zunger self-interaction correction to the local spin density approximation can now be brought under the umbrella of Kohn-Sham theory, the development of more sophisticated functionals and optimized effective potential methods suggests that general-purpose self-interaction-free density functionals will be developed soon and implemented within Kohn-Sham theory. Such functionals may well include full exact exchange plus highly nonlocal correlation based in part upon unitarily-invariant iso-orbital indicators such as $\tau_W^\sigma(r)/\tau_\sigma(r)$.

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