

Orbital currents in the Colle-Salvetti correlation energy functional and the degeneracy problem

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Abstract

Popular density functionals for the exchange-correlation energy typically fail to reproduce the degeneracy of different ground states of open-shell atoms. As a remedy, functionals which explicitly depend on the current density have been suggested. We present an analysis of this problem by investigating functionals that explicitly depend on the Kohn-Sham orbitals. Going beyond the exact-exchange approximation by adding correlation in the form of the Colle-Salvetti functional we show how current-dependent terms enter the Colle-Salvetti expression and their relevance is evaluated. A very good description of the degeneracy of ground-states for atoms of the first and second row of the periodic table is obtained.

I. INTRODUCTION

Common approximations to the exchange-correlation functional of density functional theory (DFT) [1, 2] and spin-DFT (SDFT) [3] often fail to reproduce the degeneracy of different ground states. An illustrative example are ground states of open-shell atoms where one usually and erroneously obtains different total energies for states with zero and non-vanishing current density. The local spin density approximation (LSDA) gives rather small splittings (of the order of 1 kcal/mole), but generalized gradient approximations (GGAs) and meta-GGAs can introduce splittings of 10 kcal/mol [4, 5, 6, 7, 8, 9, 10, 11].

These spurious energy splittings would vanish if the exact exchange-correlation functional could be used. The exchange-correlation energy functional can be represented in terms of the exchange-correlation hole function. Considering current-carrying states, Dobson showed how the expression for the exchange-hole curvature has to be changed by including current-dependent terms [12]. Later, Becke found the same kind of terms in the short-range behavior of the exchange-correlation hole, and observed that they also enter the spin-like correlation-hole function [13]. For open-shell atoms, inclusion of these current-dependent terms results in spurious energy splittings of less than 1 kcal/mole [9]. Along these lines, Maximoff et al. [10] worked out a correction for the system-averaged exchange hole of the Perdew-Burke-Ernzerhof (PBE) GGA [14], which improves the corresponding spurious splittings. Alternatively, Tao and Perdew [11, 15] proposed a scheme for the extension of existing functionals using ideas of current density functional theory (CDFT) [16, 17] which, again, improves the description of the degeneracy.

The performance of the exact-exchange (EXX) energy functional - which, by definition, describes the exchange hole correctly - has been evaluated for the spurious splittings in DFT and SDFT [18]. In the EXX-DFT (i.e., spin-restricted calculations using one and the same Kohn-Sham potential for spin-up and spin-down orbitals) the degeneracy is well reproduced to within 0.6 kcal/mole but, surprisingly, in EXX-SDFT (i.e., spin-unrestricted calculations using two Kohn-Sham potentials, one for spin-up and one for spin-down orbitals) spurious splittings up to 3 kcal/mole are obtained. In particular, current-carrying states always have higher total energies than states without current. This observation motivated the applications of the optimized-effective-potential (OEP) method [19, 20, 21]

generalized to current-spin-density functional theory (CSDFT) to these current-carrying states [22]. As expected, EXX-CSDFT total energies for current-carrying states are lower than those of EXX-SDFT. However, this lowering is too small to give a substantial improvement of the spurious energy splittings. These studies lead to the conclusion that correlation is needed for any further improvement.

The construction of a correlation energy functional compatible with EXX is a difficult task [23, 24, 25], but for spherical atoms it was found that EXX combined with the Colle-Salvetti (CS) functional for correlation [26, 27, 28] leads to very accurate total energies [29]. The CS functional has been used to derive the popular Lee-Yang-Parr (LYP) functional [30], which is most commonly used together with Becke’s exchange functional [31] (BLYP) and in hybrid schemes such as B3LYP [32, 33]. On the other hand, the CS correlation energy functional also has its limitations [34, 35, 36]. In particular, while short-range correlations are well described [35], very important long-range correlations are missing. These correlations often cannot be ignored in molecules and solids, but are negligible in atoms. This fact, together with the encouraging results for spherical atoms [29], indicates that it is appropriate to employ the CS functional to analyze the degeneracy problem for open-shell atoms beyond EXX. Furthermore, the expression of the CS functional also allows a reconsideration of the relevance of the orbital currents as ingredient of correlation functionals.

Although the general density functional formalism to deal with degenerate ground states includes densities which can only be obtained by a weighted sum of several determinantal densities [37, 38], as in many previous investigations [8, 9, 10, 11] we only consider densities which may be represented by a single Slater determinant of Kohn-Sham orbitals.

II. THEORY

Going beyond the EXX approximation, we here consider the correlation-energy functional of Colle and Salvetti [26]. This expression relies on the assumption that the correlated two-body reduced density matrix may be approximated by the Hartree-Fock (HF) two-body reduced density matrix $\rho_2^{HF}(\mathbf{r}_1, \mathbf{r}_2)$, multiplied by a Jastrow-type correlation factor. After a series of approximations, the following expression is obtained for the cor-

relation energy

$$E_c = -4a \int d\mathbf{r} \frac{\rho_2^{HF}(\mathbf{r}, \mathbf{r})}{\rho(\mathbf{r})} \left\{ \frac{1 + b\rho^{-\frac{8}{3}}(\mathbf{r}) \left[\nabla_s^2 \rho_2^{HF} \left(\mathbf{r} + \frac{\mathbf{s}}{2}, \mathbf{r} - \frac{\mathbf{s}}{2} \right) \Big|_{s=0} \right] e^{-c\rho^{-\frac{1}{3}}(\mathbf{r})}}{1 + d\rho^{-\frac{1}{3}}(\mathbf{r})} \right\} \quad (1)$$

where $\rho_2^{HF}(\mathbf{r}, \mathbf{s})$ is expressed in terms of the average and relative coordinates $\mathbf{r} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$ and $\mathbf{s} = \mathbf{r}_1 - \mathbf{r}_2$. Here, $\rho(\mathbf{r})$ is the electron density and the constants $a = 0.049$, $b = 0.132$, $c = 0.2533$, $d = 0.349$ are determined by a fitting procedure using the Hartree-Fock (HF) orbitals for the Helium atom.

Following Lee, Yang and Parr, this expression can be restated as a formula involving only the total charge-density, the charge-density of each Hartree-Fock orbital and their gradient and Laplacian [30]. In this derivation, the single-particle orbitals are tacitly assumed to be real. We denote the resulting expression as CSLYP. In the following, we relax this restriction and consider complex orbitals. We then proceed in analogy to the inclusion of current-dependent terms in the Fermi-hole curvature [9, 12] and in the extension of the electron-localization-function (ELF) [39] for time-dependent states [40]. As a consequence, in addition to the term already present in CSLYP expression, the current densities of the single-particle orbitals appear in the final formula. In order to obtain this expression, which in the following will be denoted as JCSLYP, we rewrite the Laplacian of the Hartree-Fock (HF) two-body reduced density matrix in Eq.(1) in terms of the original particle coordinates

$$\nabla_s^2 \rho_2^{HF} \left(\mathbf{r} + \frac{\mathbf{s}}{2}, \mathbf{r} - \frac{\mathbf{s}}{2} \right) \Big|_{s=0} = \left(\frac{1}{4} \nabla_1^2 + \frac{1}{4} \nabla_2^2 - \frac{1}{2} \nabla_1 \cdot \nabla_2 \right) \rho_2^{HF}(\mathbf{r}_1, \mathbf{r}_2) \Big|_{\mathbf{r}_1 = \mathbf{r}_2}. \quad (2)$$

where

$$\rho_2^{HF}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) - \frac{1}{2} \sum_{\sigma} \rho_{1,\sigma}^{HF}(\mathbf{r}_1, \mathbf{r}_2) \rho_{1,\sigma}^{HF,*}(\mathbf{r}_1, \mathbf{r}_2). \quad (3)$$

Here,

$$\rho_{1,\sigma}^{HF}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{k=1}^{N_{\sigma}} \psi_{k,\sigma}(\mathbf{r}_1) \psi_{k,\sigma}^*(\mathbf{r}_2), \quad (4)$$

is the first-order HF density matrix (for a single Slater determinant) expressed in terms of the single-particle orbitals $\psi_{k,\sigma}(\mathbf{r})$. The corresponding spin-density is simply given by

$$\rho_{\sigma}(\mathbf{r}) = \rho_{1,\sigma}^{HF}(\mathbf{r}, \mathbf{r}). \quad (5)$$

Allowing the single-particle orbitals $\psi_{k,\sigma}(\mathbf{r})$ to be complex, a given orbital not only gives the contribution $\rho_{k,\sigma}(\mathbf{r}) = |\psi_{k,\sigma}(\mathbf{r})|^2$ to the density, but also the contribution $\mathbf{j}_{p\ k,\sigma}(\mathbf{r}) = \text{Im}(\psi_{k,\sigma}(\mathbf{r})\nabla\psi_{k,\sigma}^*(\mathbf{r}))$ to the paramagnetic current density which is given by

$$\mathbf{j}_{p,\sigma}(\mathbf{r}) = \sum_{k=1}^{N_\sigma} \mathbf{j}_{p\ k,\sigma}(\mathbf{r}) . \quad (6)$$

After some straightforward algebra, the Laplacian of the second-order HF reduced density matrix takes the final form

$$\begin{aligned} \nabla_s^2 \rho_2^{HF} \left(\mathbf{r} + \frac{\mathbf{s}}{2}, \mathbf{r} - \frac{\mathbf{s}}{2} \right) \Big|_{s=0} &= \frac{1}{4} \rho(\mathbf{r}) \nabla^2 \rho(\mathbf{r}) - \frac{1}{4} (\nabla \rho(\mathbf{r}))^2 - \frac{1}{4} \sum_{\sigma} \rho_{\sigma}(\mathbf{r}) \nabla^2 \rho_{\sigma}(\mathbf{r}) \quad (7) \\ &+ \frac{1}{4} \sum_{\sigma} \rho_{\sigma}(\mathbf{r}) \left[\sum_{k=1}^{N_\sigma} \frac{(\nabla \rho_{k,\sigma}(\mathbf{r}))^2}{\rho_{k,\sigma}(\mathbf{r})} \right] + J(\mathbf{r}) \end{aligned}$$

where

$$J(\mathbf{r}) = \sum_{\sigma} \rho_{\sigma}(\mathbf{r}) \left[-\frac{\mathbf{j}_{p\sigma}^2(\mathbf{r})}{\rho_{\sigma}(\mathbf{r})} + \sum_{k=1}^{N_\sigma} \frac{\mathbf{j}_{p\ k,\sigma}^2(\mathbf{r})}{\rho_{k,\sigma}(\mathbf{r})} \right] \quad (8)$$

contains all the current-dependent terms. Alternatively, Eq. (7) may also be expressed in terms of the non-interacting kinetic energy density

$$\tau_{\sigma}(\mathbf{r}) = \frac{1}{2} \sum_{k=1}^{N_\sigma} |\nabla \psi_{k,\sigma}(\mathbf{r})|^2 = \frac{1}{8} \sum_{k=1}^{N_\sigma} \frac{(\nabla \rho_{k,\sigma}(\mathbf{r}))^2}{\rho_{k,\sigma}(\mathbf{r})} + \frac{1}{2} \sum_{k=1}^{N_\sigma} \frac{\mathbf{j}_{p\ k,\sigma}^2(\mathbf{r})}{\rho_{k,\sigma}(\mathbf{r})} \quad (9)$$

as

$$\begin{aligned} \nabla_s^2 \rho_2^{HF} \left(\mathbf{r} + \frac{\mathbf{s}}{2}, \mathbf{r} - \frac{\mathbf{s}}{2} \right) \Big|_{s=0} &= \frac{1}{4} \rho(\mathbf{r}) \nabla^2 \rho(\mathbf{r}) - \frac{1}{4} (\nabla \rho(\mathbf{r}))^2 - \frac{1}{4} \sum_{\sigma} \rho_{\sigma}(\mathbf{r}) \nabla^2 \rho_{\sigma}(\mathbf{r}) \\ &+ \sum_{\sigma} (2\rho_{\sigma}(\mathbf{r})\tau_{\sigma}(\mathbf{r}) - \mathbf{j}_{p\sigma}(\mathbf{r})^2) . \quad (10) \end{aligned}$$

Comparison of Eq.(7) and Eq.(10) shows that $J(\mathbf{r})$, as defined in Eq.(8), also contains current-dependent terms coming from the kinetic energy density. Thus, this would also suggest to reconsider the gradient expansion of τ for current-carrying states. Important consequences maybe expected for all approximated exchange-correlation functional involving the kinetic energy density as ingredient, such as the CS functional, and meta-GGAs. This issue will be specifically considered in a future work. In the next section, we assess the performance of the CS functional, and, in particular, the relevance of $J(\mathbf{r})$, in reproducing the degeneracy of atomic states.

III. RESULTS AND DISCUSSION

We consider ground states of open-shell atoms having densities that can be represented by a single Slater determinant of Kohn-Sham orbitals. Due to the symmetry of the problem, these Slater determinants are eigenstates of the z -component of both spin and orbital angular momentum. The single-particle orbitals are generally complex-valued and states with different total magnetic quantum numbers, M_L , correspond to different current densities. By means of an accurate exchange-correlation functional the same total energies would be obtained. In the previous section, we have shown how current-dependent terms enter the expression of the CS functional when complex-valued orbitals are considered. Here, we evaluate the performance of EXX plus the CS functional in reproducing the degeneracy and study the effect of the current-dependent terms, in SDFT and DFT calculations.

We consider atoms of the first and second row of the periodic table: these are the reference cases for which a vast amount of numerical data is available [8, 9, 10, 11, 18, 22]. In analogy to the procedure where Hartree-Fock orbitals are used as input to the CS formula, we have evaluated the correlation energies in a post-hoc fashion using Kohn-Sham (KS) orbitals. We expand the KS orbitals in Slater-type basis functions (QZ4P of Ref. [42]) for the radial part, multiplied with spherical harmonics for the angular part. We obtain the KS orbitals from self-consistent EXX-only calculations employing the approximation of Krieger, Li, and Iafrate (KLI) [41], which has been shown to be extremely good at least for small systems [21]. In principle a functional should be evaluated with KS orbitals obtained from self-consistent calculations, and this is certainly possible for the CS functional [29]. However, thanks to the variational nature of DFT, it is common experience to observe only minor quantitative differences between post-hoc and self-consistent evaluation of total energies. This is the reason why the functionals designed for solving the degeneracy problem are typically evaluated in a post-hoc manner [9, 10, 11].

Table I shows the spurious energy splittings (difference in the total energies) between Kohn-Sham Slater determinants with total magnetic quantum number $|M_L| = 1$ and $M_L = 0$, from our SDFT and DFT calculations. The deviation of these total energies from the exact values is plotted in Fig. (1), where again the spurious energy splittings are visi-

Atom	SDFT (DFT)	
	Δ_{JCSLYP}	Δ_{CSLYP}
B	0.8 (-0.3)	2.4 (1.4)
C	0.9 (-0.1)	-3.2 (-4.3)
O	-0.6 (-1.9)	0.9 (-0.4)
F	-0.1 (-1.5)	-3.5 (-5.1)
Al	0.4 (-0.5)	1.1 (0.2)
Si	0.5 (-0.4)	-1.2 (-2.2)
S	0.1 (-1.6)	1.1 (-0.7)
Cl	0.7 (-1.3)	-1.1 (-3.2)
me	0.3 (-1.0)	-0.4 (-1.8)
mae	0.5 (1.0)	1.8 (2.2)

TABLE I: Spurious energy splittings, $\Delta = E(|M_L| = 1) - E(M_L = 0)$ in kcal/mol for open-shell atoms, computed in SDFT (DFT results in parenthesis for comparison). Correlation energy has been added to the KLI-EXX energies including (JCSLYP) and neglecting (CSLYP) the current terms of Eq. (7). The last row shows the mean error (me) and mean absolute (mae) of the spurious splittings.

ble. These results highlight the importance of including $J(\mathbf{r})$ in Eq. (7). In particular, it is remarkable to observe that SDFT splittings are within 0.9 kcal/mol (with a mean error of 0.3 kcal/mol and a mean absolute error of 0.5 kcal/mol), and the corresponding DFT spurious energy splittings are less than 1.9 kcal/mol (with mean errors of 1.0 kcal/mol). It is worthwhile to note that in several cases inclusion of correlation leads to current-carrying states ($|M_L| = 1$) with lower total energy than zero-current states ($M_L = 0$). These results are in contrast to EXX-only [18] cases where: (a) the zero-current states are always lowest in energy and (b) the spurious energy splittings are always smaller in DFT than in SDFT.

Going beyond EXX by including correlation in the form of CS functional accurate total energies can be obtained within the OEP method [29]. Figure (1) and Table II show the deviations from exact total energies for the states with different magnetic quantum

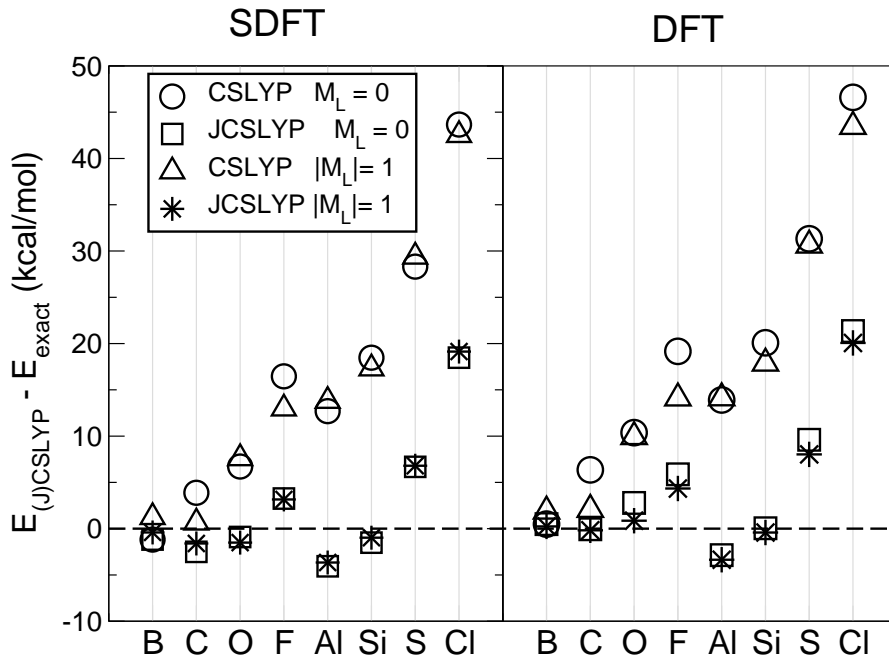


FIG. 1: Deviation from exact total energies for SDFT and DFT calculations employing the CS functional, including (JCSLYP) and not including (CSLYP) the current-dependent term J in Eq. (7). States with different magnetic quantum numbers M_L are plotted. Exact total energies are taken from Ref. [29] and references therein.

numbers, i.e. different current-carrying states. This further emphasizes the importance of proper inclusion of $J(\mathbf{r})$ in Eq. (7).

IV. CONCLUSIONS

We have shown that going beyond the exact-exchange approximation by including correlation energy in the form of the Colle-Salvetti functional leads to a very good description of the degeneracy of open-shell atoms in both SDFT and DFT calculations. Comparing DFT and SDFT results for the first and second row of the periodic table, on average we observe a reduction of the spurious energy splittings and better total energies for SDFT. Furthermore, we have also shown how current-dependent terms enter the expression of the Colle-Salvetti functional. If these terms are neglected, the degeneracy is not well described and the total energies are also less accurate. Thus, this analysis reconfirms the advantage of properly including the orbital current dependent terms as an

	JCSLYP (CSLYP)			
	SDFT	DFT	SDFT	DFT
$ M_L $	0	0	1	1
me	2.3 (16.1)	4.7 (18.5)	2.6 (15.7)	3.7 (16.8)
mae	4.8 (16.4)	5.4 (18.5)	4.7 (15.7)	4.7 (16.8)

TABLE II: Mean error (me) and mean absolute error (mae) in the total energies for the CS functional, including (JCSLYP) and not including (CSLYP results in parenthesis) the current-dependent term J in Eq. (7), in kcal/mol. Exact total energies are taken from Ref. [29] and references therein.

ingredient in correlation functionals.

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