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REGULAR ARTICLE

The self-interaction error and the description of non-dynamic electron correlation in density functional theory

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Abstract The self-interaction error (SIE) plays a central role in density functional theory (DFT) when carried out with approximate exchange-correlation functionals. Its origin, properties, and consequences for the development of standard DFT to a method that can correctly describe multi-reference electron systems by treating dynamic and non-dynamic electron correlation on an equal footing, is discussed. In this connection, the seminal work of Colle and Salvetti on wave function-based correlation functionals that do no longer suffer from a SIE is essential. It is described how the Colle–Salvetti correlation functional is an anchor point for the derivation of a functional multi-reference DFT method.

Keywords Colle–Salvetti functional · Self-interaction error · Non-dynamic electron correlation · Multi-reference DFT · CAS-DFT

1 Introduction

Electron correlation plays a crucial role when describing chemical systems and processes with quantum chemical methods. Of special interest, and at the same time particularly challenging for computational chemistry, are situations where short-range dynamic electron correlation coexists with long-range, non-dynamic electron correlation. Such situations are found for molecules with (quasi)-degenerate states, Jahn–Teller systems, dissociating multiple bonds, conjugated low-spin biradicals, etc. The most widely used method of contemporary computational chemistry, Kohn–Sham density functional theory (KS-DFT) [1, 2], is in principle capable of describing both dynamic and non-dynamic correlation. However, the available approximations for the exchange and correlation (XC) functional in KS-DFT (see, e.g., [3–16]) focus on a suitable description of dynamic electron correlation whereas the description of non-dynamic correlation effects within standard KS-DFT is problematic [17].

The treatment of long-range electron correlation in the framework of DFT has been an active field of research for a long period, and a variety of approaches has been suggested. Most of these approaches follow either strategy (1) or (2).

(1) Standard DFT is applied in such a way that non-dynamic electron correlation is mimicked non-specifically via the XC-functional or by introducing additional degrees of freedom when optimizing the single-determinant DFT wave function. (see, e.g., [17–19]).
In this case, errors of the standard XC-functionals are utilized to account for the missing correlation effects. Proper use of this approach requires that the errors of

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Dedicated to the memory of Professor Oriano Salvetti and published as part of the Salvetti Memorial Issue.

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standard-DFT XC-functionals have been analyzed and understood. The advantage of this approach is its simplicity; however, its applicability is limited. Some XC-functionals are specially calibrated for the description of non-dynamic correlation in special cases, e.g., for weakly bound complexes [7, 16] or for transition states [16].

Strategy (1) is applied for the description of bond dissociation reactions, low-spin biradicals, etc. utilizing broken-symmetry (BS)-spin-unrestricted (U) DFT [17–19], combined in some cases with extrapolation schemes [18, 20].

(2) One develops hybrid methods where the non-dynamic electron correlation is described explicitly, e.g., by a multi-reference approach or an additional term in the correlation functional. In this approach, the use of standard-DFT is restricted to the description of exchange (possibly) and dynamic correlation [21–42]. Strategy (2) is more general than strategy (1) in that it, in principle, can be used to describe any pattern of non-dynamic electron correlation. A crucial point in its proper application is the suitable separation between dynamic and non-dynamic correlation to avoid any double-counting of correlation effects [24–26, 29, 30, 35, 39]. This implies two requirements: (i) The KS-DFT correlation functional used must not cover any portion of non-dynamic correlation, i.e., it must be restricted to short-range correlation effects. (ii) Also, the XC functional must not spuriously mimic long-range attraction or repulsion inside the system. Conversely, that component of the approach used to account for non-dynamic electron correlation should not introduce any portion of the dynamic correlation; if it does, this portion has to be quantified and deducted when determining the KS-DFT correlation energy.

Our previous work involves methods in the realm of both strategy (1) [17–19] and strategy (2) [28, 35, 36, 39]. In the following, we will focus on that part of our method development work that follows strategy (2); not the least because our work in this field has greatly benefited from the work of Colle and Salvetti [23–25, 29].

The specific errors in a DFT calculation depend on the XC-functional used. One error that is common to a wide class of functionals is the self-interaction error (SIE) [43]. For a system consisting just of one electron, DFT predicts an non-physical self-interaction energy. This problem has already been noticed by Fermi and Amaldi in the early 1930 [44] in connection with the Thomas–Fermi approximation [45, 46]. A thorough analysis in the framework of DFT was performed by Perdew and Zunger [43], who suggested an explicit correction term that makes any XC-functional SIE-free. An alternative way of avoiding the SIE of approximate XC-functionals was suggested by Colle and Salvetti already in 1975 who used wave function theory (WFT) to develop the first SIE-free C-functional [23]. The Colle–Salvetti (CS) functional laid the basis for the work of Lee et al. to develop the LYP correlation functional, [9] which is also SIE-free.

In the description of non-dynamic correlation, the SIE can play two different roles: if strategy (1) is used, the SIE may improve the accuracy of standard DFT by mimicking part of the non-dynamic electron correlation of a given molecule [17, 18, 47–54]. However, within the framework of strategy (2) the SIE has to be avoided, at least with regard to the long-range part of electron–electron interactions.

The current work is organized as follows. In Sect. 2, we will briefly summarize the origin and the features of the SIE and explain its role when following strategy (1). Section 3 is devoted to multi-reference DFT and the question how dynamic and non-dynamic electron correlation effects can be handled at the DFT level in a more general way based on strategy (2). Finally, in Sect. 4 conclusions of this work are presented.

2 Origin and features of the self-interaction error

Indication of the SIE is already provided by the electron density distribution calculated with standard XC-functionals [53, 54]. This becomes obvious when comparing densities obtained from exchange-only DFT calculations directly with MP or coupled cluster densities and then investigating the changes in the DFT electron density caused by adding the correlation functional. Such studies reveal that the DFT density is influenced most strongly by the exchange part, to which the correlation part adds only minor corrections. If Hartree–Fock (HF) exchange is replaced by the local-density approximation (LDA) or the generalized gradient approximation (GGA) exchange, the molecular electron density distribution will change in a typical way that reminds of the changes caused by the inclusion of dynamic electron correlation at the MP2, MP4, [55] or CCSD(T) [56] levels of theory [17, 53, 54]. A thorough analysis of the density changes caused by X-functionals such as Becke88 (B) [4] or Perdew-Wang91 (PW91) [5–6] leads to the conclusion that at this level already strong pair and some higher correlation effects are mimicked where it is not clear whether these might be characterized as short-range (dynamic) or long-range (non-dynamic) electron correlation effects [53]. It has to be noted in this connection that the short-range, dynamic and the long-range, non-dynamic correlation effects, in spite of their different character, may lead to similar features of the one-electron density.

In view of these observations two questions arise: (a) If correlation is already included (in whatever way) by the X-functional, what role does the C-functional play? (b) Why does a standard X-functional mimic (dynamic or non-dynamic) correlation effects? These questions can be answered by again comparing density changes as they are caused by the C-functional and in addition investigating the exchange-correlation hole.

An LDA correlation functional (VWN, VWN5 [8] or Perdew local correlation (PL) [43]) increases the electron density distribution in the atom, bond, and (inner) non-bonding regions whereas it decreases the density in the van der Waals regions [53, 54]. These changes are rather small when compared with those caused by the X-functional and largely independent of the molecule investigated. They can be explained by the fact that a LDA C-functional leads to an attractive local potential that becomes stronger the higher the density is [17]. Accordingly, negative charge is shifted from regions with low electron density to regions with high electron density. This implies that correlation effects are exaggerated because the magnitude of the local density decides on the redistribution of negative charge rather than a specific electron correlation effect as in the case of a WFT-based correlation method such as MP [55] or CC [56, 57].

The CS correlation functional [23, 24] largely avoids the problem of exaggerating electron correlation because it was derived with the help of WFT to account for both local and non-local correlation effects and therefore does not solely depend on the magnitude of the local electron density. Compared to an LDA correlation functional, the CS functional moves some of the density from the bond and valence regions back to the van der Waals regions because the non-local electron correlation effects counterbalance the dependence of the local correlation effects on high densities.

GGA correlation functionals such as PW91 [5, 6] lead to density changes that are intermediate to those caused by LDA and those caused by the CS functional. Electron density is redistributed from the core and bond regions to the outer valence regions rather than the van der Waals regions as the CS-functional does. For the GGA C-functionals, the basic error of the LDA C-functionals (attractive potential for high densities) still exists, however the consequences of the error are less severe. In regions where the reduced gradient of the density, $\nabla\rho/\rho^{4/3}$, is small (e.g., bond regions) but ρ relatively large, the GGA correlation density becomes smaller than the LDA correlation density. In the nonbonding regions between the atoms the reduced gradient is relatively large and ρ relatively small with the consequence that a larger GGA correlation density results as in the LDA case.

At the nuclei, the GGA correlation and exchange potential become both singular [17]. The singularity for the correlation potential is repulsive whereas that of the exchange functional is attractive with the result that the two singularities partly compensate each other with regard to their consequences. The main effect of the gradient corrections to the correlation potential is a redistribution of electron density from the core and bond regions into the outer valence regions of the atoms, thus reducing slightly the effects of the LDA correlation potential.

As regards its impact on the density distribution, the DFT C-functional plays a much smaller role than electron correlation does in general in WFT. One can compare DFT correlation with the higher order correlation effects included by coupled cluster methods such as CCSD or CCSDT [58, 59]. Low-order correlation effects such as pair or three-electron effects mostly lead to an expansion of the electron density and to more diffuse molecular orbitals. This causes longer bonds, smaller bond angles, lower atomic charges, and smaller effective electronegativities. Higher order correlation effects are essentially disconnected correlation effects characterized by a complicated coupling between two or more low-order correlation effects whereas connected correlation effects with $N > 4$ electrons do not play a significant role. The coupling between low-order correlation interactions reduces the changes in the density caused by the diagonal low-order correlations, i.e., the electron density becomes somewhat more contracted, bond lengths shorten, bond angles widen, atomic charges and effective electronegativities become larger, and bond polarities increase. This is the reason why CCSD or CCSDT reduce and revert trends in molecular properties obtained at the MP2 or MP4 levels of theory [58, 59]. According to the changes in the electron density distribution caused by C-functionals, DFT correlation seems to be comparable with the high order correlation effects observed in WFT rather than the corresponding low-order diagonal correlations.

It remains to be clarified how the low-order correlation effects, which are also present in the DFT density distribution, are mimicked by the X-functional. For this purpose, the DFT exchange (X)-hole has to be investigated and requires that points (i)–(v) have to be considered.

(i) The analysis of the DFT X-hole implies that it is referenced to an exact X-hole, which suitably is taken from a HF calculation. For the purpose of eliminating differences in the DFT and HF X-hole caused by differences in the one-particle densities, both X-holes are calculated with the same set of HF orbitals.

(ii) The X-hole of a many-electron system ($N > 2$) can be split into an intraelectronic part that accounts for the self-exchange of the electrons and an interelectronic part that results from the Fermi interaction of different electrons or, in other words, the antisymmetry of the

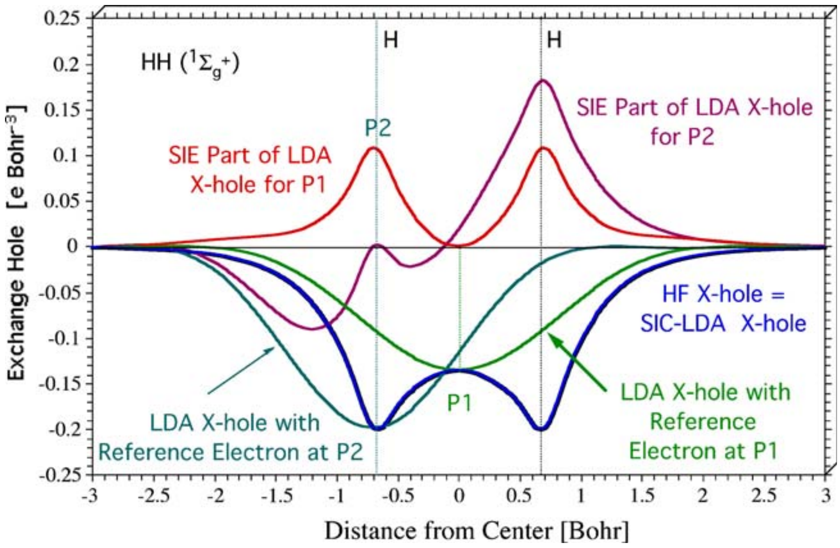

Fig. 1 One-dimensional cut through the X-hole calculated for H_2 in its $^1\Sigma_g{}^+$ ground state with with Dunning's cc-pVTZ basis at 0.742 Å along its bond axis at the HF, SIC-LDA (*both bold blue line*), and LDA (X-only; *green and bluegreen lines*) levels of theory for positions P1 (center of H_2 bond) and P2 (position of first H nucleus) of the reference electron. The SIE part of the LDA X-hole is given by the *red and purple lines* for P1 and P2. For the purpose of simplifying the comparison, HF orbitals are used in all calculations

wave function. For reasons of simplicity, we constrain the following discussion to a spin-coupled two-electron system such as the H_2 molecule in its $^1\Sigma_g{}^+$ ground state so that the interelectronic part of the X-hole does not play any role and the X-hole becomes identical to the intraelectronic part.

(iii) For a one-electron system (e.g., $H_2{}^+$) with $\int d^3r\, \rho_\alpha(\mathbf{r}) = 1$, $\rho_\beta \equiv 0$, the correct XC-functional must lead to an electron density distribution that fulfills Eqs. 1 and 2.

$$E_J[\rho_\alpha] + E_X[\rho_\alpha, 0] = 0, \tag{1}$$

$$E_C[\rho_\alpha, 0] = 0, \tag{2}$$

which simply mean that a single α electron does not interact with itself, i.e., the self-repulsion energy of the electron given by $E_J[\rho_\alpha]$ is canceled by the self-exchange energy $E_X[\rho_\alpha, 0]$ covered by the X-functional. Also, a single electron does not possess any *self-correlation energy* $E_C\,[\rho_\eta, 0]$. An approximate XC functional may violate either condition (1), (2) or both and, accordingly, self interaction corrections have to be introduced into DFT to obtain a SIE-free method. Given that the exchange interaction occurs only between electrons of like spin, Eq. 1 remains valid for a spin-coupled two-electron system, e.g., the H_2 atom; an analogous relationship holds for the β spin density.

(iv) The HF X-hole (see Fig. 1, we consider here always just one of the two possible spin values) takes the form of the negative of the $\sigma_g{}^2$ density of H_2 and reflects the self-exchange of its two electrons. It is delocalized having two troughs at the positions of the H nuclei. Accordingly, it reflects the electronic structure of the H_2 molecule in the same way as the electron density distribution $\rho(\mathbf{r})$ does.

(v) In the general case, the X-hole changes its form in dependence of the position of the reference electron. Hence, one may expect that a detailed account of the form of the X-hole requires a large (in the extreme an infinite) number of positions of the reference electron and therefore makes the analysis tedious. However, in reality only two or three positions of the reference electron are sufficient to identify general features of the X-hole, which are needed for the identification of correlation effects accounted for by a given X-functional.

In Fig. 1, the LDA X-hole is compared with the HF X-hole. It depends on the position of the reference electron (Fig. 1, position P1: reference electron is at the center of the bond; position P2: reference electron is at the left H nucleus) and is, contrary to the HF X-hole, unstructured. It is always localized and centered at the position of the reference electron where one has to keep in mind that for reasons of comparison in Fig. 1 the same electron density is used. The exact and the LDA X-hole have in common that they are negative everywhere and that they are normalized to -1. The lowest point of the LDA X-hole for H_2 is equal to the negative electron density at this point, which means that at P1 the LDA hole is shallower and more diffuse whereas at P2 the hole becomes deeper and more contracted.

Self-interaction corrected LDA (SIC-LDA) possesses an X-hole that is identical to the HF X-hole provided the same HF orbitals are used (Fig. 1) [48]. Hence, it is static and delocalized in the same way as the HF X-hole. The SIE part of the LDA X-hole is obtained by subtracting the SIC-LDA hole from the LDA hole. Accordingly, it can be both positive and negative. Since both the LDA and the SIC-LDA X-hole integrate to -1, the SIE part of the LDA

X-hole integrates to zero. Although the SIE part depends as the LDA X-hole on the position of the reference electron, a typical pattern emerges for the SIE part (Fig. 1).

The SIE part is always zero at the position of the reference electron and increases the probability of finding the second electron in the opposite part(s) of the H_2 molecule, i.e., if the reference electron is at one (position P2) or closer to one nucleus, the other electron will be at or in the vicinity of the second nucleus; if it is at the center of the bond (position P1), the other electron will be found with equal probability at either the first or the second nucleus (Fig. 1). Although the X-hole adopts a somewhat different form for GGA functionals, the same general observations can be made in this case [50].

It is obvious from Fig. 1 that the SIE converts the delocalized, structured SIC-LDA X-hole into an unstructured, spherically symmetric localized LDA X-hole. Accordingly, it must adopt a structure that is related to wave function and electron density $\rho(\mathbf{r})$ where this relationship has to be seen in dependence of the position of the reference electron. At P1, the SIE part reflects the electronic structure close to the nuclei; at P2 it gives the situation at the other nucleus. Clearly, the SIE part of the LDA X-hole mimics long-range left–right electron correlation. By this, the electron density changes in a way that is typically found for wave function methods including left–right electron correlation.

Contrary to WFT, the non-dynamic electron correlation effects introduced by an X-functional with SIE are nonspecific, i.e., they will always appear, independently of the electronic system described. This improves the single-determinant DFT description of electron systems with multi-reference character, which otherwise can only be correctly treated with multi-configurational wave function methods, but provides no possibility of differentiating between electron systems with different multi-reference character. Because of the left–right correlation mimicked by the SIE, DFT can perform much better than any other single-determinant method. At the same time, this implicit introduction of non-dynamic electron correlation effects provides a major obstacle for a systematic improvement of DFT.

When applying one of the strategies (1) and (2) discussed in the introduction, the SIE and its role in connection with the description of electron correlation has always to be considered. An improvement of DFT via the XC-functional has to be adjusted to the SIEs of both X and C parts. For example, a combination of B-exchange [4] with LYP-correlation [9] as found in the widely used BLYP functional is problematic as B-exchange mimics left–right electron correlation in the way described above whereas the LYP functional is SIE-free because it excludes all equal-spin correlation. Hence, a partial cancellation of the SIEs of X- and C-part as found for the PWPW91 functional [47, 53, 54] is not possible and the SIE is at its maximum. In terms of C-effects included, the situation for the BLYP functional is somewhat more transparent than for the PWPW91 functional since the electron correlation effects are better identified in the former case (for PW91 correlation, the SIE introduces correlation effects that are difficult to characterize [47]).

Similarly, any new XC-functional (GGA, meta-GGA, hybrid) has always to be analyzed with regard to the SIEs included or excluded. The situation is complicated and cannot be handled in a systematic manner [47–54]. Even larger problems of identifying correlation effects arise when the form of the DFT wave function leads to an inclusion of extra correlation effects as it is the case for BS-UDFT [17–19] or Restricted Ensemble Kohn–Sham (REKS) DFT [49]. If these methods are applied with BLYP or other XC-functional suffering from an SIE, a double counting of electron correlation effects is the consequence: Non-dynamic electron correlation is introduced both by the method (BS-UDFT or REKS) and by the X-functional. Therefore, results become unpredictable and are difficult to analyze [49].

If one develops hybrid methods where the non-dynamic correlation effects are described explicitly (strategy 2), e.g., by using a multi-reference approach or an additional term in the C-functional, one has to abandon the use of SIE-contaminated XC-functionals altogether. For example long-range correlation as needed for the description of dispersion interactions is poorly described by the majority of approximate C-functionals in use today [60, 61]. The problem can be solved if a dispersion functional is added that reproduces the exact $1/R^6$ dependence between two electronic systems separated by distance R (R approximately equal to the sum of the van der Waals radii) and interacting via dispersion forces. However, such a remedy would be in vain if the XC-functional used leads to artificial long-range attraction/repulsion forces and by this contaminates or even annihilates the effect of the dispersion functional. Hence, one has to cut off first the long-range part of the XC-functional and replace it by exact exchange and an accurate dispersion functional. This can be done by splitting the Coulomb potential $\mathrm{v}(r) = 1/r$ according to Eq. 3

$$\frac{1}{r} = \frac{1-\mathrm{erf}(\mu r)}{r} + \frac{\mathrm{erf}(\mu r)}{r} \tag{3}$$

into a short-range and a long-range part and adjust their domains with a suitable control parameter μ [62–64]. The short-range part is then described in the usual way where the XC-functional describing this part may or may not possess a SIE.

There is also need for suppressing SIEs when setting up CAS-DFT (Sect. 3). In this case, the X-part is described correctly by the CAS wave function and accordingly the correlation part described by a C-functional must not have any SIE. In this situation, it is of advantage to choose a wave-function based C-functional such as the CS-functional that does not suffer from a SIE. This we will discuss in more detail in the next section.

3 Accounting for non-dynamic and dynamic correlation effects: CAS-DFT

The occurrence of non-dynamic electron correlation implies a multi-reference (MR) character of the wave function, i.e., the total wave function is dominated by a number of configuration state functions (CSFs) with non-negligible weights rather than a single CSF. This is difficult to describe with standard KS-DFT using approximate XC-functionals. DFT relates the ground state of the real many-particle system to a fictitious system of non-interacting electrons. The latter move in an effective potential adjusted in such a way that the reference system has the same electron density as the real electron system. One can use the adiabatic connection scheme [65] and replace the effective potential in the reference state adiabatically via a continuum of intermediate states by the real electron–electron interaction with the help of the perturbation parameter λ (Fig. 2). In Fig. 2, the adiabatic connection scheme is schematically shown for the situation of an electron system that encounters just dynamic electron correlation (Fig. 2a) and one that encounters both dynamic and non-dynamic electron correlation (Fig. 2b).

If the electron–electron interaction parameter λ is continuously increased from 0 (situation of the reference state with noninteracting electrons) to 1 (real state), dynamic electron correlation will adopt its full magnitude. This is indicated in Fig. 1 by increasing the weighting coefficients of the excited CSFs Ψ_i ($i =$ 1, 2, …) to their finite, but still small values whereas the weighting coefficient of the ground state CSF Ψ_0 decreases to some value below, but still close to 1. In the case of an electron system with both dynamic and non-dynamic electron correlation, at least one of the excited state CSFs adopts for some value λ_x ($\lambda_x < 1$; Fig. 2b) a large value whereas the weighting coefficient of Ψ_0 is drastically decreased. Although the weight(s) of Ψ_1 (Ψ_2,…) are still below that of Ψ_0, the wave function is no longer dominated by the ground state CSF but by those of the two (three or more) lowest CSFs.

WFT uses for the treatment of systems with non-dynamic correlation a MR wave function from the beginning, such as the complete-active-space self-consistent field (CASSCF [66, 67]) or the generalized valence-bond (GVB) [68] method. However, CASSCF or MCSCF methods are inefficient for the description of dynamic electron correlation, which requires a huge number of electronic configurations with tiny weights in the wave function.

Accordingly, a simultaneous description of non-dynamic and dynamic correlation requires hybrid methods where each kind of electron correlation is described in a suitable way. A number of such hybrid methods rest completely in the realm of WFT, such as the different flavors of CASSCF-based perturbation theory [69, 70] or

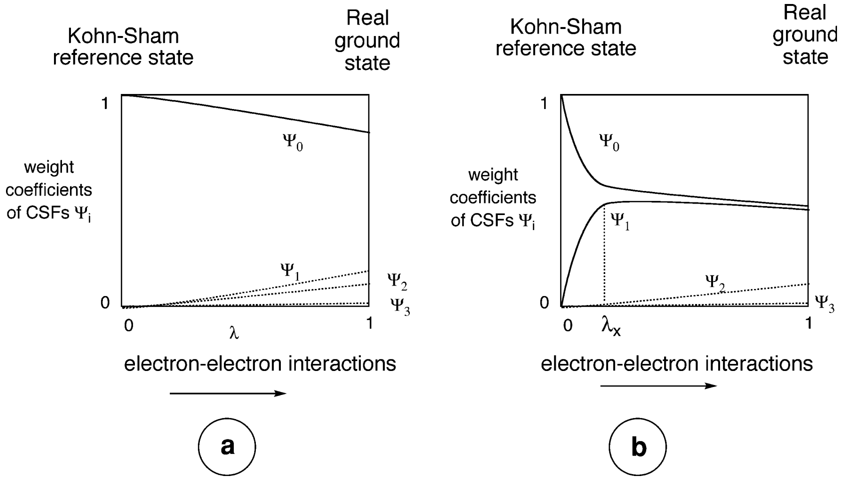

Fig. 2 Schematic illustration of dynamic and non-dynamic electron correlation with the help of the adiabatic connection scheme and the composition of the wave function in terms of configuration state functions (CSFs) Ψ_i given by their weighting coefficients w_i. The perturbation parameter λ increases the relative strength of the electron–electron interactions from the KS reference state ($\lambda = 0$) to the real ground state ($\lambda = 1$). **a** Electron system with dynamic electron correlation. **b** Electron system with multi-reference character leading to both dynamic and non-dynamic electron correlation

GVB-MP2 [71]. However, there are also attempts to develop hybrid methods combining the power and versatility of MR-WFT with the efficiency of DFT.

A general problem with such combined MR-DFT approaches is the double counting of correlation energy: The MR wave function covers not only the non-dynamic electron correlation but also part of the dynamic electron correlation. DFT correlation functionals, which scan the MR wave function only locally, are not sensitive to any dynamic electron correlation already accounted for, and include dynamic correlation a second time thus artificially increasing the correlation energy. In the approach by Lie and Clementi [21, 22] and the GVB-LSDA method developed by Kraka et al. [27, 28], this problem was handled by keeping the active space of the MR wave function as small as possible. However, in a generally applicable MR-DFT approach, double-counting has to be detected and canceled explicitly.

These problems were early recognized by Colle and Salvetti, who performed a long-standing research work on a cost-effective description of dynamic electron correlation based on HF or MR wave functions. In 1975 [23], Colle and Salvetti suggested a functional for the *a posteriori* determination of the correlation energy based on a HF calculation, thus providing an alternative to a configuration-interaction (CI) calculation. The derivation of the CS-functional rested upon a Jastrow-type wave function [72], where the Jastrow factor models the local correlation cusp and contains parameters for both the depth and the extent of the local C-hole. The local gain in correlation energy was expressed in a simple analytic expression containing the local density $\rho(\mathbf{r})$ and the pair density $P(\mathbf{r},\mathbf{r}')$; more specifically, the on-top pair density $P(\mathbf{r},\mathbf{r})$ and the mixed gradient $\partial/\partial\mathbf{r}\ \partial/\partial\mathbf{r}'\ P(\mathbf{r},\mathbf{r}')\big|_{\mathbf{r}'=\mathbf{r}}$. The parameters in this expression were calibrated against accurate CI calculations for the He atom.

The original CS-functional had been designed for closed-shell systems without significant non-dynamic correlation. In 1979, Colle and Salvetti extended their approach to open-shell systems and systems with multi-reference character [24, 25, 29]. In this generalized approach, the reference function may be either a HF or a MR-SCF wave function. A straightforward combination of the original CS-functional with a MR wave function would have led to the aforementioned double-counting of a part of the dynamic correlation energy. For the purpose of avoiding this double-counting, Colle and Salvetti introduced a local measure for the quality of the reference wave function. This measure is designed in such a way that it compares the curvature K_0 of the reference wave function Ψ_0 at the coalescence point $\mathbf{r_1} = \mathbf{r_2}$

$$K_0 = \frac{\partial^2}{\partial\mathbf{r}_1^2}\Psi_0(\mathbf{r}_1,\sigma_1,\mathbf{r}_2,\sigma_2,\ldots,\mathbf{r}_N;\sigma_N)|_{\mathbf{r}_2=\mathbf{r}_1} \tag{4}$$

with its counterpart K_{HF} for the HF reference wave function Ψ_{HF} that is obtained from Ψ_0 if all except the lowest configuration are eliminated,

$$K_{\mathrm{HF}} = \frac{\partial^2}{\partial\mathbf{r}_1^2}\Psi_{\mathrm{HF}}(\mathbf{r}_1,\sigma_1,\mathbf{r}_2,\sigma_2,\ldots,\mathbf{r}_N;\sigma_N)|_{\mathbf{r}_2=\mathbf{r}_1} \tag{5}$$

If $\Psi_0 = \Psi_{\mathrm{HF}}$, i.e., if no multi-reference wave function is used, $K_0 \equiv K_{\mathrm{HF}}$ throughout space. If Ψ_0 contains some of the dynamic correlation effects, it will be $|K_0| > |K_{\mathrm{HF}}|$; if, in particular, Ψ_0 were the exact wave function, $|K_0| \to \infty$ would hold due to the derivative discontinuity of the wave function for $\mathbf{r_1} = \mathbf{r_2}$ (which in turn gives rise to the correlation cusp). The CS C-functional is then modified in a way that, depending on K_0 and K_{HF}, the local contribution to the correlation energy is scaled down (for $|K_0| > |K_{\mathrm{HF}}|$) or set to zero (for $|K_0| \to \infty$), so that the CS correlation energy covers only that part of the dynamic correlation energy not covered by the MR wave function.

The idea to use a local measure for the quality of the reference wave function has been used by Miehlich, Savin, and Stoll (MSS) [26, 30] and later adapted in our CAS-DFT approach [35, 36, 39]. At each position, in addition to the real density $\rho(\mathbf{r})$, one calculates the reference density $\rho_{\mathrm{ref}}(\mathbf{r})$ one would obtain if all active orbitals in the wave function were doubly occupied. The ratio $s(\mathbf{r}) = \rho_{\mathrm{ref}}(\mathbf{r})/\rho(\mathbf{r})$, where $s(\mathbf{r}) \geq 1$, is then a measure for the local size of the active space: For $s(\mathbf{r}) = 1$, all active orbitals are fully occupied locally, i.e., the wave function looks as a HF wave function locally and contains no dynamic correlation. Conversely, $s(\mathbf{r}) \gg 1$ indicates that a large set of active orbitals is present locally, i.e., the wave function should contain a large amount of the dynamic correlation for this position, which should be eliminated from the DFT correlation energy. For $s(\mathbf{r}) \to \infty$, all local correlation effects are contained in the MR wave function, and the DFT C-energy should be put to zero locally. The elimination of local correlation contributions from the DFT C-energy is handled by introducing a scaling factor $f(\rho, \rho_{\mathrm{ref}})$ with

$$\begin{aligned} f(\rho,\rho_{\mathrm{ref}}) &= 1 \quad &&\text{for} \quad \rho = \rho_{\mathrm{ref}} \\ 0 < f(\rho,\rho_{\mathrm{ref}}) &< 1 \quad &&\text{for} \quad \rho < \rho_{\mathrm{ref}} \\ f(\rho,\rho_{\mathrm{ref}}) &\to 0 \quad &&\text{for} \quad \rho_{\mathrm{ref}} \to \infty \end{aligned} \tag{6}$$

and calculating the corrected DFT C-energy according to

$$E_c^{\mathrm{MSS}} = \int \mathrm{d}^3 r f(\rho,\rho_{\mathrm{ref}})\epsilon_c[\rho]|_{\mathbf{r}}. \tag{7}$$

The scaling factor f is calibrated based on a recalculation of the correlation energy for the homogeneous electron gas where the space of virtual orbitals is restricted in order to model the impact of different ρ_{ref} values. The results of these calculations are parameterized once and for ever into an analytic expression, which is then used in production calculations. The original MSS approach shows a number of limitations, which we had to overcome when developing CAS-DFT.

3.1 Distinction between active and inactive orbitals

In the original MSS approach, it is assumed that all occupied orbitals are active, i.e., involved in the description of the non-dynamic correlation effects. In practice, however, only those orbitals relevant for non-dynamic electron correlation are involved into the active space to keep the numerical cost at a reasonable level. Core orbitals as well as valence orbitals not involved in non-dynamic electron correlations are treated as "inactive", i.e., at the same level as in a HF calculation. The DFT C-functional should thus fully account for the dynamic electron correlation involved in these orbitals. However, the scaling factor *f* defined above falsely decreases the DFT C-energy contributions from the inactive orbitals and thus overcompensates the double-counting of the correlation energy.

For CAS-DFT, we developed two alternatives to remedy this shortcoming:

CAS-DFT 1 For the purpose of modeling the situation in a real CASSCF calculation with both active and inactive orbitals, we consider in the homogeneous electron gas only orbitals above a limiting energy as active whereas electrons in orbitals with energies below the limiting energy are considered to be passive. The value of the limiting energy is used to model the size of the inactive space relative to that of the active one. The calculations were parameterized in an analytic expression for the generalized scaling factor *f*′. Within the framework of this approach, the DFT correlation energy gets the form

$$E_c^{\text{CAS-DFT1}} = \int d^3 r\, f'(\rho_{\text{act}}, \rho_{\text{inact}}, \rho_{\text{ref}})\epsilon_c[\rho]|_{\mathbf{r}}. \tag{8}$$

CAS-DFT 2 In the CAS-DFT2 approach, we distinguished between active and inactive orbitals by explicitly adding a correlation term accounting for the latter:

$$E_c^{\text{CAS-DFT2}} = E_c^{\text{MSS}} + \int d^3 r [f(\rho_{\text{inact}}, \rho_{\text{ref}}) - f(\rho_{\text{inact}}, \rho)]\epsilon_c[\rho_{\text{inact}}]|_{\mathbf{r}}. \tag{9}$$

where $\rho_{\text{inact}}(\mathbf{r})$ is the density related to the inactive orbitals. The CAS-DFT2 approach did thus not require a reparameterization for the scaling factor *f*.

3.2 Open-shell versus closed-shell states

The original MSS approach was implemented for closed-shell states only. We extended the approach to also handle open-shell states according to (1) and (2):

(1) *Generalization of f to the open-shell case*. The scaling factor *f* has to reflect the local spin polarization $\zeta(\mathbf{r}) = [\rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})]/\rho(\mathbf{r})$. We generalized the calculation of *f* performed in [26] to the case of a spin-polarized homogeneous electron gas and adjusted the parameterization of *f* accordingly.

(2) *Proper distinction of equal-spin and opposite-spin correlation in the calculation of f.* The relative contribution of equal-spin correlation to the total correlation energy is much larger in the homogeneous electron gas than in real electron systems. Consequently, the role of equal-spin correlation is overestimated in the determination of *f*, which eventually results in an overstabilization of open-shell states relative to closed-shell states [39]. Adapting a suggestion by Stoll, Pavlidou and Preuß (SPP) [73], we recalculated *f* for both open-shell and closed-shell situations in a way that equal-spin correlation effects were eliminated completely.

3.3 Balanced description of high-spin and low-spin open-shell states

In a singlet open-shell state, it is $\zeta(\mathbf{r}) \equiv 0$. The open-shell version of CAS-DFT based on (1) and (2) of Sect. 3.2 describes open-shell singlet states in the same way as closed-shell states, thus resulting in a destabilization of the former states relative to their high-spin isoelectronic counterparts. Hence, it is necessary to describe high-spin and low-spin open-shell states on an equal footing. We accomplished such a description by employing a modified version of the effective unpaired-electron density introduced by Davidson et al. [74, 75], which identifies singly occupied orbitals, no matter whether part of a high-spin or low-spin state, as indicators for an open-shell configuration.

3.4 Reparameterization of the scaling factor *f*

In the course of our work, it turned out that the parameterization of *f* suggested by MSS is not flexible enough for the required generalization of *f*. We therefore developed an alternative parameterization model, which reflects boundary conditions for *f* more properly and allows to reproduce the *f* factor with sufficient accuracy.

For the testing of the CAS-DFT method, we used the three lowest electronic states of methylene, i.e., the $^3B_1$, $^1A_1$, and $^1B_1$ states. Methylene is a suitable test example for computational schemes. In spite of the fact that it contains just six valence electrons, methylene provides a wide range of electronic features (open-shell vs. closed-shell states, high-spin vs. low-spin open-shell states, coexistence of non-dynamic and dynamic electron correlation). We calculated the $^3B_1$, $^1A_1$, and $^1B_1$ states for varying sizes of the active space and different levels of refinement for the DFT C-functional. These tests clearly corroborated the reasoning that had led to improvements in the development of CAS-DFT described in Sects. (3.1)–(3.3) and showed that each of these steps was relevant to obtain a balanced description of the three states investigated. The work clearly confirmed the fact that one cannot construct a functioning MR-DFT approach by simply adding a DFT functional to a MR-WFT function, as was already pointed out by Colle and Salvetti in 1979 [24, 25]. In WFT-based hybrid methods such as CASPT2, the dynamic correlation operator scans the reference wave function in terms of many-electron configurations, which provides a natural basis for a separation of non-dynamic and dynamic correlations. In a MR-DFT approach, where the DFT functional scans the reference wave function just in terms of local one- and two-electron properties, one has to make sure that all required information on the reference wave function is passed to the DFT functional. However, if this is done properly, one will be able to develop an approach that is competitive in its quality to CASPT2 and comparable methods, at a considerably lower computational cost level. In CASPT2, the perturbational calculation of the dynamical correlation energy may require about the same CPU time as the CASSCF step whereas the calculation of the DFT correlation energy implies only negligible extra cost, i.e., CASDFT is equally expensive as a conventional CASSCF calculation.

A crucial point in the development of CAS-DFT was the proper choice of the DFT C-functional. In view of the discussion given in this and the previous chapter, the following requirements have to be fulfilled by a CAS-DFT C-functional:

(1) In distinction to standard DFT, the CAS-DFT-C-functional has to be evaluated on the basis of a many-electron wave function rather than a set of KS orbitals. That is, it should utilize the information contained in the density $\rho(\mathbf{r})$ and the pair density $P(\mathbf{r},\mathbf{r}')$.
(2) There is no SIE in the multi-reference part of the energy functional, neither for the X-part nor for non-dynamic correlation part. Consequently, the DFT-C-functional has to be SIE-free to avoid unidentified and uncontrollable electron interaction effects.
(3) The CAS-DFT-C-functional should be strictly restricted to short-range (dynamic) electron correlation to exclude a double-counting of correlation effects already accounted for by the multi-reference part of the functional.
(4) The CAS-DFT-C-functional should be sensitive to the differences in dynamic correlation between closed-shell and low-spin open-shell states.

These requirements are fulfilled by the CS-functional, which therefore is a suitable choice for the DFT-C-functional in CAS-DFT. The crucial point is that the CS-functional has been derived in a wave function context with a finite system (He atom) as reference, which has the following consequences:

(a) The CS-functional is defined in terms of $\rho(\mathbf{r})$, $P(\mathbf{r},\mathbf{r})$, and $\partial/\partial\mathbf{r}\ \partial/\partial\mathbf{r}' P(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}$.
(b) For a one-electron system, $P(\mathbf{r},\mathbf{r}') \equiv 0$. By virtue of this, CS is able to detect single-electron states and is thus SIE-free.
(c) There is no long-range electron correlation in the He atom. Consequently, the CS-functional is designed for a description of short-range electron correlation only.
(d) The on-top pair density $P(\mathbf{r},\mathbf{r})$ is sensitive to the difference between closed-shell and low-spin open-shell states in distinction to the spin-resolved densities $\rho_{\alpha,\beta}(\mathbf{r})$ used in standard KS-DFT.

In view of this, it is appropriate to emphasize that the work of Colle and Salvetti has been crucial for the development of CAS-DFT, namely by

(1) introducing a local measure for the quality of the reference wave function,
(2) providing the appropriate DFT C-functional.

It should be mentioned that in 1990 Colle and Salvetti suggested an alternative MR-DFT approach [29]. Given that the local measure used in their 1979 work was constructed in an ad-hoc fashion, Colle and Salvetti developed a method that does not require any ad-hoc correction factor. The basic idea of the 1990 method was to account dynamic electron correlation before rather than after taking the multi-reference character into account. For this purpose, the correlation energy was calculated separately with the original CS-functional for each CSF to be included into the MR wave function. In addition, transition Hamilton matrix elements were calculated between different CSFs, incorporating the dynamic correlation effects within each of the CSFs. The (correlated) energies of the individual states and the correlated transition Hamilton matrix elements were then used to set up a Hamilton matrix for the set of CSFs. Diagonalization of this Hamilton matrix led to the energy spectrum of the multi-reference system to be described. In the terminology of multi-reference perturbation theory, this approach can be characterized as "perturb then diagonalize" strategy [76]. In this respect, it can be considered as a predecessor of the REKS method developed later by Filatov and Shaik [33, 34].

4 Conclusion and outlook

Despite the wide use of DFT in computational chemistry, origin, properties, and consequences of the SIE of approximate XC-functionals are hardly known, often overlooked, or wrongly considered as being negligible. Apart from the importance of considering the SIE when analyzing DFT results, especially in the case of odd-electron systems and charge transfer reactions, it plays also an important role when describing electron systems with multi-reference-character and trying to assess the reliability of standard KS-DFT. In the latter cases, the SIE improves DFT results by artificially including left–right correlation. However, this fact must not be misunderstood as a guarantee that DFT with SIEs can correctly describe MR electron systems. The inclusion of non-dynamic electron correlation via the the SIE of the X-part is done in a non-specific way and therefore cannot adjust to the situation of multi-reference systems with specific non-dynamic electron correlation effects. If the SIE-induced correlation effects lead to an improvement of DFT results it is certainly an improvement for the wrong reason that provides an uncertain starting point for further method or XC improvements. Especially problematic are those cases where an improvement of the XC functional leads to a deterioration of DFT results. This is often an indication of a reduction of the X-SIE, as it happens when converting a GGA XC functional into a hybrid functional with a significant portion of exact exchange. The advantages of the improved XC functional often can only be made visible when including non-dynamic electron correlation effects via the form of the wave function as, e.g., in a BS-UDFT or REKS calculation.

Although it is not directly relevant for the discussion presented in this work, it has to be mentioned that definition of the SIE is no longer unambiguous for many-electron systems. This problem has recently been discussed by a number of authors. Ruzsinsky et al. [77, 78] studied diatomic molecules with fractional occupation numbers in the dissociation limit and pointed out the difficulties of getting XC functionals which are not only one- but also many-electron SIE. Cohen et al. [79] interpret the one- and many-electron SIEs as delocalization errors which can be best understood when studying fractional charge distributions. Körzdörfer et al. [80] showed that the variance of the Perdew–Zunger SIE-corrected XC energy functional [43] with respect to orbital rotations is directly related to the problem of defining the SIE for many electron systems and suggest an optimized effective potential (OEP) version of the Perdew–Zunger functional, which handles this problem in a better way. In all these studies it is emphasized that the SIE is one of the most serious problems of DFT, which has not been solved so far in a generally satisfying way.

Until the early 90s, WFT and DFT constituted two disjunct realms within the field of electronic structure calculations. This segregation was aggravated by the fact that WFT was used nearly exclusively by chemists whereas DFT was preferred by physicists. Colle and Salvetti were among the first to combine the strengths of WFT and DFT in hybrid approaches. Their work demonstrated both the potential and the challenge of such hybrid approaches: DFT-like functionals allow an effective but still cheap description of the dynamic correlation effects missing in a MR wave function. However, one has to be aware that WFT and DFT employ different languages: In a pure WFT method, e.g., CASPT2, the perturbation approach scans the MR wave function in terms of many-body configurations, which effectively eliminates a double-counting of correlation contributions. On the contrary, a DFT C-functional assesses only local information from the MR wave function and is blind to the configurations contained in the wave function. When developing a MR-DFT approach, one has to convey the relevant information to the DFT C-functional via suitable local properties. However, if this problem is satisfactorily solved, MR-DFT methods will provide reliable descriptions for a wide range of multi-reference electron systems, as has been demonstrated by the use of CAS-DFT in these cases [35, 36, 39].

Today, the combination of WFT- and DFT-based techniques becomes more and more accepted. The development of MR-DFT methods is a field of active research. Apart from this, modern DFT functionals employ ingredients stemming from WFT: Hybrid X-functionals [10, 11] use the WFT exchange expression to determine a portion of the X-energy. Meta-GGA functionals [12, 15, 16] use local indicators combining derivatives of the one-particle density and the KS density matrix to detect single-electron regions and eliminate the SIE of the C-functional. An extension of this idea can be found in the X-functional by Kümmel and Perdew [81], where a local indicator is used to vary the portion of exact X-in the X-functional on a per-point basis, so that the SIE may be incorporated where it is desirable to mimic non-dynamic electron correlation and excluded in single-electron regions.

In all these developments, the CS functional has played, as outlined in this article, an important role. Nevertheless, it should not be elided that there has been criticism as to the usefulness of the CS functional. Singh et al. [82] pointed out that the CS wave function functional is not properly normalized and the Coulomb hole sum rule is violated among some other deficiencies, which are typical of most other correlation functionals currently in use. Tao et al. [83] and Caratzoulas and Knowles [84] demonstrated that the CS functional lacks long-range electron correlation, which is why the CS correlation energy is incorrect in the limit of a homogeneous system. It should be noted, though, that the lack of long-range corelation does not pose a problem in CASDFT because in this case long-range electron correlation is described by the multi-reference wave function. More recently, Moscardo et al. [85, 86] suggested modifications of the Colle–Salvetti approach to remedy the inconsistencies pointed out in the literature [82–84].

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