Range-separated multiconfigurational density functional theory methods

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Abstract
Range-separated multiconfigurational density functional theory (RS MC-DFT) rigorously combines density functional (DFT) and wavefunction (WFT) theories. This is achieved by partitioning of the electron interaction operator into long- and short-range components and modeling them with WFT and DFT, respectively. In contrast to other methods, mixing wavefunctions with density functionals, RS MC-DFT is free from electron correlation double counting. The general formulation of RS MC-DFT allows for merging any ab initio approximation with density functionals. Implementations of RS MC-DFT aim at increasing both versatility and accuracy of the underlying methods, while reducing the computational cost of the ab initio problem. Variants of the RS MC-DFT approach can be divided into single-determinant-based range-separated methods and range-separated multideterminantal WFT methods. In these approaches the electron correlation energy is described both by a pertinent short-range density functional and by the wavefunction theory. We review the short-range functionals and correlated wavefunction theories employed in the framework of RS MC-DFT. We discuss applications of the RS MC-DFT methods to ground-state properties of molecules and to noncovalent interactions. Time-dependent linear-response theory and direct approaches to excited states are also presented. For each area of applications, we assess advantages of RS MC-DFT over conventional DFT and ab initio methods.

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1 INTRODUCTION

Electronic structure methods may be divided into those originating from the wavefunction theory (WFT) and from the density functional theory (DFT). Foundations of both WFT and DFT are exact: WFT is directly linked to many-electron Schrödinger equation, while DFT is rooted in the Hohenberg–Kohn theorem. Approximations of WFT can be
systematically improved, at a cost of a rapidly growing computational burden. In contrast, DFT has always relied on approximate functionals. Although there exists no methodical way of developing exchange-correlation functionals, both physical insight and exact constraints have led to DFT models of accuracy useful for chemical applications. At the same time, DFT methods dominate computational chemistry in terms of efficiency, as their computational cost is at least one order of magnitude lower compared to WFT-based approaches. Enormous progress in the functional development notwithstanding, even the best-performing approximations are less reliable when applied to systems where long-range or static electron correlation effects come into play.

Taking into account the pros and cons of WFT and DFT methods, a question arises if they can be combined in a way that preserves their firm footing in the exact theory, and makes them benefit from each other’s strengths in practical implementations. A positive answer was given by Savin et al. who separated the electron interaction operator into short- and long-range regimes and described them with DFT and WFT, respectively. Even though the original idea was to cure the inability of DFT approximations to treat nearly degenerate systems, potential benefits for WFT were also envisaged: “Please notice that due to the disappearance of the electron–electron interaction potential for \( r_{12} \rightarrow 0 \) no cusp will appear in \( \Phi \) and thus the expansion in terms of Slater determinants can be expected to be shorter than in the usual configuration interaction calculations.” In other words, removal of the electron cusp from the wavefunction opens a way of achieving a satisfactory accuracy at a lower cost, thanks to more compact wavefunctions and smaller basis sets. The benefits for DFT from combining it with WFT is that the spin-symmetry dilemma is avoided and static electron correlation is accounted for without breaking the spin-symmetry of electron density. Moreover, the long-range electron correlation, inadequately treated or altogether missing in density functional approximations, can be captured by the wavefunction part.

The plan of this overview is as follows. In Section 2 we present the range-separated multiconfigurational density functional theory (RS MC-DFT), which is behind the methods combining DFT and WFT via range-separation—the subject of this work. In the same section we also discuss practical realizations of the range-separated electron interaction operator, strategies of choosing the value of the range-separation parameter, development of the short-range exchange-correlation functionals, and wavefunction methods, which have been employed in various implementations of RS MC-DFT. Section 3 is devoted to ground-state properties, while Section 4 focuses on intermolecular interactions. RS MC-DFT methods for excited states and their performance are a subject of Section 5. Summary and perspective on RS MC-DFT is given in Section 6.

## Theory and Implementations

### Exact formalism

The RS MC-DFT theory as proposed by Savin et al. is based on partitioning of the electron–electron Coulomb interaction operator, \( r_{12}^{-1} \), into short-range (SR) and long-range (LR) components, \( \tilde{\nu}_{ee}^{SR}(r_{12}) \) and \( \tilde{\nu}_{ee}^{LR}(r_{12}) \), respectively,

\[
\frac{1}{r_{12}} = \tilde{\nu}_{ee}^{LR}(r_{12}) + \tilde{\nu}_{ee}^{SR}(r_{12}).
\]

The total electron interaction operator \( \tilde{V}_{ee} \) is decomposed accordingly as

\[
\tilde{V}_{ee} = \tilde{V}_{ee}^{LR} + \tilde{V}_{ee}^{SR},
\]

\[
\tilde{V}_{ee}^{LR/SR} = \sum_{i>j} \tilde{\nu}_{ee}^{LR/SR}(r_{ij}).
\]

The essential conditions for the long-range part are that it is finite at the electron–electron coalescence, \( r_{12} \rightarrow 0 \), and reduces to the Coulomb interaction in the large-separation limit

\[
\lim_{r_{12} \rightarrow 0} \tilde{\nu}_{ee}^{LR}(r_{12}) = \text{const},
\]

\[
\lim_{r_{12} \rightarrow \infty} \tilde{\nu}_{ee}^{LR}(r_{12}) = \frac{1}{r_{12}}.
\]
By assumption, short-range interaction takes over in the short-distance limit

$$\lim_{r_{12} \to 0} \rho^{\text{SR}}_{\text{ee}}(r_{12}) = \frac{1}{r_{12}},$$

(6)

and vanishes faster than $1/r_{12}$ when electrons are far from each other, $\lim_{r_{12} \to \infty} \rho^{\text{SR}}_{\text{ee}}(r_{12}) = 0$.

The motivation for RS MC-DFT has been to describe the long-ranged electron interaction with a many-configurational wavefunction, while leaving the electron-cusp region for the density functional. The exact ground state range-separated density functional is constructed using Levy’s constrained search formalism

$$E_0 = \min_{\rho} \left\{ \min_{\Psi} \left\langle \Psi \left| \hat{T} + \hat{V}_{\text{ne}} + \hat{V}^{\text{LR}}_{\text{ee}} \right| \Psi \right\rangle + E^{\text{SR}}[\rho] \right\},$$

(7)

where $\hat{T}$ and $\hat{V}_{\text{ne}}$ are, respectively, the kinetic energy and electron–nuclei interaction operators, and $\rho$ stands for electronic density. The functional $E^{\text{SR}}[\rho]$ has been defined as the difference of universal functionals corresponding to full- and long-range electron interaction operators

$$E^{\text{SR}}[\rho] = \min_{\Psi} \left\langle \Psi \left| \hat{T} + \hat{V}_{\text{ne}} + \hat{V}^{\text{LR}}_{\text{ee}} \right| \Psi \right\rangle - \min_{\Psi} \left\langle \Psi \left| \hat{T} + \hat{V}^{\text{LR}}_{\text{ee}} \right| \Psi \right\rangle.$$

(8)

The double minimization in Equation (7) is equivalent to minimization with respect to the antisymmetrized electronic wavefunction

$$E_0 = \min_{\Psi} \left\{ \left\langle \Psi \left| \hat{T} + \hat{V}_{\text{ne}} + \hat{V}^{\text{LR}}_{\text{ee}} \right| \Psi \right\rangle + E^{\text{SR}}[\rho_{\Psi}] \right\},$$

(9)

where the electron density $\rho_{\Psi}$ corresponds to the wavefunction $\Psi$. The wavefunction minimizing the expression in the curly bracket, which will be denoted as $\Psi^{\text{LR}}$, is the ground state eigenfunction

$$\hat{H}^{\text{LR}} \Psi^{\text{LR}} = E_0 \Psi^{\text{LR}},$$

(10)

of the Hamiltonian $\hat{H}^{\text{LR}}$

$$\hat{H}^{\text{LR}} = \hat{T} + \hat{V}_{\text{ne}} + \hat{V}^{\text{LR}}_{\text{ee}} + \hat{V}^{\text{SR}}[\rho_{\Psi^{\text{LR}}}],$$

(11)

which includes the long-range electron interaction operator and the short-range local potential $\hat{V}^{\text{SR}}$. The latter follows as a functional derivative of $E^{\text{SR}}[\rho]$

$$\hat{V}^{\text{SR}}[\rho] = \sum_{i} \frac{\delta E^{\text{SR}}[\rho]}{\delta \rho(r_i)}.$$
\[ E_0 = \left\langle \psi^{LR} \right| \hat{T} + \hat{V}_{ne} + \hat{V}^{LR}_{ee} \left| \psi^{LR} \right\rangle + E^{SR}[\rho_{\text{ee}}]. \] (14)

The short-range functionals single out the short-range Hartree functional, \( E_{\text{SR}}^H[\rho] \) and the exchange-correlation functional \( E_{\text{SR}}^{xc}[\rho] \):

\[ E^{\text{SR}}[\rho] = E_{\text{SR}}^H[\rho] + E_{\text{SR}}^{xc}[\rho], \] (15)

where \( E_{\text{SR}}^H[\rho] \) is computed with the short-range operator \( \hat{v}^{\text{SR}}_{ee}(r_{12}) \)

\[ E_{\text{SR}}^H[\rho] = \frac{1}{2} \int \rho(r_1) \hat{v}^{\text{SR}}_{ee}(r_{12}) \rho(r_2) dr_1 dr_2. \] (16)

Due to range separation of the electron interaction, description of the electron correlation is also partitioned between the wavefunction part and the SR functional. It is worthwhile to stress, that RS MC-DFT, based on Equations (1) and (9), avoids correlation double counting in a rigorous manner.

Implementation of the RS MC-DFT method requires selecting a particular form of the long-range electron interaction operator, Equation (1), developing a complementary short-range functional \( E^{\text{SR}} \), Equation (15), and choosing the approximation for the WFT to be employed in the variational equation shown in Equation (10).

2.2 | Range-separated electron interaction operator

Practical realization of range-separation involves introducing a parameter \( \mu \), the inverse of which determines the cut-off in the scale of electron–electron distances at which the wavefunction and density functional parts operate. By definition, the parameter should smoothly switch between the limiting cases, \( \mu \) tending to 0 and \( \infty \). In the former case, the LR electron interaction vanishes and the long-range wavefunction, see Equations (10) and (11), reduces to a Kohn–Sham determinant \( \Phi_{\text{KS}} \)

\[ \mu \to 0: \, \hat{v}^{\text{LR}}_{ee}(r_{12}) = 0, \, \psi^{LR} = \Phi_{\text{KS}}. \] (17)

In the large-\( \mu \) limit, the long-range operator \( \hat{v}^{\text{LR}}_{ee} \) converges to Coulomb interaction and the energy recovered by the SR density functional drops to 0

\[ \mu \to \infty: \, \hat{v}^{\text{LR}}_{ee}(r_{12}) = \frac{1}{r_{12}}, \, E^{\text{SR}}[\rho] = 0. \] (18)

One of the first choices for the long-range electron interaction function was to use a Yukawa-like potential and introduce a parameter \( \mu \) in its exponent\(^5,8,9\)

\[ \hat{v}^{\text{LR}}_{ee}(r_{12}) = \frac{1 - e^{-\mu r_{12}}}{r_{12}}. \] (19)

This form satisfies Equations (4) and (5), so the two crucial conditions are met: divergence at \( r_{12} = 0 \) is avoided and the complementary \( \hat{v}^{\text{SR}}_{ee}(r_{12}) \) potential vanishes faster than \( 1/r_{12} \) at infinity. One of the practical difficulties with the Yukawa potential is the incompatibility of the LR operator in Equation (19) with the Gaussian basis set functions, widely used in most quantum chemistry packages, that renders two-electron integrals computation inefficient.

Two other choices have been considered. In the first one, the singularity in the long-range interaction operator is removed using the error function\(^6\)
\[ \hat{v}_{ee, \text{LR}}^{\text{LR}}(r_{12}) = \frac{\text{erf}(\mu r_{12})}{r_{12}}, \]

(20)

In the second one, in addition to the error function, the Gaussian function is employed to attenuate the electron interaction at short-range. The resulting erfgau operator reads

\[ \hat{v}_{ee, \text{erfgau}}^{\text{LR}}(r_{12}) = \frac{\text{erf}(\mu r_{12})}{r_{12}} - \frac{2\mu}{\sqrt{\pi}} e^{-\frac{1}{\mu^2} r^2}. \]

(21)

It is worth noticing, that these forms of the long-range operators have been also explored in other methods, in particular in the hybrid long-range corrected (LC) density functionals. Both erf and erfgau LR operators conform to the limiting conditions Equations (4) and (5). Their appealing feature is that computation of two-electron integrals requires only simple modifications of the integral codes that rely on Gaussian basis set functions. The main difference between the two \( \hat{v}_{ee, \text{LR}}^{\text{LR}} \) operators is their short-range behavior. While \( \hat{v}_{ee, \text{LR}}^{\text{LR}}(r_{12}) \) achieves a nonzero value at \( r_{12} = 0 \), \( \hat{v}_{ee, \text{erfgau}}^{\text{LR}}(r_{12} \rightarrow 0) = 2\pi^{-1/2}\mu \), the \( \hat{v}_{ee, \text{erfgau}}^{\text{LR}} \) function and its derivative vanish at \( r_{12} = 0 \). As can be seen in Figure 1, the wavefunction- and density functional electron interaction domains largely overlap if the erf function is used. In contrast, the erfgau function strictly prevents the LR operator from describing electron interaction in the short-range regime. Therefore, it seems that the erfgau function is better suited for the RS MC-DFT approach than its \( \hat{v}_{ee, \text{erfgau}}^{\text{LR}} \) counterpart. However, implementations of the RS MC-DFT methods have shown that erfgau does not offer higher accuracy than the functionals based on the error function. Moreover, the binding potential in the short-range region of the erfgau electron interaction is unphysical, which could affect its performance. For these reasons the erfgau operator was eventually abandoned. Practically, all currently used implementations of the RS MC-DFT approaches are based on the erf interaction.

The range-separated electron interaction operator involves a parameter which separates the two domains. The separation is not sharp, and for the erf interaction, Equation (20), with \( \mu = 0.5 \text{ bohr}^{-1} \) corresponding to the cutoff radius \( r_c = 1/\mu = 1 \) bohr, there is a broad overlap of the ranges, centered around \( r_c \), where both \( \hat{v}_{ee, \text{lr}}^{\text{LR}} \) and \( \hat{v}_{ee, \text{sr}}^{\text{SR}} \) have non-negligible values, cf. Figure 1. Increasing the value of \( \mu \) extends the range in which \( \hat{v}_{ee, \text{lr}}^{\text{LR}} \) dominates over its SR counterpart toward smaller distances \( r_{12} \), so that the LR wavefunction has to capture a greater amount of electron correlation. The physical meaning of the range-separation parameter has been exploited in Ref. 18 to fix the \( \mu \) value for a given system. In this work, RS MC-DFT has been applied to describe the interaction energy of rare gas dimers. The range-separation parameter was set for each dimer as the inverse of half the interatomic distance \( R_0 \), namely \( \mu = (R_0/2)^{-1} \). With this choice, the LR wavefunction part describes the interatomic electron interaction, while the SR functional recovers intraatomic electron correlation.

**Figure 1** Left panel: Long- and short-range electron interaction potentials, \( \frac{\text{erf}(\mu r_{12})}{r_{12}} \) (LR) and \( 1 - \text{erf}(\mu r_{12}) \) (SR) for \( \mu = 1.0 \) and \( \mu = 0.4 \). Dots indicate position of the cutoff radius \( r_c = 1/\mu \). Right panel: Behavior of the wavefunction in the electron–electron coalescence region for Coulomb electron interaction (1/\( r_{12} \)) and LR erf interaction (\( \mu = 1.0 \) and \( \mu = 0.4 \), cf. Ref. 27. \( \theta \) is the angle between position vectors \( r_1 \) and \( r_2 \) of two electrons and \( |r_1| = |r_2| = 1 \)
As the scale of the required electron interaction separation is local and system dependent, one might consider designing a local \( \mu \) and linking the corresponding cutoff radius \( r_c \) to the Wigner–Seitz radius \( r_s = \left[ \frac{3}{(4\pi \rho)} \right]^{1/3} \). Interacting electrons enclosed in the Wigner–Seitz sphere, where density is assumed to be close to homogeneous, would be well described by the local short-range functional. Although the idea of a local \( \mu \) is appealing, its implementation would greatly increase the complexity of two-electron integrals evaluation. Notice, that system-specific choices of \( \mu \) risk violating size-extensivity and size-consistency conditions. To avoid these problems, in Ref. 19 the system-averaged parameter \( \langle \mu \rangle = (1/r_s) \) has been employed. In Ref. 20 Toulouse et al. employed a locally determined range-separation function, \( \mu(r) \), in the SR functional part, leaving the wavefunction part with a global range-separation parameter. A local \( \mu(r) \) function has allowed to remove the unwanted long-range interaction effects from the short-range local functional and improved its accuracy. As pointed out in Ref. 20, special care should be taken when using different range-separating \( \mu \) in the long-range Hamiltonian and the short-range functionals, to avoid exchange and correlation double counting. A solution to this problem would be to impose the condition \( \mu(r) > \mu \) on the local \( \mu(r) \) in the SR functional, if \( \mu \) is the global parameter.

The optimal choice of the global system- and application-independent parameter remains an open issue. Ideally, the ground state energy, cf. Equation (14), does not depend on the assumed value of the parameter, but this would only happen if the exact short-range functional were used. With approximate SR functionals, the results are, inevitably, parameter-dependent. Moreover, this dependence is related to the accuracy of the functional, that is, more accurate functional should be less sensitive to the choice of \( \mu \). One of the first estimations of the optimal value of the range-separation parameter was provided by Gerber and Ángyán who evaluated formation enthalpies of molecules from the G2 subset with RS MC-DFT (in fact, a single-determinantal wavefunction \( \Psi^{LR} \) was used in the framework of Equation (9)) and obtained \( \mu = 0.5 \text{ bohr}^{-1} \) as the recommended value minimizing the average error. In the work of Goll et al. this value has been confirmed as a reasonable choice also for applications with correlated WFT methods.

Investigation undertaken by Fromager et al. explored the possibility of establishing a single, universal value of \( \mu \). The proposed definition of universality assumed decomposition of electron correlation into dynamic and static components and assigned the short- and long-range electron interaction to the former and the latter parts, respectively. Such an approach circumvents the system and geometry dependence of the optimal, global \( \mu \). According to the adopted definition, for systems with no static correlation effects the universal value of \( \mu \) should correspond to the largest value for which the wavefunction \( \Psi^{LR} \) is mainly single determinantal. For description of multireference systems or systems involving dispersion interaction, the universal \( \mu \) should be large enough to obtain a sufficiently correlated \( \Psi^{LR} \) capable of capturing either static- or long-range correlation effects. Based on numerical tests for energies of small atoms and molecules, and several dissociation energy curves, the universal \( \mu \) value was set to 0.4 \text{ bohr}^{-1}. Search for the universal \( \mu \) parameter has been extended to a set of actinide compounds in Ref. 25. Although \( \mu = 0.3 \text{ bohr}^{-1} \) was identified as the optimal choice, it was confirmed that RS MC-DFT energies remain reasonably accurate if a larger value, \( \mu = 0.4 \text{ bohr}^{-1} \), is used. Therefore, the universal range-separated parameter obtained in the studies of Fromager et al. is close to the value of 0.5 \text{ bohr}^{-1} obtained by Gerber et al.

A global and universally valid \( \mu \) makes the calculation of two-electron integrals efficient and avoids breaking the size-extensivity and size-consistency conditions. Nevertheless, insisting on the single value of \( \mu \) may limit the accuracy of RS MC-DFT methods, in particular for excited states (see Section 5). Choosing a system-dependent \( \mu \) value, for example, by enforcing satisfaction of the extended Koopmans theorem, could in principle improve the accuracy, but comes at the price of losing size-consistency.

### 2.3 Short-range exchange and correlation density functionals

The critical challenge in the development of RS MC-DFT has always been to devise the best approximation to the SR exchange-correlation functional. One should stress that finding the exact SR functional is as an insurmountable problem as in the full-range Kohn–Sham formulation of DFT. Clearly, if the exact SR functional were known, it would mean that the full-ranged functional is also within reach, so going through the RS MC-DFT procedure would be pointless.

A choice of the long-range electron interaction operator in RS MC-DFT calls for the development of a density functional corresponding to the complementary, short-ranged, interaction. It is the exchange-correlation part of the SR functional, cf. Equation (15),
\[ E_{xc}^{SR}[\rho] = E_{xc}^{SR}[\rho] - E_{xc}^{SR}[\rho], \quad (22) \]

which requires approximation. When the long-range electron interaction operator tends to zero, cf. Equation (17), the SR exchange-correlation functional reduces to the standard xc functional, namely

\[ \lim_{\rho_{sr}^{LR} \to 0} E_{xc}^{SR}[\rho] = E_{HK}[\rho] - \langle \Phi_{KS}[\rho] \mid T \mid \Phi_{KS}[\rho] \rangle - E_H[\rho] = E_{xc}[\rho], \quad (23) \]

where \( E_{HK}[\rho] \) is the universal Hohenberg–Kohn functional, \( E_{ls}[\rho] \) is the Hartree energy corresponding to Coulomb electron interaction, and \( \Phi_{KS}[\rho] \) denotes a Kohn–Sham determinant corresponding to \( \rho \). In the other limiting case, \( \forall_{r_{12}} \mu_{se}^{LR}(r_{12}) = 1/r_{12} \), cf. Equation (18), the short-range functional vanishes, \( E_{xc}^{SR}[\rho] = 0 \). Construction of the exact exchange-correlation functional corresponding to a modified electron interaction is not a simpler task than finding a functional for the Coulomb interaction. However, a short-ranged nature of \( E_{xc}^{SR}[\rho] \) implies that approximate functionals should be better transferable than in the case of \( E_{xc} \).

In most approximations \( E_{xc}^{SR} \) is decomposed into the short-range exchange energy functional

\[ E_{xc}^{SR}[\rho] = \langle \Phi_{KS}[\rho] \mid V_{SR}^{perl} \mid \Phi_{KS}[\rho] \rangle - E_{xc}^{SR}[\rho], \quad (24) \]

that is, taking a Kohn–Sham determinant \( \Phi_{KS} \) as the reference, similarly to the conventional KS-DFT, and the remaining correlation functional\(^5,28\)

\[ E_{c}^{SR}[\rho] = E_{c}^{SR}[\rho] - E_{xc}^{SR}[\rho]. \quad (25) \]

Since by construction the short-range exchange-correlation functional is responsible for describing interacting electrons in the short-range, it was natural to assume a homogeneous electron gas (HEG) with modified interaction as a model system for functional development and design local SR approximations

\[ E_{xc}^{SR}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}^{SR}[\rho](\mathbf{r}) d\mathbf{r}, \quad (26) \]

where the exchange or correlation energy density \( \epsilon_{xc}^{SR}[\rho] \) corresponds to HEG of the density \( \rho \). Defining the long-range exchange-correlation functional as \( E_{xc}^{LR}[\rho] = E_{xc}^{SR}[\rho] - \langle \Phi_{KS}[\rho] \mid T' \mid \Phi_{KS}[\rho] \rangle - E_{ xc}^{LR}[\rho] \), in analogy to its full-range counterpart given in Equation (23), allows one to write the SR functional presented in Equation (22) in the equivalent form reading\(^ \[ E_{xc}^{SR}[\rho] = E_{xc}[\rho] - E_{ xc}^{LR}[\rho]. \]

One of the first local short-range functionals was proposed for the Yukawa-like potential, Equation (19). The local SR exchange functional was obtained analytically.\(^5,9\) The Fermi-hypernetted-chain approximation\(^5\) and coupled cluster calculations\(^9\) were performed for the HEG with the modified SR electron interaction leading to a local approximation to the correlation functional \( \epsilon_{c}^{SR}[\rho] \).

Exact expression for the short-range local-density exchange functional can also be derived for the erf interaction, see Equation (20), as demonstrated in Ref. 6. In the same work the local short-range correlation functional corresponding to the erf potential was presented. The model was based on coupled cluster calculations carried out for the Coulomb- and long-range interacting HEG, for a number of electron densities and the range-separation parameter values. The working form of the SR local correlation functional at a given \( \mu \) was obtained as a difference of the Coulomb- and long-range-interacting correlation energy density of HEG multiplied by a ratio of the standard local correlation in the VWN approximation\(^29\) to its SR counterpart in the \( \mu = 0 \) limit.

Asymptotic expansions in terms of \( \mu \) for the exact SR exchange and correlation functionals corresponding to erf and erf-gau interactions have been derived by Toulouse et al.\(^13\) In particular, the first two terms in the large-\( \mu \) expansion of the SR correlation \( \mu^{-3} \) term, was found by Gori-Giorgi
et al.\textsuperscript{30} were shown to be local functionals of the on-top pair density. The on-top pair density is defined as the electron pair-density function $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ evaluated at a coalescence of the position of two electrons, $\mathbf{r}_1 = \mathbf{r}_2 = r^{31}$

$$\Pi(\mathbf{r}) = \rho_2(\mathbf{r}, \mathbf{r}) = N(N-1) \int \cdots \int |\Psi(x_1, \ldots, x_N)|^2 d\sigma_1 \ldots d\sigma_N d\mathbf{r}_3 \ldots d\mathbf{r}_N |_{\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}}. \quad (27)$$

This important result has opened new possibilities in constructing SR correlation functionals by including their dependence not only on the electron density, but also on a two-electron quantity—the on-top pair density. Rational formulas, interpolating between the $\mu = 0$ and $\mu \to \infty$ have been proposed\textsuperscript{13} for the SR exchange and correlation energy functionals.

Local approximation for the correlation functional has further been elaborated in Ref.\ 14, both for the erf and erfau electron interactions. The results obtained from the coupled cluster method for the HEG with modified interactions\textsuperscript{32} have been fitted by a simple analytic function. Its form accounted for the leading term in the $\mu \to \infty$ expansion. The SR correlation functional has been combined with the exact form of SR local exchange for both erf and erfau functions.

One of the limitations of the short-range exchange-correlation functionals developed in Refs. 6, 13, 14 was their spin-independence, which practically restricted the applications to spin-unpolarized systems. To overcome this, a local spin-dependent SR functional was designed by Paziani et al.\textsuperscript{28} by generalizing definition of the short-range functional in Equation (8) to its spin dependent variant as

$$E^{\text{SR}}[\rho_\alpha, \rho_\beta] = \min_{\Psi \rightarrow \rho_\alpha, \rho_\beta} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle - \min_{\Psi \rightarrow \rho_\alpha, \rho_\beta} \langle \Psi | \hat{T} + \hat{V}^{\text{LR}}_{\text{ee}} | \Psi \rangle, \quad (28)$$

($\rho_\alpha$ and $\rho_\beta$ are $\alpha$ and $\beta$ components of electron density, respectively) and looking for the exchange and correlation energy densities, see Equation (26), as functions of the electron density $\rho = \rho_\alpha + \rho_\beta$, spin polarization $\zeta = (\rho_\alpha - \rho_\beta) / \rho$, and the range-separation parameter $\mu$: $e_{\text{SR}}^{\text{LR}}[\rho, \zeta, \mu] = e_{\text{LR}}^{\text{SR}}[\rho, \zeta, \mu] - e_{\text{SR}}^{\text{LR}}[\rho, \zeta, \mu]$, where $e_{\text{SR}}^{\text{LR}}$ and $e_{\text{LR}}^{\text{SR}}$ are exchange and correlation energy per electron of the HEG model with, respectively, Coulomb and long-range electron interaction. The functional was developed for the erf long-range electron interaction operator. The analytic expression for the spin-polarized exchange energy of HEG, $e_{\text{LR}}^{\text{SR}}[\rho, \zeta, \mu]$, was given. The correlation energy $e_{\text{SR}}^{\text{LR}}[\rho, \zeta, \mu]$ was presented in a form of a compact function fitted to diffusion quantum Monte Carlo energy values computed for a range of $\rho$, $\zeta$, and $\mu$ values. Exact $\mu \to 0$ and $\mu \to \infty$ asymptotics for the local correlation energy $e_{\text{SR}}^{\text{LR}}[\rho, \zeta, \mu]$ were derived and imposed on the proposed correlation functional.

A validation of correlation and exchange energies obtained with a local approximation to the SR functional (srLDA) against accurate reference values revealed that even for few-electron systems srLDA gives poor results when applied with intermediate or small values of the range separation parameter.\textsuperscript{20} To fix this, models which can be considered as first nonlocal exchange-correlation SR functionals have been proposed in Ref. 13. They have been constructed as rational interpolations between a conventional (full-range) density functional at $\mu = 0$ and a correct $\mu$-expansion in the large-$\mu$ limit. Fromager et al. adopted this development in Ref. 24, where a gradient-corrected functional consisted of the short-range variant of the PBE exchange model developed in Ref. 33 combined with the SR correlation functional interpolating between the standard PBE correlation at $\mu = 0$ and the asymptotic expansion of the SR local functional at $\mu \to \infty$.

In Ref. 20 Toulouse et al. devised a more rigorous approach to SR gradient-corrected functionals involving a product of the local SR functional and modified PBE enhancement functions. Dependence on the reduced separation parameter $\tilde{\mu} = \mu / (2k_F)$ was introduced and the coefficients in the enhancement function for exchange were fixed by imposing a correct large-gradient expansion and the Lieb–Oxford bound.\textsuperscript{44} The short-range PBE (srPBE) correlation functional was proposed by exploiting the low- and high-density gradient limits and the density uniform scaling condition. Another variant of the srPBE functional for erf interaction was introduced by Goll et al.\textsuperscript{18} In the exchange part, the $\mu$-dependence was incorporated only into the gradient coefficient of the enhancement function. For the latter the formula proposed in Ref. 20 was employed, but it was scaled to retrieve PBE exchange with unmodified interaction at the $\mu \to 0$ limit, and damped in the large-$\mu$ limit. In the correlation part, the form of the enhancement function originally proposed for the PBE functional with Coulomb interaction was retained. The coefficient multiplying quadratic gradient was simply scaled by a ratio of the srLDA correlation energy densities, $e_{\text{SR}}^{\text{LR}}(\mu, \rho) / e_{\text{SR}}^{\text{LR}}(0, \rho)$\textsuperscript{\textsuperscript{46}}. Both the $\alpha_2$ factor and the parameter in the damping function introduced into the exchange functionals were fitted to the exchange-correlation
energy of the helium atom. The closed-shell srPBE density functional developed in Ref. 18 was generalized to open shell systems in Ref. 21.

Similar as in conventional DFT, short-range GGA functionals have been followed by meta-GGA approximations. The meta-GGA models include the kinetic energy density as an input, in addition to the electron density and its gradient employed in GGA. Goll et al. 35 have proposed a meta-GGA model based on the srPBE 18,21 and the unmodified TPSS 36 functionals. The expressions for the exchange and correlation functionals interpolate between the srPBE and TPSS ($\mu = 0$ limit) by means of the range-separation parameter-dependent exponential function. Application of the short-range TPSS to thermochemistry has shown that it performs slightly better than srPBE (see also Section 3.2). In Refs. 37, 38 a simple scaling has been applied to adopt any GGA or meta-GGA correlation functional to the short-range electron interaction. The local scaling factor was a ratio of the srLSDA functional by Paziani et al. 28 to the local spin density correlation functional. There exists a plethora of short-range exchange functionals proposed within the LC-DFT methods, see for example, Ref. 12. In general, they have not been matched with the short-range correlation functionals (in LC-DFT methods, conventional, i.e., full-range, correlation functionals are used), so their use in RS MC-DFT is not straightforward.

Gradient corrections substantially increased the accuracy of RS MC-DFT, which also manifested in much lower sensitivity to changes of the range-separated parameter compared to the local functionals. 18,21 Unfortunately, short-range GGA exchange-correlation functionals still suffer from fractional charge and fractional spin errors, although to a lesser extent than the full-range approximations. 39 Consequently, potential energy surfaces modeled with range-separated multiconfigurational methods will be inaccurate in the stretched-bond regions, even if the wavefunction part accounts for the multireference effects. This deficiency is well illustrated in Figure 2 for dissociation energy curves of the H$_2$ molecule. The curve obtained with the CAS(2,2) wavefunction is improved around the equilibrium geometry by the CAS-srPBE method, as a result of accounting for the short-range correlation energy in the srPBE functional, but CAS-srPBE fails in the dissociation limit due to the fractional spin error. The error is visibly lower, though, than that of the standard PBE functional.

A remedy for the charge and spin errors is the on-top pair density function, available from the LR wavefunction, as an additional variable into the SR functionals. One of the possible routes is to view spin densities as alternative variables, $\rho_{\alpha/\beta}^{alt}$, in the spin DFT 7 and express them by charge density and the on-top pair density functions as 31

$$
\rho_{\alpha/\beta}^{alt}(\mathbf{r}) = \rho^c(\mathbf{r}) \left( 1 \pm \sqrt{1 - \frac{2\Pi(\mathbf{r})}{\rho^c(\mathbf{r})^2}} \right),
$$

where $\Pi(\mathbf{r})$ is the on-top pair density function, see Equation (27), equal to the electron pair density function at the electron coalescence point. In Figure 2 reduction of the static correlation error (fractional spin error) achieved by employing the alternative densities is visible for the H$_2$ molecule. Replacing the conventional spin densities in the srPBE functional 21 by the auxiliary ones leads to the accurate dissociation limit.

![Figure 2](image-url)
As it has been mentioned, the on-top pair density emerges in the large-μ asymptotic expansion of the SR correlation energy functional.\textsuperscript{13,30} In particular, the first two terms, quadratic and cubic in \( \mu^{-1} \), depend on the correlated on-top pair density corresponding to Coulomb electron interaction. This feature can be exploited to develop new approximations to the short-range correlation functionals either based on the standard definition, Equation (25), or using the alternative formulation.\textsuperscript{30,41}

\[
E_{\text{c,md}}^{\text{SR}}[\rho] = E_{\text{c,md}}^{\text{LR}}[\rho] - \left\langle \Psi_{\text{c,md}}^{\text{LR}}[\rho] \right| \left( \hat{T} + \hat{V}_{\text{ne}} + \hat{V}_{\text{ee}} \right) \left| \Psi_{\text{c,md}}^{\text{LR}}[\rho] \right\rangle,
\]  

where the multiconfigurational long-range wavefunction \( \Psi_{\text{c,md}}^{\text{LR}}[\rho] \) minimizes the energy \( \left\langle \Psi \right| \hat{T} + \hat{V}_{\text{ne}} + \hat{V}_{\text{ee}} \left| \Psi \right\rangle \) under the \( \rho_{\text{on-top}} = \rho \) condition, see Equation (7). Such a definition, based on a multisdeterminantal (md) wavefunction, offers an important advantage over its standard, KS-wavefunction based counterpart given in Equation (25). Namely, the total energy corresponding to Equation (30) simply reads

\[
E_0 = \left\langle \Psi_{\text{c,md}}^{\text{LR}} \right| \hat{T} + \hat{V}_{\text{ne}} + \hat{V}_{\text{ee}} \left| \Psi_{\text{c,md}}^{\text{LR}} \right\rangle + E_{\text{c,md}}^{\text{SR}}[\rho_{\text{on-top}}],
\]  

\( \Psi_{\text{c,md}}^{\text{LR}} \) satisfies the eigenequation in Equation (10), so the exchange is fully absorbed in the wavefunction part and the density functional is responsible only for a small fraction of the correlation. This reduces both the spin- and charge fractional errors. The local approximation to \( E_{\text{c,md}}^{\text{SR}}[\rho] \) was formulated by Toulouse et al.\textsuperscript{41} To go beyond the local model, Ferté et al.\textsuperscript{42} proposed an interpolation scheme based on the known large-μ asymptotics of the SR correlation functional. In this approach, one interpolates between the \( \mu \to 0 \) limit, at which \( E_{\text{c,md}}^{\text{SR}}[\rho] \) reduces to the conventional full-range functional, and the large-μ limit. Importantly, in this way the correlation functional could incorporate the on-top function corresponding to the underlying wavefunction \( \Psi_{\text{c,md}}^{\text{LR}} \), while previous local approximations relied on the on-top function of the HEG. The first nonvanishing term in the large-μ limit is linear in \( \mu^{-3} \).\textsuperscript{41} This stays in contrast to the correlation function as defined in Equation (25) that decays less rapidly, that is, as \( \mu^{-2} \), this is understandable since it describes a greater portion of the correlation energy than \( E_{\text{c,md}}^{\text{SR}} \).

The interpolated on-top pair density dependent functional introduced by Ferté et al.\textsuperscript{42} is connected with the PBE correlation functional at \( \mu = 0 \). Unlike the local approximation to \( E_{\text{c,md}}^{\text{SR}}[\rho] \), the gradient-corrected PBE-based functional does not overestimate the correlation energy. The drawback of using the multideterminantal correlation functional shown in Equation (31) is that self-consistent calculation of the ground state energy must proceed via the computationally costly optimized effective potential (OEP) procedure.\textsuperscript{43} Alternatively, the correlation energy can be computed from the wavefunction a posteriori, that is, after solving the variational problem, Equation (9), with a SR correlation functional approximated using Equation (25), and employing the resulting wavefunction \( \Psi_{\text{c,md}}^{\text{LR}} \) to compute the ground state energy from Equation (31).\textsuperscript{42}

Short-range functionals developed for the electron interaction partitioning based on the error function, which has dominated implementations of the RS MC-DFT methods, are collected in Table 1.

Finally, efforts to develop relativistic short-range functionals suitable for the relativistic formulation of RS MC-DFT\textsuperscript{44} are worth mentioning. The design of the relativistic SR exchange functional in the local approximation was the first step,\textsuperscript{44} very recently followed by its correlation counterpart.\textsuperscript{45} Applications of the heavy ions have shown that the local exchange approximation is inaccurate and possible improvements may be achieved by including density gradient corrections or the on-top exchange pair density as auxiliary variables.\textsuperscript{46}

2.4 Wavefunction theories in RS MC-DFT

The exact wavefunction is characterized by sharp features at short interparticle distances. At the electron coalescence point, \( r_{12} \to 0 \), the Coulomb electron interaction diverges and wavefunction develops the electron cusp, see Figure 1. The electron cusp condition\textsuperscript{48} imposes that the wavefunction is linear in \( r_{12} \) in the short-distance. In RS MC-DFT the Coulomb interaction is replaced with the long-range operator finite at \( r_{12} \to 0 \) (Equation (4)) which removes the cusp in the resulting LR wavefunction, see Equation (10). In particular, if the error function is used, Equation (20), the LR wavefunction is linear in \( r_{12}^2 \) around the coalescence point, cf. Figure 1.\textsuperscript{27,41} The range-separated description remains accurate, since correlation effects at short interelectron separations are recovered by the short-range density functional.
Consequently, the LR wavefunction can be correctly represented with lower-level approximations than in the case of electron interaction acting at the full range. As confirmed in actual implementations, the multiconfigurational or configuration interaction wavefunctions used within RS MC-DFT may be applied with shorter expansions in the single determinantal space compared to the full-range ab initio models.\(^1\)\(^9\),\(^4\)\(^2\) This feature is illustrated in Figure 3 which presents the convergence of the Be dimer energy with the number of determinants included in the wavefunction for the selected CI method (results obtained with the Coulomb and long-range erf operators are marked as “CIPSI” and “lrCIPSI + srPBE,” respectively).\(^4\)\(^2\) If the CASSCF approach is employed, the size of the active space can be considerably smaller than in the case of Coulomb electron interaction. The benefit for the coupled cluster theories adapted to the long-range variant is that the double excitation level often provides sufficient accuracy and costly triples can be avoided.\(^2\)\(^1\),\(^4\)\(^9\),\(^5\)\(^0\) The efficiency of the WFT is achieved on condition of a judicious choice of the range separation parameter, that is, it should be small enough so that the short-range correlation effects are removed from the wavefunction part.

A proper description of the dynamic electron correlation requires accounting for the electron cusp, which in the WFT methods involves large basis sets. By contrast, conventional density functional approximations require much shorter basis set expansions to represent electron density with the Kohn–Sham orbitals. Although the RS MC-DFT approaches do not replicate the impressive convergence behavior of full-range DFT, numerous studies have demonstrated that they benefit from removing singularity in the modified electron interaction operator and incorporation of the short-range exchange-correlation functionals. More specifically, when applied with the typical values of the range-separation parameter RS methods gain a clear advantage over the underlying ab initio models in terms of convergence of the energy with the basis set size. An illustrative comparison of the convergence behavior of range-separated methods (closed symbols) and their full-range variants (open symbols) is shown in Figure 4 (adapted from Ref. 51).

| Type/name | Variables\(^a\) | Description | Reference |
|-----------|-----------------|-------------|-----------|
| Local/srLDA | \(\rho\) | Local approximation for \(E_{SR}^{\rho}\) | 13,14 |
| Local/srLSDA | \(\rho, \zeta\) | Local spin-density approximation for \(E_{SR}^{\rho,\zeta}\) | 28 |
| GGA/srPBE | \(\rho, \nabla \rho\) | PBE-based model for \(E_{SR}^{\rho}\) | 20 |
| GGA/srPBE(GWS) | \(\rho, \zeta, \nabla \rho\) | PBE-like \(E_{SR}^{\rho,\zeta}\), PBE limit recovered at \(\mu = 0\) | 18,21 |
| GGA/PBEHSERI | \(\rho, \nabla \rho\) | Modified PBE for \(E_{SR}^{\rho}\) and PBE-srLDA interpolation for \(E_{SR}^{\rho}\) | 24 |
| Meta-GGA/srTPSS | \(\rho, \zeta, \nabla \rho, \tau\) | TPSS-like approximation for \(E_{SR}^{\rho,\zeta}\) | 35 |
| Local/md(srLDA) | \(\rho\) | Local approximation to \(E_{SR}^{\rho,md}\), see Equations (30) and (31) | 47 |
| Beyond local/md (srPBEon-top) | \(\rho, \nabla \rho, \Pi_{\psiLR}\) | On-top pair density dependent approximation for \(E_{SR}^{\rho,md}\), see Equations (30) and (31) | 42 |

\(^a\)The spin polarizability is denoted by \(\zeta\), \(\tau\) is the kinetic energy density, and \(\Pi_{\psiLR}\) indicates the on-top pair density function, see Equation (27), evaluated from a LR multiconfigurational wavefunction.

FIGURE 3 Convergence of the standard CIPSI and lrCIPSI + srPBE total variational energies (measured with respect to their respective FCI limits) as a function of the number of selected determinants for the Be\(_2\) molecule (internuclear distance of 3 bohr) with aug-cc-pCVTZ basis set. All electrons are correlated. The range-separation parameter used is \(\mu = 0.5\) bohr\(^{-1}\). Reprinted with permission from Ref. 42; copyright 2019 AIP Publishing

Consequently, the LR wavefunction can be correctly represented with lower-level approximations than in the case of electron interaction acting at the full range.
In essence, introduction of DFT into wavefunction theories via range separation of the electron interaction allows for capturing short-range correlation in an efficient manner, and at the same time improves the convergence with the basis set size of the chosen ab initio model.

Similar to standard ab initio methods, their LR counterparts can be divided into single- or multireference approaches. In the case of the former, first the optimal single determinantal wavefunction \( \Phi^{LR} \) is found in the SCF way for the LR Hamiltonian

\[
\Phi^{LR} = \arg\min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}^{LR} | \Phi \rangle + E_{\text{SR}}^{\text{Hxc}}(\rho_\Phi) \right\}. \tag{32}
\]

This step is common for all range-separated hybrids (RSH) methods. The RSH energy

\[
E_{\text{RSH}} = \left\langle \Phi^{LR} | \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}^{LR} | \Phi^{LR} \right\rangle + E_{\text{SR}}^{\text{Hxc}}(\rho_{\Phi^{LR}}) \tag{33}
\]

includes the exact long-range exchange energy, but misses the (long-range) correlation, \( E_c^{LR} \). The latter is recovered from the post-SCF WFT and the final ground state energy follows from

\[
E_0 = E_{\text{RSH}} + E_c^{LR} \left[ \Phi^{LR} \right]. \tag{34}
\]

In principle, the ground state energy could be obtained in a self-consistent way, by minimizing the expression in Equation (34) with respect to the electron density, in agreement with the variational formulation of the RS MC-DFT approach, cf. Equation (7). The effect of self-consistency on the energy is small and in most implementations of the RSH methods, the \( E_c^{LR} \) is added on top of the RSH energy. Several ways of obtaining \( E_c^{LR} \) have been explored in the literature. First was the nonlinear Rayleigh–Schrödinger perturbation theory, which in the second order yields the correlation correction of the same form as that of MP2—the only difference lies in the two-electron integrals, which involve the long-range interaction \( \hat{v}_{ee}^{LR}(r_{12}) \). At the same time, single reference (or RSH-based) range-separated methods employing the coupled cluster (CC) approximations were introduced. Any CC approach can be adapted to the RS MC-DFT framework in a straightforward manner, by simply replacing the Hartree–Fock determinant used as a reference WF in standard CC methods with \( \Phi^{LR} \), computing two-electron integrals with the \( \hat{v}_{ee}^{LR}(r_{12}) \) operator, and including a short-range potential, Equation (12), in a one-electron Hamiltonian. Finally, in Refs. 55, 56, it has been shown how to derive a long-range correlation energy from the formally exact adiabatic-connection fluctuation–dissipation density-functional theory based on range separation. The resulting approximations are based on the random phase approximation (RPA) with the long-range electron interaction, and the RSH + RPA variants have been widely used since then, cf. Sections 3 and 4.
The RSH + $E^{LR}_c$ methods should be distinguished from the long-range corrected (LC) hybrid density functional methods (also known as range-separated hybrid exchange, RSHX) of Hirao et al. Although LC-DFT approaches also employ electron interaction separation, they are not multiconfigurational. The range separation is employed only in the exchange energy functional, while the total correlation energy is described by a standard correlation density functional. The LC-DFT approximations, the subject of the recent reviews, will not be discussed in this work.

Returning to RS MC-DFT, apart from single-reference RSH approaches, truly multiconfigurational methods have been developed. These variants of RS MC-DFT are often referred to as MC-srDFT. They employ multideterminantal (md) wavefunctions $\Psi_{md}$ obtained by minimizing the functional with the long-range electron interaction and the short-range Hartree-exchange-correlation density functional

$$\Psi_{md}^{LR} = \arg\min_{\Psi_{md}} \left\{ \langle \Psi_{md} | \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}^{LR} | \Psi_{md} \rangle + E^{SR}_{Hxc} [\rho_{\Psi_{md}}] \right\}.$$  \(35\)

To describe nearly degenerate or strongly correlated systems, the MCSCF, CASSCF, RASSCF, or CI wavefunction models have been used in Equation (35), cf. for example Refs. 11, 24, 42, 60 and discussion in Sections 3–5. Multideterminantal wavefunction models are typically deficient in describing dynamic correlation of the long-range nature, and thus not suitable for predicting molecular interactions. This can be cured by adding the long-range correlation derived from multireference second-order perturbation method or by applying the long-range multideterminantal adiabatic connection formalism. The total energy is then obtained as a sum

$$E_0 = \langle \Psi_{md}^{LR} | \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}^{LR} | \Psi_{md}^{LR} \rangle + E^{SR}_{Hxc} [\rho_{\Psi_{md}^{LR}}] + E^{LR}_c [\Psi_{md}^{LR}].$$  \(36\)

The computational cost of the wavefunction component of RS MC-DFT, already reduced due to shorter expansion of the wavefunction or lower excitation level of the determinants, can be further decreased by introduction of local techniques known from other ab initio methods. The local-correlation and density fitting computational procedures have been successfully implemented in the framework of RS MC-DFT.

The RS MC-DFT approach was also formulated without invoking the many-electron wavefunction. Instead, reduced quantities such as one-electron reduced density matrix, Green's function, or matrix product states in the framework of density matrix renormalization group (DMRG) theory have been used.

The RS MC-DFT theory provides a general framework for combining practically any ab initio method with DFT via range-separation. Several implementations are available in widely used quantum chemistry packages. The rigorous foundation of the RS methods assures that electron interaction is not doubly counted. This feature is worth emphasizing when comparing RS MC-DFT with other approaches employing DFT to efficiently treat dynamic correlation within a WFT formalism. For recent reviews of the combined DFT-WFT methods see Refs. 59, 74, 75.

In the rest of the paper we adhere to the RS MC-DFT notation to refer to a general theory and relevant approximations. We also use the WFT-srDFT abbreviation, where WFT is replaced by the actual ab initio method (MP2, CC, RPA, CAS, etc.), and srDFT indicates the SR functional (e.g., srLDA or srPBE). Occasionally, the RSH + WFT notation is invoked to stress a single-reference character of a given method (see Table 2). Notice that RSH methods, defined by Equations (33) and (34), for example a combination of the long-range MP2 with SR functionals, may be referred to either as MP2-srDFT or RSH + MP2, both forms are used in the literature. Naming conventions and acronyms of the RS MC-DFT methods are collected in Table 2.

### 3 | GROUND STATE APPLICATIONS

#### 3.1 | Dissociation of covalent bond

Molecular dissociation energy curves are standard benchmarks for the RS MC-DFT methods. The H$_2$ molecule is often used as a paradigm system, since the accurate prediction of its potential energy curve requires accounting for both dynamical correlation in the equilibrium and for static correlation in the dissociation limit. In contrast to equilibrium geometries, the dissociation limit poses a serious challenge for local and gradient-corrected SR functionals, which suffer from a sizable fractional-spin error (cf. Figure 2). When typical $\mu$ values between 0.3 and 0.5 bohr$^{-1}$ are employed, the
DFT functional contributes also in the regime where static correlation effects dominate. This becomes a major source of errors even for MC-srDFT schemes which incorporate multideterminantal wavefunctions, cf. Equation (35).\cite{11,19,24,43} For example, Pollet et al.\cite{19} have shown that combination of multireference configuration interaction with a local short-range functional cannot recover more than 75% of the correlation energy in the stretched H₂ molecule ($R_{H-H} = 3.0$ bohr) at $\mu = 0.45$ bohr$^{-1}$ even with a large configuration space.

The RSH methods based on different RPA flavors are in general not capable of handling strongly correlated systems and fail at dissociation.\cite{76,77,78} In this context it is worth to mention the RSH built upon singlet-pair coupled cluster CCD₀ model\cite{38} studied by Garza et al.\cite{37} The proposed LC-CCD₀-DFT approximations rely on same-spin correlation from meta-GGA functionals\cite{36,83} and describe long-range correlation with direct RPA (dRPA). On the example of BH and N₂ molecules, the authors demonstrated that dRPA effectively reduces the wrong high-energy dissociation limit that plagues the base CCD₀ approach.

To date, two strategies have been proposed to remove the fractional-spin error from the existing short-range density functional approximations. The first one is the use of alternative spin densities, see Equation (29), as variables of the spin functionals.\cite{7,31} To incorporate the on-top pair density function into the existing short-range functionals. In their work on RS MC-DFT based on pair coupled cluster doubles (pCCD) ansatz, Garza et al.\cite{37} applied the auxiliary spin densities together with srLDA\cite{28} and srPBE\cite{57,84} models. The resulting pCCD-srDFT methods (originally named LC-pCCD-DFT) gave correct potential energy curves for H₂, linear hydrogen chains and symmetric dissociation of water both in the equilibrium and in the dissociation limit. The erroneous pCCD-srDFT behavior when breaking multiple bonds, illustrated for formaldehyde and N₂, results from the limitation of pCCD itself. The use of auxiliary spin densities as arguments of the srPBE functional\cite{18} has also been explored in the work of Hapka et al.\cite{62} The authors devised a MC-srDFT formalism corrected for long-range dynamic correlation and applied it with CASSCF wavefunctions. Both the shape of the potential energy curves and dissociation energies of H₂, N₂, H₂O, and F₂ molecules confirmed that the use of alternative spin densities improves the accuracy of MC-srDFT. For instance, the reported dissociation energy of

### Table 2: Acronyms for RS MC-DFT methods discussed in the overview

| Acronym | WFT model | Original notation | Reference |
|---------|-----------|-------------------|-----------|
| Single-determinantal WFT methods |
| MP2-srDFT | MP2 | RSH + MP2 | 52 |
| RPA-srDFT | RPAX | RSH + RPAX | 55 |
| dRPA | LC-ωLDA-dRPA | 76 |
| JMP2 | LC-ωLDA-JMP2 | 77 |
| SOSEX | LC-ωLDA-SOSEX | 78 |
| RPAX-SO2 | RSH + RPAX-SO2 | 79 |
| GF2-srDFT | GF2 | srVWN5-lrGF2 | 26 |
| CC-srDFT | CCSD, CCSD(T) | sr-DFT/lr-CC | 18 |
| pCCD | LC-pCCD-DFT | 37 |
| CCD₀ | LC-CCD₀-DFT | 38 |
| Multideterminantal WFT methods |
| CI-srDFT | MRCI | DFT-CI | 11 |
| RAS-CI | RAS-srDFT | 60 |
| CIPSI | lrCIPSI+srPBE | 42 |
| MCSCF-srDFT | CASSCF | 24,80 |
| NEVPT2-srDFT | NEVPT2 | 61 |
| lrAC₀-srDFT | CASSCF | lrAC₀-postCAS | 62 |
| APSG-srDFT | APSG | lrAPSG | 81 |
| DMRG-srDFT | DMRG | 66 |

**Note:** The column marked as “original notation” refers to the acronym used in the original work, when different from the conventions adopted in this work.
the nitrogen molecule was equal to 9.77 eV (at $\mu = 0.5$ bohr$^{-1}$), which is close to the accurate value of 9.91 eV$^{85}$ and stays in contrast to 15.73 eV obtained from MCSCF-srPBE calculations employing unmodified electron density as input of the SR functional.$^{24}$

The second approach to eliminate fractional-spin error from srDFT models follows from the alternative decomposition of the short-range energy proposed by Toulouse et al.$^{41}$ Recall that the partitioning of Equation (30) changes the demand put on the short-range correlation functional. In contrast to the conventional MC-srDFT energy expression, cf. Equation (14), the alternative definition of the ground state energy absorbs the entire exchange in the wavefunction part, cf. Equation (31). Consequently, the correlation functional does not need to compensate for the errors in the approximate exchange functional. First calculations based on the alternative separation were performed by Stoyanova et al.$^{43}$ and relied on the local approximation to the md correlation functional.$^{41}$ The MCSCF-based range-separated models introduced in Ref. 43, including a self-consistent formulation of Equation (31) via OEP, showed improvement upon standard MCSCF-srLDA in terms of both the relative shape of the dissociation curves and dissociation energies. For $H_2$ the error in the dissociation energy was reduced from 27% in MCSCF-srLDA to 7%, while for $N_2$ the respective values were 63% and 20%. Nevertheless, this effect relies partially on error compensation, since within the typical range of $\mu$ values the local $E^\text{SR}_{c,\text{md}}$ functional proved to systematically overestimate the correlation energies. Moreover, for $H_2$, $N_2$, and symmetric dissociation of water unphysical bumps in the intermediate region of dissociation energy curves occurred.

A recent progress in the development of md correlation energy functionals led to a new gradient-corrected on-top pair density functional, see Section 2.3 and Ref. 42. The total energy obtained from Equation (31) by combining the functional with long-range selected CI wavefunction gave excellent description of $H_2$ and $Li_2$ potential energy curves, clearly surpassing the accuracy of the method relying on the local approximation. Note that in the lithium dimer both dynamic and static correlation effects contribute to a similar extent at all interatomic distances, making it a good test for MC-srDFT based on multireference wavefunctions.$^{11,19,43,86}$ similar to heteroatomic BH or LiH$^{19,38,65}$ The results for model systems obtained with alternative spin densities$^{37,62}$ and multideterminantal correlation functionals$^{42,87}$ confirm that the self-interaction error may be effectively minimized with the use of the on-top pair density.

### 3.2 Thermochemistry and kinetics

Description of chemical transformations with range-separated methods has been attempted starting from the study of Ángyán and Gerber$^{52}$ which adopted the ideas of Savin and his coworkers by mixing srDFT with long-range HF exchange. The first application of RSH + WFT, see Equation (34), to thermochemical properties was presented by Goll et al.$^{35}$ who analyzed the performance of coupled-cluster-srDFT hybrids. For atomization energies of the G2 dataset$^{23}$ the range-separated methods proved superior to both full-range DFT and CCSD(T). In the case of CCSD(T)-srPBE the mean absolute error (MAE) amounted to 5.0 kcal/mol, which meant reduction by a factor of three compared to full-range PBE and by a factor of two with respect to CCSD(T). Going from the srPBE to srTPSS lowered the errors even further (MAE = 2.9 kcal/mol). This is in contrast to CC-srDFT results for noncovalent interactions$^{18,21}$ and dipole moments,$^{49}$ where a weaker dependence on the short-range functional was observed. The omission of triple excitations, that is, coupling to CCSD instead of CCSD(T), had only minor effect on the accuracy increasing the MAE value on average by 0.2 kcal/mol, regardless of the underlying functional.

The CC-srDFT hybrids of Ref. 35 did not offer any advantage over the parent methods in calculations of ionization potentials (IPs), electron affinities (EAs), and proton affinities from the G2 dataset, for example, the CCSD(T)-srPBE scheme predicted IPs with MAE of 0.15 eV which was identical to the PBE value and inferior to CCSD(T) result (MAE = 0.09 eV). A similar level of accuracy for IP and EA calculations was reported using other RSH approaches. For comparison, mean average errors from dRPA-srPBE calculations$^{78}$ of IPs on the same dataset amounted to 0.21 eV. A combination of srLDA and second-order Green’s function theory (GF2) developed by Kananenka and Zgid$^{26}$ was able to predict IPs of atoms and small molecules with a mean error of 0.24 eV. As indicated by the study of Śmiga et al.$^{88}$ both the range-separated MP2 hybrid and its self-consistent RS-OEP2 formulation provide a similar level of accuracy when applied with $\mu = 1.0$. The self-consistent OEP formulation of RPA-srDFT introduced by Hesselmann and Ángyán$^{54}$ provided IPs which deviated by no more than 0.27 eV from the CCSD(T) reference for $\mu > 0.75$ bohr$^{-1}$.

Another group of RSH + WFT approaches, carefully characterized for molecular thermochemistry and kinetics, combines DFT with approximate long-range correlation energy, cf. Equation (34) from ring coupled-cluster doubles formulation of RPA.$^{89}$ The methods introduced by Scuseria and coworkers$^{76–78,90,91}$ were tested on a range of properties including
atomization energies from the G2 set, atomization energies and barrier heights from the AE6BH6 test set of Refs. 92, 93, the hydrogen transfer and nonhydrogen transfer barrier heights from the HTBH38/04 and NHTBH38/04 test sets, respectively. Best overall results, with MAE in the 1.0–2.7 kcal/mol range, were achieved with the dRPA-srPBE approach (denoted LC-ωPBE-dRPA in the original work) in which \( \mu \) was set to 1.15 bohr\(^{-1} \) and the long-range RPA correlation was scaled by a factor of 1.63 to account for the self-interaction error.\(^{76,78} \) Slightly larger errors were obtained with the second-order screened exchange (SOSEX) variant of RPA in which the one-electron self-interaction error is explicitly removed.\(^ {78,91} \) Janesko and Scuseria have also explored a RSH flavor of the “Coulomb-only” MP2 approach (without accounting for exchange integrals), referred to as JMP2. With srLDA as the underlying functional and no additional scaling of long-range correlation, the method performed similar to dRPA-srLDA on the aforementioned test sets, and gave slightly better result compared to the latter for activation and reaction enthalpies of 1,3-dipolar cycloadditions.\(^ {97} \)

A study of Mussard et al.\(^ {98,99} \) compared the accuracy of MP2-srDFT and RPA-srDFT for atomization energies from the AE49 dataset\(^ {100} \) and forward/reverse reaction barrier heights from the DBH24/08 dataset.\(^ {101} \) The RPAx-SO2-srDFT method with exchange, based on the Szabo and Ostlund’s formulation,\(^ {102} \) combined with srPBE\(^ {21} \) was identified as one of the best-performing RPA schemes (the RPA correlation was not scaled). Although both range-separated MP2 and RPAx-SO2 methods yielded similar MAE values, that is, between 4 and 5 kcal/mol on atomization energies and ca. 3 kcal/mol on barrier heights, the RPAx-SO2 approach offered better accuracy for noncovalent interactions.\(^ {79} \) Another advantage of the Szabo-Ostlund’s-based variant is the lack of triplet instabilities,\(^ {79,103} \) since only singlet excitations are included in this approximation. For comparison of RSH and LC-DFT methods performance on benchmark datasets of atomization energies and barrier heights, see Figure 5.

Several chemical reactions involving strong electron correlation effects have been investigated with MC-srDFT methods. Sharkas et al.\(^ {86} \) verified the accuracy of range-separated MCSCF for two 1,3-cycloadditions from the O3ADD6 dataset of Ref. 104. The set contains reactions of ozone either with ethylene or with acetylene, each characterized by three stationary points: the initial van der Waals complex, the transition state and the cycloadduct. Although the MCSCF-srPBE method clearly outperformed MCSCF, the MAE value of the latter was as large as 11.5 kcal/mol compared to 4.27 kcal/mol of the former, the relative errors in description of the van der Waals systems and transition states exceeded 50%. This was attributed to the lack of long-range dispersion forces and limitations of the srPBE model.

Hedegård et al.\(^ {66} \) applied DMRG-srPBE to study ligand-dissociation reactions in two complexes of Cu and Pt atoms from the WCCR10 benchmark set\(^ {105} \) (system-independent \( \mu = 0.4 \) bohr\(^{-1} \) value was applied). The authors demonstrated that the effective recovery of dynamic correlation by the short-range functional makes DMRG-srDFT results

![Figure 5](image-url)

**Figure 5** Mean absolute errors (MAE in kcal/mol) in AE6, G2 and AE49 atomization energies, BH6 and HTBH38/04 hydrogen transfer barrier heights, NHTBH38/04 nonhydrogen transfer barrier heights and DBH24 barrier heights. LC-LDA and LC-PBE denote results from LC-ωLDA and LC-ωPBE calculations presented in Refs. 78 and 84, respectively. The dRPA*-srLDA label stands for LC-ωLDA + dRPA calculations of Ref. 78, whereas dRPA*-srPBE and SOSEX*-srPBE denote LC-ωPBE + dRPA and LC-ωPBE + SOSEX results of Ref. 91. Methods marked with a star include scaling of the long-range RPA correlation contribution. Results marked as dRPA-srPBE, RPAx-SO2-srPBE, and MP2-srPBE refer to RSH + dRPA, RSH + RPAx-SO2, and RSH + MP2 calculations from Ref. 98.
more stable with the size of the active space compared to pure DMRG calculations. Another relevant observation was the strong dependence of ligand-binding energies from DMRG-srDFT calculations on the underlying DFT model. For the Cu-complex dissociation energies obtained with srPBE of Ref. 24 spanned the 216.5–225.1 kJ/mol range, depending on the size of the active space, which perfectly matched the 226.7 kcal/mol reference value. Yet, coupling the DMRG wavefunction to the srPBE functional of Goll et al.18 deteriorated the results by approximately 20 kJ/mol. The opposite effect was observed for the Pt-complex for which srPBE of Ref. 18 led to significantly better agreement with the experiment.

3.3 Energy gradients: geometry optimization, dipole moments

Analytical energy gradients were derived and implemented for both MP2106 and RPA-based107 RSH approaches. The first development was presented by Chabbal et al.106 who validated MP2-srDFT on the Truhlar dataset108 of noncovalent dimers. Overall, the mixed MP2 method leads to more accurate geometries compared to the ones obtained with plain LDA or PBE functionals. The largest differences were observed for charge-transfer (CT) complexes which are challenging for nonhybrid functionals due to significant charge delocalization. For example, the MAE in intermonomer distances was reduced from 35.4 pm in PBE to 8.2 pm in MP2-srPBE. As shown by Mussard et al.,107 even finer description of the CT dimers may be achieved with range-separated RPA-variants (MAE values ranging from 2.3 pm to 2.5 pm depending on the employed RPA model). Moving beyond weak interactions, Chabbal et al.109 applied MP2-srDFT to the problem of bond length alternation of conjugated polymers. The RSH approach performed exceptionally well for polyyacetylene closely following the benchmark CCSD(T) results. Significantly larger deviations from the reference were observed for two conformations of polymethineimine. In line with other properties studied in the RSH framework, geometries from both MP2 and RPA hybrids exhibited only weak dependence on the basis set size.

Fromager et al.25 investigated the influence of the \( \mu \) parameter on the equilibrium geometries of \( \theta^6 \) actinide compounds calculated with the CAS-srPBE method. For heavy element systems in which static correlation effects are small (ThO\(_2\), PaO\(_2^+\), UO\(_2^{2+}\), UN\(_2\), and CUO) the MC hybrid with the optimal \( \mu \) values between 0.3 and 0.4 bohr\(^{-1}\) remained in close agreement with standard DFT and CCSD(T) results (maximal deviation in bond lengths with respect to CCSD(T) did not exceed 3 pm). In the case of the neptunyl (VII) ion, NpO\(_2^{3+}\), which features pronounced static correlation, the CAS-srDFT methods favored bent equilibrium geometry while WFT-based results predict a linear structure. This discrepancy was attributed to the deficiencies in the short-range LDA and PBE functionals.

An interesting application of RSH methods for ground-state properties are dipole moment calculations of the group-11 transition metal hydrides and halides performed by Goll et al.49 In agreement with previous reports in the literature,110,111 full-range DFT performed poorly for these system—the MAE values of CuX, AgX, and AuX (X = H, F, Cl, Br, I) dipole moments ranged from 1.01 D for LDA to 0.48 D for B3LYP. Combining CCSD via range-separation with either srLDA or srPBE functionals reduced the mean errors by one order of magnitude. Addition of perturbative triples practically did not change the results with MAE of 0.07 D for both functionals.

3.4 Basis-set incompleteness

A separate development worth mentioning in the context of RS MC-DFT are density-based corrections for basis-set incompleteness of the WFT methods. The formalism established by Giner et al.112 employs correlation energy functionals with multideterminantal reference to recover solely correlation effects outside of a given basis set. Contrary to range-separation in RS MC-DFT, the correction relies on splitting of the electron–electron interaction directly in a given one-electron basis set. To date, the density-based complete basis set (CBS) corrections have been combined with several WFT models in computations of total energies and IPs,112,113 excitation energies,113 atomization energies, and potential energy curves of strongly correlated systems.87

Let us provide the reader with an overview of Section 3, which focused on applications posing a challenge to RS MC-DFT methods. At present, dissociation of covalent bonds may be accurately described using short-range functionals depending on the on-top pair density (either explicitly42 or through the use of alternative spin densities37,62). Regarding molecular thermochemistry and kinetics, best-performing variants of RSH match the accuracy of generalized Kohn–Sham (i.e., global hybrid functionals and LC-DFT).35,91 A true gain from turning to range-separated schemes is expected for systems which require multiconfigurational treatment. Although first results obtained with CASSCF86 and DMRG66
wavefunctions are encouraging, they have also pointed to the need for proper representation of dispersion forces and careful selection of the short-range functional.

4 | NONCOVALENT INTERACTIONS

4.1 | Model systems: rare-gas dimers, alkali-metal dimers, metallophilic interactions

The introduction of RSH + $E^{LR}_{\text{loc}}$ methods, cf. Equations (33) and (34), was motivated mainly by their potential application to noncovalent interactions. While semilocal density functional approximations cannot capture long-range dynamic correlation effects, that is, dispersion forces, the range-separated treatment assigns this task to the wavefunction method. In this way, RSH can be considered as extension of DFT to weak intermolecular interactions. At the same time, removal of the electron cusp from the long-range problem relaxes the requirement for large basis sets and long configuration expansions (or high excitation terms) on the ab initio side.

The idea of employing range-separation of the Coulomb operator for calculation of van der Waals forces within the Kohn–Sham framework was first explored by Kohn et al. The authors derived the expression for the long-range correlation contribution to the energy using the adiabatic connection–fluctuation–dissipation theorem and applied it to describe asymptotic interaction in He–He and H–He diatoms. The emergence of short-range functionals several years later gave rise to the MP2-srDFT and CC-srDFT hybrids, soon followed by range-separated RPA models.

The established benchmark for methods targeting accurate description of van der Waals complexes are interaction energy curves of rare gas dimers. In the work introducing the MP2-srDFT approach, Ángyán and coworkers presented encouraging results obtained with the srLDA approximation and a single value of the range-separation parameter of $\mu = 0.5$ bohr$^{-1}$. For Ne$_2$, Ar$_2$, and Kr$_2$ the hybrid performed on a par with or better than CCSD(T) (in the same basis set), both in terms of the predicted dissociation energies and positions of the minima. Larger discrepancies occurred for He$_2$, where the MP2-srLDA curve was too repulsive deviating by almost 40% from the benchmark dissociation energy. As expected, at large intermolecular distances the hybrid matched pure MP2—the dispersion energy shows the correct asymptotic behavior, and is reproduced only at the uncoupled level of theory, that is, assuming nonrelaxed polarizabilities of the monomers. This was clearly reflected in systematic overestimation of the $C_6$ coefficients from MP2-srLDA calculations. The study also revealed that the short-range DFT component lowers the basis set superposition error compared to standard MP2 or CCSD(T). These observations were confirmed by Gerber and Ángyán in a more detailed analysis, which included also mixed dimers and results from LDA, PBE, and TPSS calculations. The improved basis set convergence of MP2-srDFT with respect to pure ab initio approaches was pointed out in both studies. A later work of Franck et al. demonstrated that the long-range MP2 correlation contribution converges exponentially with the cardinal number $X$, which is in contrast to the $X^{-3}$ convergence behavior of the standard full-range MP2 (for basis set convergence of MP2 versus MP2-srDFT for rare gas dimers see also Figure 4).

Homo- and heterodimers composed of He–Xe rare gas atoms were chosen as the first test systems for the CC-srDFT methods developed by Goll et al. The coupling between srPBE and CCSD(T) leads to excellent results—with augmented Dunning basis sets of a quadrupole-zeta quality mean deviations from the experimental data amounted to 0.04 Å for the equilibrium bond lengths, 14 $\mu E_h$ for the dissociation energies and 3.0 cm$^{-1}$ for the harmonic frequencies. Similar accuracy was already obtained with the triple-zeta basis set. In fact, CCSD(T)-srPBE in the triple-zeta basis was three times as accurate as CCSD(T) in the quadrupole-zeta basis when comparing dissociation energies. An important observation was that the short-range functional makes the perturbative triples correction redundant, that is, the CCSD-srPBE model practically reproduced range-separated CCSD(T) results. Substituting srLDA for srPBE did not affect equilibrium distances and harmonic frequencies, but had a visible effect on dissociation energies increasing the mean error by ca. 20 $\mu E_h$. Although the MP2-srPBE approach performed worse than the CC hybrids, it still matched the accuracy of full-range CCSD(T) results obtained with larger, quadrupole-zeta basis set. In particular, the MAE value of dissociation energies from range-separated MP2 reached 56 $\mu E_h$ in the triple-zeta basis, while the respective MAE from pure CCSD(T) in the quadrupole-zeta basis was 58 $\mu E_h$.

The CCSD(T)-srDFT method was generalized to open-shell systems by Goll et al. Results obtained for a group of alkali-metal rare-gas dimers, AmRg (Am = Li-Cs, Rg = Ne-Xe), matched the high level of accuracy attained for rare-gas dimers, being at the same time superior to those obtained with the full-range CCSD(T). As an example, mean error in dissociation energies was as low as 23 $\mu E_h$ with a triple-zeta basis and the result remained virtually unchanged with the basis set of quadrupole zeta quality. The respective error in CCSD-srPBE calculations (in a triple-zeta basis set) had a
larger value of $41 \mu E_h$, which still was closer to the experimental reference than CCSD(T) at the quadrupole-zeta level (MAE value of $64 \mu E_h$). The change of the short-range functional coupled to CC had only a marginal effect on the quality of the potential energy curves.

Rare gas dimers served as initial tests for different range-separated schemes that incorporate long-range RPA correlation. In Ref. 51 Toulouse et al. presented a comprehensive comparison of RSH methods applied to homo- and heteroatomic dimers. In this work, the srPBE functional was coupled either with long-range RPA, MP2 or CCSD(T), the $\mu$ value was set to 0.5 bohr$^{-1}$ and large, aug-cc-pV5Z Dunning basis sets were employed. The RPAx-srPBE method (referred to as RSH + RPAX in the original work) performed nearly identically to MP2-srPBE for equilibrium properties and offered a distinct advantage over the direct RPA scheme in which exchange contributions, present in RPAX, are neglected. Among the tested RSHs, RPAx-srPBE gave best representation of the interaction energy curves at medium and large distances, while CCSD(T)-srPBE systematically overestimated in these regions. (The latter result was in contrast to the findings of Goll et al., which indicated that some CCSD(T)-srPBE interaction energies reported in Ref. 18 were far from convergence with the basis set size.) The mean absolute percentage errors in the van der Waals $C_6$ coefficients of Ref. 51 amounted to 9% for RSH + RPAX and 29% CCSD(T)-srPBE calculations, respectively.

Janesko et al. demonstrated that the RSH approach combining short-range LDA with long-range direct RPA correlation may afford very good description of rare gas dimers, if the long-range correlation is additionally scaled by an empirical factor, $c_{\text{RPA}}$. The dRPA-srLDA method (denoted LC-oLDA + dRPA in the original works) with $\mu$ and $c_{\text{RPA}}$ parameters tuned to 1.2 bohr$^{-1}$ and 1.5, respectively, reproduced both the binding energies and $C_6$ coefficients with accuracy on a par with CCSD(T). Potential energy curves obtained with the scaled range-separated SOSEX formulation of RPA (which includes the exchange kernel) were too attractive, especially when coupled with the short-range PBE model.

Following the path explored for single-determinantal functions by Kohn et al. and Toulouse et al. in Ref. 62 Pernal and coworkers applied the multiconfigurational adiabatic connection formalism to derive long-range correction for multideterminantal functions. The correction was combined with CASSCF wavefunctions, and the srPBE functional, the latter depending on alternative spin densities introduced in Equation (29). As demonstrated on the example of the He–Ne interaction, the method recovered the proper $R^{-6}$ asymptotic behavior of the dispersion energy and markedly improved upon its full-range counterpart at medium- and short-intermonomer separations.

Kullie and Saue adapted range-separated MP2 for relativistic calculations using 4-component Dirac–Coulomb Hamiltonian. This allowed for spectroscopic constants calculations in heavy rare gas systems, that is, the radon (Rn) and eka-radon (Uuo) homodimers. Shee et al. obtained first 2-component relativistic CCSD(T) and CCSD(T)-srLDA results for these complexes and found good agreement with MP2-srDFT binding energies. Both CC- and MP2-based RSHs came closer to the full-range CCSD(T)/CBS benchmark than their full-range WFT counterparts in the same basis set. Nevertheless, choosing basis sets of quadrupole-zeta quality, instead of terminating at the triple-zeta level, as well as correlating the subvalence $(n - 1)d$ shell had nonnegligible effects, and were required to approach the CBS limit.

Several studies applied RS MC-DFT methods to alkaline-earth dimers. Gerber and Ángyán were first to illustrate the substantial improvement in all equilibrium properties brought by MP2-srDFT with respect to both full-range MP2 and LDA. Toulouse et al. performed an extended investigation which included also range-separated RPA and CC approaches. Although none of the RSH schemes succeeded at describing the Be$_2$ dimer potential (relative binding energy errors ranged from $-70\%$ in dRPA-srPBE to $60\%$ in CCSD(T)-srPBE), the CCSD(T)-srPBE hybrid greatly improved upon the pure CCSD(T) results and achieved a remarkable accuracy for both Mg$_2$ and Ca$_2$ (mean relative errors in binding energies and equilibrium distances did not exceed 2%). The long-range variant of second-order n-electron valence state perturbation theory (NEVPT2) developed by Fromager et al. predicted magnesium and calcium dimers dissociation curves with a reasonable accuracy, comparable to range-separated MP2 results. This favorable behavior was not conserved when NEVPT2-srDFT was applied to Be$_2$. Even though the method correctly predicted position of the van der Waals minimum, accounting for the multireference character of beryllium did not result in accurate binding energy, which was overestimated by almost 40%. So far, the challenging mixture of static and dynamic correlation effects in the Be$_2$ dimer was best captured in the MC-srDFT framework by a combination of selected CI and short-range multideterminant correlation functionals, cf. Equation (30). Ferté et al. showed that their gradient-corrected on-top pair density functional coupled with CI not only did considerably improve upon full-range CI, but also gave a potential energy curve in excellent agreement with the exact reference at all interatomic distances.
Attractive forces between closed-shell metal atoms or ions, known as metallophilic interactions, were also examined with RS MC-DFT methods. Liu et al.\textsuperscript{127} employed range-separated MP2 and CC hybrids to study the prototype (AuH)\textsubscript{2} and (HAuPH\textsubscript{3})\textsubscript{2} complexes. Based on comparison with both full-range WFT results and empirical models from other works,\textsuperscript{128,129} the authors recognized CCSD(T)-srPBE as the best approach for description of aurophilic interactions. Alam and Fromager\textsuperscript{130} investigated metallophilic attraction in A-frame molecules of the [S(MPH\textsubscript{3})\textsubscript{2}] type (M = Cu, Ag, Au) using range-separated MP2 and NEVPT2 schemes. With $\mu = 0.4$ bohr\textsuperscript{-1}, both the single- and multireference RS MC-DFT variants remained in good agreement leading to potential energy curves closely matching the full-range CCSD(T) results.

### 4.2 Benchmark datasets for noncovalent interactions

A common protocol to establish the performance of a method for intermolecular interactions of different nature and strength are calculations on balanced benchmark datasets of noncovalently bound dimers.\textsuperscript{131} The first such evaluation of RSHs was presented in Ref. 63. To reduce the computational cost of MP2-srDFT and CC-srDFT approaches and access larger systems, Goll and coauthors\textsuperscript{63} applied local-correlation approximation\textsuperscript{132} for the long-range ab initio components. Numerical demonstration was carried out on the database of Zhao and Truhlar\textsuperscript{108} containing weak interaction, dipole complex, charge-transfer complex, and hydrogen-bond subsets. The range-separated CC hybrids provided consistent accuracy for all types of interactions with mean errors ranging from 8% to 13%. Similar to what was observed for diatomic molecules, the CC hybrids were essentially insensitive to triples. The MP2-srDFT method differed from its CC counterpart only in the case of weakly interacting (i.e., van der Waals) complexes for which the mean absolute relative error (MARE) reached 20%. The range-separated CCSD(T) hybrid combined with srPBE performed similar to the full-range CCSD(T) method for all test sets except for the hydrogen bonded complexes, where CCSD(T) yielded MARE of 5% and CCSD(T)-srPBE deviated by 10%–11% from the reference. Hydrogen-bonded dimers were also the only systems sensitive to the short-range functional—replacing srPBE with srLDA increased MAEs by a factor of two.

In a subsequent development, Goll et al.\textsuperscript{50} lowered the computational effort of range-separated MP2 and CC even further by introducing density fitting (DF) approximations for calculation of electron repulsion integrals. The DF formulations of RSH approaches were tested on the S22 dataset\textsuperscript{133} of Hobza and coworkers, with the main focus put on analysis of local MP2 (denoted DF-LMP2-srDFT). In line with findings of Ref. 63, range-separated MP2 systematically overestimated interaction energies in hydrogen-bonded complexes. MAE of DF-LMP2-srPBE calculations for this subset amounted to 1.6 kcal/mol, whereas the respective error for full-range DF-LMP2 was 0.95 kcal/mol. In turn, for the van der Waals and mixed (i.e., featuring strong electrostatic and dispersion interactions) subsets the local RSH\textsuperscript{+MP2} reduced the errors compared to pure DF-LMP2 from to 0.56 to 0.47 kcal/mol and from 0.30 to 0.17 kcal/mol, respectively.

The first application of dRPA-srLDA beyond rare gas dimers were calculations on the dataset of Zhao and Truhlar\textsuperscript{108} carried out by Janesko et al.\textsuperscript{139} The excellent performance of this approach achieved by rescaling of the long-range RPA correlation was confirmed also for stronger interactions. The mean relative errors ranged from 2% for dimers with dominating dipole interactions to 14% in weakly bonded complexes. In contrast to CC- and MP2-srDFT, the dRPA hybrids matched the full-range CCSD(T) accuracy for hydrogen bonded systems giving MAE of 0.49 kcal/mol (0.38 kcal/mol in pure CCSD(T)). This favorable result was attributed mainly to the large $\mu = 1.2$ bohr\textsuperscript{-1} value (compared to $\mu = 0.5$ bohr\textsuperscript{-1} chosen by Goll et al.\textsuperscript{50,63}) which reduces the overbinding character of the short-range DFT functional.

Zhu et al.\textsuperscript{56} and Toulouse et al.\textsuperscript{79} verified the performance of RPA-srDFT approaches on the S22 dataset of Jurečka et al.\textsuperscript{133,134} The RPAX-srDFT and RPAX-SO2-srDFT variants, which include the exchange terms, provided better accuracy than MP2-srDFT for all subsets, reducing the total MAEs by more than a factor of two. Relatively large errors in the 0.8–1.0 kcal/mol range persisted for hydrogen-bonded systems. The RPAX-SO2-srPBE method gave best overall accuracy with the MARE value of 3.7% (corresponding to MAE of 0.41 kcal/mol) and has been recommended as the range-separated RPA method of choice for noncovalent interactions.\textsuperscript{79} The RPAX-SO2 formulation avoids the numerical integration over the adiabatic connection, a clear advantage over the RPAX model.\textsuperscript{55,56} In contrast to RSH, full-range dRPA and RPAX,\textsuperscript{55} analyzed in Ref. 56 using small basis sets, deviated from the benchmark by 2.6 and 2.10 kcal/mol, respectively, in terms of MAEs. As shown by Eshuis and Furche,\textsuperscript{135} employing larger basis substantially reduces the errors of dRPA leading to MARE of 8.5% and MAE of 0.41 kcal/mol on the same dataset.
Performance of the range-separated methods compared with straight ab initio approaches for complexes of the S22 dataset is presented in Table 3. Focusing on the RPA variants, it can be noticed that RPAX-SO2-srPBE is comparable in accuracy to the more expensive CCD-srPBE method. When confronted with the dRPA results, RPAX-SO2-srPBE is more accurate for the dispersion-dominated and mixed complexes, and performs similarly in hydrogen-bonded systems. Regarding full-range RPA variants that include exchange integrals, test calculations on the S22 dataset are reported for the RPAX2 model introduced by Hesselmann. The method achieved a

| Complex                              | MP2  | dRPA | MP2-srPBE | RPAX-SO2-srPBE | CCD-srPBE | Reference |
|--------------------------------------|------|------|-----------|----------------|-----------|-----------|
| Hydrogen bonded complexes            |      |      |           |                |           |           |
| Ammonia dimer                        | −2.68| −2.74| −3.13     | −3.18          | −3.20     | −3.17     |
| Water dimer                          | −4.36| −4.52| −5.34     | −5.39          | −5.41     | −5.02     |
| Formic acid dimer                    | −15.99| −17.91| −21.20    | −20.98         | −20.94    | −18.80    |
| Formamide dimer                      | −13.95| −15.42| −17.44    | −17.27         | −17.25    | −16.12    |
| Uracil dimer C_{2h}                  | −18.41| −19.54| −22.62    | −22.15         | −22.00    | −20.69    |
| 2-Pyridoxine/2-aminopyridine         | −15.56| −16.23| −18.86    | −18.20         | −18.08    | −17.00    |
| Adenine/thymine WC                   | −14.71| −15.93| −18.26    | −17.69         | −17.62    | −16.74    |
| MAE                                  | 1.70 | 0.75 | 1.34      | 1.05           | 0.99      |           |
| MARE                                 | 12.66| 6.79 | 8.28      | 6.60           | 6.44      |           |
| Complexes with predominant dispersion contribution |      |      |           |                |           |           |
| Methane dimer                        | −0.39| −0.40| −0.46     | −0.51          | −0.51     | −0.53     |
| Ethene dimer                         | −1.18| −1.20| −1.45     | −1.47          | −1.45     | −1.50     |
| Benzene/methane                      | −1.47| −1.26| −1.62     | −1.43          | −1.40     | −1.45     |
| Benzene dimer C_{2h}                 | −4.25| −2.42| −4.08     | −2.61          | −2.40     | −2.62     |
| Pyrazine dimer                       | −6.00| −3.83| −5.97     | −4.34          | −4.14     | −4.20     |
| Uracil dimer C_{2}                   | −9.80| −9.64| −11.76    | −10.13         | −9.94     | −9.74     |
| Indole/benzene                       | −7.13| −4.30| −6.95     | −4.48          | −4.17     | −4.59     |
| Adenine/thymine stack                | −13.24| −11.52| −15.11    | −12.02         | −11.72    | −11.66    |
| MAE                                  | 1.01 | 0.22 | 1.42      | 0.14           | 0.14      |           |
| MARE                                 | 27.96| 10.33| 28.48     | 2.54           | 4.01      |           |
| Mixed complexes                      |      |      |           |                |           |           |
| Ethene/ethyne                        | −1.39| −1.27| −1.62     | −1.57          | −1.55     | −1.51     |
| Benzene/water                        | −2.98| −3.14| −3.49     | −3.30          | −3.29     | −3.29     |
| Benzene/ammonia                      | −2.21| −2.13| −2.49     | −2.29          | −2.27     | −2.32     |
| Benzene/hydrogen cyanide             | −4.37| −4.09| −5.31     | −4.71          | −4.65     | −4.55     |
| Benzene dimer C_{2v}                 | −3.09| −2.49| −3.33     | −2.70          | −2.61     | −2.71     |
| Indole/benzene T-shaped              | −6.10| −5.41| −6.55     | −5.57          | −5.44     | −5.62     |
| Phenol dimer                         | −6.79| −6.48| −8.05     | −7.43          | −7.35     | −7.09     |
| MAE                                  | 0.27 | 0.30 | 0.54      | 0.09           | 0.10      |           |
| MARE                                 | 7.55 | 8.46 | 12.91     | 2.16           | 2.51      |           |
| Total MAE                            | 0.99 | 0.41 | 1.10      | 0.43           | 0.41      |           |
| Total RMSD                           | 1.35 | 0.50 | 1.46      | 0.71           | 0.68      |           |
| Total MARE                           | 16.06| 8.53 | 16.56     | 3.77           | 4.32      |           |

**Table 3 Interaction energies (in kcal/mol) for the complexes of the S22 dataset**

*Note:* The MP2-srPBE results are taken from Ref. 56; the RPAX-SO2-srPBE and CCD-srPBE energies are reprinted from Ref. 79. The full-range dRPA and MP2 results are taken from Refs. 135 and 134, respectively. All calculations employed the aug-cc-pVDZ basis set, except for dRPA which employed def2-QZVP. The CCSD(T)/CBS estimates of Ref. 134 serve as reference. MAE and RMSD (given in kcal/mol) denote the mean absolute error and root mean square deviation, respectively; MARE (given in percent) is the mean absolute relative error.
slightly higher accuracy than RPAX-SO2-srPBE when comparing relative percentage errors (MARE values amounted to 3.4% and 3.7%, respectively). A larger difference occurred in the MAE values: RPAX2 deviated by 0.16 kcal/mol from the reference, while the corresponding RPAX-SO2-srPBE value was 0.41 kcal/mol (note that RPAX2 results were extrapolated to the CBS limit, whereas RPAX-SO2-srPBE results of Ref. 79 were obtained in the aug-cc-pVDZ basis set).

Outside the realm of molecular complexes, the range-separated MP2 approach was generalized to periodic systems by Sansone et al.138 The method was implemented with Gaussian-type basis functions and local treatment of long-range MP2 correlation contribution. Cohesive energy calculations revealed that $\mu$ value of 0.5 bohr$^{-1}$ is a good choice also for solids. The study concluded that RSH + MP2 affords better accuracy compared to pure DFT and MP2 not only for ionic and covalent solids, but also for van der Waals and molecular crystals bound by weak interactions.

In Ref. 139 Szalewicz and coworkers introduced a benchmark dataset composed of 10 dimers of a mixed type, each represented at intermonomer separations sampling the repulsive wall, minimum, and the asymptotic region. In a blind test study, the authors validated DFT-based methods capable of handling noncovalent interactions—both MP2-srPBE and RPAX-SO2-srPBE were included in the evaluation. Comparison with CBS-extrapolated CCSD(T) revealed that the RSHs systematically overestimated interaction energy curves, also at large intermonomer distances. Regarding the overall performance, the range-separated RPA hybrid gave median unsigned percentage error of 7.7%. Other methods with median errors in the 5%-8% range were: the vdW-DF2 functional140 with nonlocal correlation, two meta-GGA functionals from the Minnesota family (M06141 and M11142), and LC-DFT models corrected for dispersion (including the LC-ωPBE functional84 combined with the D3143 correction). The median error of MP2-srPBE calculations reached 10.2% which was the result next to last. Note that MP2-srDFT and RPAX-SO2-srDFT involve virtual orbitals and, without additional approximations, scale with the fifth or sixth power of the system size, respectively, that is, they are up to two orders of magnitude more computationally demanding than the other mentioned DFT methods. The three top contenders in the blind test were the symmetry-adapted perturbation theory based on DFT description of the monomers, SAPT(DFT),144 the popular B3LYP-D3145 functional, and the dlDFT + D functional146 which predicted interaction energies with median percentage errors of 2.6%, 3.4%, and 4.2%, respectively.

A brief summary of RS MC-DFT performance for noncovalent interaction is appropriate at this point. Combining srDFT with CC proved beneficial only for dispersion-bound complexes in moderate basis sets, where it brought a clear improvement over the parent DFT and CC methods.18,50,63 For stronger interactions the quality of CC-srDFT interaction energies either came close or, for hydrogen-bonded systems, deteriorated with respect to full-range CCSD(T) in the same basis set. The range-separated MP2 approach offers a lower computational cost than CC-based hybrids, but performs worse than regular MP2 for hydrogen-bonded complexes and inherits poor-quality dispersion energy of MP2 in the asymptotic regime. The RPA-srDFT approaches are superior to MP2-srDFT across all types of interactions, including better representation of the dispersion forces at large intermonomer separation.51,56,119 They are also more accurate compared to full-range RPA schemes for van der Waals (i.e., dispersion-dominated) complexes. For both mixed- and hydrogen-bonded dimers, the RPA-based RSH match the accuracy the best-performing full-range RPA schemes.

5 | EXCITED STATES FROM RS MC-DFT

5.1 | Linear response theory

Range-separated multiconfigurational DFT based on Equations (7) and (8) is a ground state theory. Van Leeuwen proved147,148 that given an initial state, a time-dependent Hamiltonian with Coulomb-interacting electron, and the corresponding electron density $\rho(t)$, there exists a local time-dependent potential for any modified electron interaction operator (unique up to a time-dependent function), which yields $\rho(t)$. Based on this theorem, Pernal149 formulated a time-dependent range-separated MC-DFT (RS TD-MC-DFT) equation for the $\psi_{LR}(t)$ wavefunction reading

$$i \frac{\partial \psi_{LR}(t)}{\partial t} = \left[ \hat{T} + \hat{V}_{\text{ext}}(t) + \hat{V}_{ee} + \hat{V}_{\text{SR}}(t) \right] \psi_{LR}(t).$$

(37)

The time-dependent (TD) Hamiltonian in the square bracket, compare with Equation (11), includes a TD external potential $\hat{V}_{\text{ext}}(t)$ and the local potential $\hat{V}_{\text{SR}}(t)$. The latter is such that the density $\rho_{\text{rel}}(\mathbf{r}, t)$, corresponding to the TD
wavefunction $\Psi^{LR}(t)$, coincides at each time with that of the exact fully interacting density $\rho(r, t)$, evolving under the influence of the same external potential $V_{\text{ext}}(t)$,

$$\rho_{\text{qslr}}(r, t) = \rho(r, t). \tag{38}$$

An equivalent time-dependent RS MC-DFT equation was derived by Fromager et al.\textsuperscript{150} from under stationary condition of the action integral principle. Considering the range-separation parameter dependence of the LR interaction, cf. Equations (17) and (18), it follows that the SR potential vanishes in the large-$\mu$ limit

$$\mu \to \infty : \vartheta^{\text{SR}}(r, t) = 0. \tag{39}$$

In the opposite, $\mu \to 0$, limit the time-dependent Kohn–Sham potential, $\vartheta^{\text{KS}}(r, t)$,\textsuperscript{151,152} is recovered

$$\mu \to 0 : \vartheta^{\text{SR}}(r, t) = \vartheta^{\text{KS}}(r, t) - \vartheta_{\text{ext}}(r, t). \tag{40}$$

Thus, varying $\mu$ between $\infty$ and 0 switches the time-dependent RS MC-DFT equation from the TD Schrödinger equation with fully interacting electrons to TD-DFT with noninteracting particles. Equation (37) is the base for linear response RS MC-DFT equations, but requires knowledge of the local time-dependent potential $V^{\text{SR}}(t)$, formally a functional of the exact interacting density $\rho(t)$. The same problem is encountered in TD-DFT, and it is resolved by adopting the adiabatic approximation to $V^{\text{SR}}(t)$. Within this approximation, the ground-state definition of $\vartheta^{\text{SR}}$, given in Equation (12), is used. The SR potential becomes a functional of the TD density,

$$\vartheta^{\text{SR}}(r, t) = \frac{\delta E_{\text{SR}}}{\delta \rho} \left[ \rho_{\text{qslr}}(r, t) \right], \tag{41}$$

where $E_{\text{SR}}$ is the ground state SR density functional. Excitation energies obtained from the RS TD-MC-DFT linear response equations are meant to be superior to those from TD-DFT in the adiabatic approximation. The latter fails to predict double excitations and underestimates charge-transfer excitations as a result of the self-interaction error.\textsuperscript{153} The wavefunction part in the TD equation is expected to recover double excitations and, since the self-interaction is reduced in approximate RS MC-DFT compared to DFT approximations,\textsuperscript{39} the CT excitations should be more accurate. The anticipated benefit for WFT is analogous as in the ground state theory, namely the efficient treatment of the SR correlation by the functional part.

The first range-separated linear-response equations derived from Equation (37) were presented in Ref. 149 in the framework of the time-dependent reduced density matrix theory.\textsuperscript{154} Next, Fromager et al.\textsuperscript{150} derived RS TD-MC-DFT linear response equations which gave access to excitation energies from variational multiconfigurational wavefunctions, cf. Equation (35). So far, RS TD-MC-DFT was applied with MCSCF\textsuperscript{150,155–157} wavefunctions and with the antisymmetrized product of strongly orthogonal geminals (APSG).\textsuperscript{81} The long-range wavefunction part was combined with SR functionals developed for ground state calculations, that is, either the local approximations\textsuperscript{14,28} or the gradient-corrected PBE-based variants.\textsuperscript{18,21} Finally, a nonvariational range-separated linear response scheme based on the second-order polarization propagator approximation has also been put forward in Ref. 155.

In all RS linear response theories the range-separation enters at two levels. First, in the LR Hamiltonian, see Equation (11), employed in both ground state calculation and RS TD-MC-DFT equations. Second, in the SR kernel obtained in the adiabatic approximation as a second-order functional derivative of the SR functional, that is

$$K^{\text{SR}}[\rho](r, r') = \frac{\delta^2 E_{\text{SR}}[\rho]}{\delta \rho(r) \delta \rho(r')}, \tag{42}$$

which appears in the Hessian matrix.\textsuperscript{81,149,150,155}

Pilot studies applied RS TD-MC-DFT to problems beyond the reach of single-reference methods. Excitation energy calculations along the dissociation curve of H\textsubscript{2}\textsuperscript{150} and asymmetric dissociation of H\textsubscript{2}O\textsuperscript{81} have shown that both MCSCF- and APSG-based range-separated approaches perform more reliably for the stretched-bond geometries than TD-HF and TD-DFT, but the errors may be still significant due to inaccuracies in the functional part. In the equilibrium geometries RS TD methods predicted accurate local excitation energies not only of a single, but also of a double character.\textsuperscript{81,150,155}
Note that double excitations emerge in linear response equations due to contributions from variations of the configuration coefficients.

Investigations of the charge transfer singlet excitations in ferrocene and a set of peptides have demonstrated that RS TD-MC-DFT methods outperform their full-range counterparts for this challenging class of transitions. At the same time, RS TD-MC-DFT remained slightly inferior compared to CAM-B3LYP (a Coulomb attenuated DFT functional). On the example of the retinal chromophore, the RS method was validated as an adequate tool for studying states of a multireference character or resulting from double excitations. The accuracy of the excitations to the lowest lying singlet states paralleled that of the more costly ab initio methods. In particular, RS TD-MC-DFT does not require access to three- and four-electron density matrices that is the computational bottleneck for the PT2 correction in CASPT2. The initial studies have also revealed that RS approaches require much smaller active spaces compared to their ab initio parent methods. For example, the low-lying singlet excited state of the retinal chromophore could be correctly described already in the CAS(6,6) active space instead of CAS(12,12) chosen in CASPT2 calculations.

In Ref. 160 the effect of the environment has been accounted for in the RS TD-MC-DFT equations by adopting the polarizable-embedding (PE) method from Ref. 161. Hedegård et al. applied the PE formulation of range-separated linear response to the uracil and acetone molecules in the aqueous environment and to the retinylidene chromophore embedded in the channelrhodopsin protein. The obtained solvent shifts stayed in close agreement both with experimental reference data and high-level WFT results. Moreover, individual excitation energies predicted by the PE variant of CAS-srDFT were significantly more accurate compared to full-range PE-CASSCF values. Again, incorporation of the srDFT functional via range-separation allowed for compact active spaces in the reference wavefunctions.

Hubert et al. validated the performance of RS TD-MC-DFT with MCSH wavefunctions for selected systems from the Thiel benchmark set. The analyzed subset included π → π* and n → π* excitations of either a valence or a mixed Rydberg-valence character of 13 organic molecules. The employed range-separated linear response method combined long-range CASSCF and short-range PBE-based functionals. The μ = 0.4 bohr⁻¹ value, recommended as universal for ground state applications in Ref. 24, turned out to be close to optimal also for description of valence, single-excitation dominated, excited states. The MAE of excitation energies from RS TD-MC-DFT calculations amounted to 0.32 eV with respect to the CASPT2 results, which was almost three times lower than that of CASSCF (the μ = ∞ limit, MAE = 0.95 eV) and TD-DFT-PBE (μ = 0 limit, MAE = 0.91 eV). The accuracy of RS TD-MC-DFT would rival the NEVPT2 method, if the valence-Rydberg mixed states were removed. For the latter, the RS approach is erratic—the srPBE functionals inherit the poor performance of the underlying PBE approximation.

In Ref. 164 Hedegård and coauthors evaluated the performance of the RS method for all singlet excitations from the Thiel set. Both excitation energies and oscillator strengths were calculated with μ set to 0.4 bohr⁻¹. For the oscillator strengths, the CAS-srPBE predictions remained in a reasonable agreement with the more accurate CC2 values. For the excitation energies, the MAEs with respect to the CASPT2 results and best theoretical estimations from Ref. 163 amounted to 0.34 and 0.32 eV, respectively. In Ref. 157 Hubert et al. reached a similarly encouraging accuracy for the excitation energies of thymine, uracil, cytosine and adenine. The authors confirmed that larger errors should be expected in the case of valence-Rydberg mixing.

Kjellgren et al. extended the linear response theory for RS MC-DFT to triplet excitations. The triplet linear response equations employing long-range CASSCF wavefunctions combined with either local or PBE-based spin density functionals were benchmarked on a set of 33 molecules. To remove the effect of triplet instability, aggravating the accuracy of the low triplet excitations, the Tamm–Dancoff approximation (TDA) was employed. As expected, TDA reduced the MAEs of RS TD-MC-DFT with respect to the CC3 benchmark from 0.4 to 0.26 eV, and from 0.29 to 0.21 eV, if srPBE or srLDA functionals were used, respectively. The corresponding MAEs of the standard (full-range) LDA and PBE were 0.44 and 0.51 eV, respectively. On the ab initio side, the full-range CASSCF linear response predicted triplet excitations with MAE of ca. 0.5 eV, depending on the active spaces selected in the calculations.

The real advantage of RS methods over RSH functionals used in TD-DFT, such as CAM-B3LYP or ωB97X, is their ability to accurately describe excitations which require multireference treatment and excitations which have a significant double character. An illustrative example is the recent study of the permanganate ion by Olsen et al. This transition metal complex is challenging to TD-DFT methods which seriously overestimate its excitation energies. Although multireference methods are more adequate, they call for large active spaces. With RS TD-MC-DFT it was possible to obtain lowest excitation energies of MnO₄⁻ in good agreement with the experimental values using the active space of 14 active electrons distributed in 12 active orbitals. This is to be compared with a significantly larger space—24 electrons in 17 orbitals—required by the RASPT2 method to achieve a similar accuracy.
It is worth mentioning that description of double excitations within linear-response RS MC-DFT could be achieved without invoking multiconfigurational wavefunction and using a single-determinant instead, if the adiabatic approximation were abandoned. Single-determinantal TD RS MC-DFT equations are equivalent to time-dependent RSH (TD-RSH) formalism. For the latter, efforts to go beyond the adiabatic approximation undertaken by Rebolini et al. included a frequency-dependent response kernel in the second-order Bethe-Salpeter approximation in the long-range domain of electron interactions. Unfortunately, only a slight improvement of excitation energies of small atoms and molecules has been observed compared to the TD-RSH results in the adiabatic approximation.

5.2 Direct excited states calculations

The time-dependent range-separated equation given by Equation (37) gives the foundation for exact linear response theory. In actual implementations, the rigor is lost due to introduction of the adiabatic approximation and the use of ground state functionals to compute the SR kernel, cf. Equation (42). As an alternative to the linear response theory, one may directly solve the LR eigenequation for the excited state of interest.

In a series of papers, Rebolini et al. considered approximate RS MC-DFT approaches aiming at correcting excited-state energies of the LR Hamiltonian $\hat{H}^{LR}$. Corrections can be derived either by considering the exact expansion in orders of $\mu$ along a range separated adiabatic connection, or from the perturbation theory. In the latter case, the $\hat{H}^{LR}$ Hamiltonian is chosen as the unperturbed operator and the perturbation is defined as $\tilde{V}_{ee} - \tilde{V}_{SR}^{SR} [\rho_0]$, cf. Equations (2) and (12). Both Rayleigh–Schrödinger and Görling–Levy perturbation theories have been applied. For the $i$th eigenstate of $\hat{H}^{LR}$ one recovers the pertinent eigenvalue in the 0th order. It was verified that already the first-order correction brings a significant improvement toward the fully interacting (exact) limit. So far, perturbation theory-based approximations in RS MC-DFT theory have been applied in proof-of-principle calculations for two- and four-electron systems, exploiting LR full configuration interaction wavefunctions and numerically exact SR potentials.

There exists another way of accessing excited states in a direct manner. Similar to the methods developed by Rebolini and coworkers, it is based on solving the eigenequation for the LR Hamiltonian. Yet, instead of using the eigenvalues of the $\hat{H}^{LR}$ operator, one simply employs both the LR wavefunction and the corresponding density in the energy functional given in Equation (14). This provides an approximation to a desired excited state energy. The main source of inaccuracy in this scheme is using ground state SR exchange-correlation functionals.

In Ref. 175 the direct approach based on the LR wavefunction of the targeted state was applied to open-shell systems. Remember, that formally in the RS MC-DFT theory, similarly to DFT, one only needs the total electron density, rather than the spin density, to determine the energy, as shown in Equations (7) and (8). In practice, for open-shell systems the local and semilocal SR DFT functionals are not expected to perform well, and for that reason approximate spin-density SR functionals were developed. Hedegård et al. implemented the variational open-shell RS MC-DFT method for LR MCSCF wavefunctions, employing local spin functionals. Numerical demonstration focused on spin-state splittings in the O$_2$ molecule and hexaaquaiiron(III) complex [Fe(H$_2$O)$_6$]$^{3+}$. The lowest excited states of both systems are of spin-multiplicity different than that of the ground state, and pose a challenge for multireference methods. To find the optimal value of the range-separation parameter for open-shell systems, the authors followed the protocol of Ref. 24. Based on the O$_2$ triplet ground state analysis, $\mu = 0.4$ bohr$^{-1}$ was recommended. The singlet–triplet splitting in the O$_2$ molecule obtained with the CAS(12,16) function coupled with the srPBE functional, fell between the CCSD(T) and CCSDT values, in a reasonable agreement with the experimental value. For the iron complex quartet-sextet spin splitting, the energy deviated only by 0.12 eV from the experiment. These encouraging results indicate that RS MC-DFT is capable of making accurate predictions of spin-splitting. At the same time, it has been suggested that the good performance for model systems could be a result of error cancellation, since the employed functionals are not self-interaction free.

The difficulty with obtaining excited states from variational calculations based on the LR Hamiltonian, Equation (11), is that the Hamiltonian is different for each state due to its dependence, via the SR potential, on the density of the state. Diagonalization of the Hamiltonian matrix in order to simultaneously find several excited states, must therefore involve construction of an effective Hamiltonian with the reference density matrix. This approach was first proposed by Pedersen, who constructed the reference density matrix by state-averaging over density matrices of states obtained in CI calculations. Casanova has followed the same path in the implementation of the RS MC-DFT scheme, but based on the restricted active space (RAS) CI model. The method has been used to study the lowest singlet states of
polyenes and acenes. Although the range-separated variant improved upon the full-range RASCI results, the predicted excited state energies showed larger variations with $\mu$ compared to energies from linear response calculations.

To circumvent problems with variational calculations using the state-specific LR Hamiltonian, Hapka et al.\textsuperscript{62} proposed a different implementation of the direct scheme. First, the state-averaged (SA) CASSCF calculations were carried out with a fully interacting Hamiltonian, leading to a set of states of interest. Next, the SA-CAS wavefunctions were employed in Equation (14) to obtain excited state energies in the RS MC-DFT framework. The noniterative approach turned out to be fairly successful—compared to CASSCF, the average errors were reduced by a factor of around 3 for singlet excitations and a factor of 2 for excitations to states of spin symmetry different than the ground state. The corresponding MAE values from RS MC-DFT were equal to 0.4 and 0.1 eV which mirrored the accuracy of CASPT2. Amending the range-separated method by addition of the long-range correlation recovered in the adiabatic connection framework,\textsuperscript{120} resulted only in a marginal improvement.

Recently, yet another non-SCF method has been applied to nonsinglet excited states from RASCI wavefunctions.\textsuperscript{176} The approach absorbs the SR exchange in the wavefunction part by representing the SR exchange functional with the Hartree–Fock expression. Hence, the energy of the excited state is obtained as a sum of the RASCI energy obtained with the full-range electron interaction, and the SR correlation functional. Although the investigated variant of RS MC-DFT gave more accurate transition energies than RASCI, it double-counts short-range correlation energy. Consequently, it will impair the results, if larger active spaces are employed.

A distinct development employs the ensemble DFT formalism generalized to range-separated interaction.\textsuperscript{177,178} Approximations based on this theory are in their infancy, and to date have been applied for model, few-electron systems (He, Be, HeH$^+$, and H$_2$).

To recapitulate the crucial benefits for excited state calculations that follow from merging TD-WFT and TD-DFT via range-separation: (1) the adiabatic approximation, which eliminates double excitations from the TD-DFT spectrum, is a less severe problem in TD RS MC-DFT methods, as double excitations are recovered by the multiconfigurational wavefunction part; (2) the wavefunction component is also responsible for improved accuracy of multireference states comparing with TD-DFT; (3) the RS direct approaches offer a significant cost reduction compared to the perturbation MC methods, for example, with CASPT2, since the dynamic correlation is captured by SR density functionals; (4) direct RS methods rival the accuracy of CASPT2, but seem to be more sensitive to the choice of the range-separation parameter than their linear-response counterparts.

6 | SUMMARY AND PERSPECTIVES

The primary motivation behind the RS MC-DFT was to overcome the inability of the approximate density functionals to treat near-degeneracy effects. This has been achieved through partitioning of the electron interaction into ranges which allowed for rigorous introduction of the WFT into DFT. Simultaneously, the removal of electron interaction singularity from the Hamiltonian in RS MC-DFT gave the opportunity to improve both the accuracy and computational efficiency of ab initio methods. Almost a quarter of a century after the pioneering works of Savin, RS MC-DFT stays an active field of research and has delivered both on DFT and ab initio fronts. Despite the increased overall accuracy and universality of the latest density functional models, static correlation remains beyond the reach of conventional DFT.\textsuperscript{2,4} Thus, merging multiconfigurational WFT with short-range functionals is a viable extension of DFT for systems with near-degeneracies. The appeal of RS MC-DFT holds also for excited states dominated by double-excitations: while adiabatic approximation precludes their investigations with TD-DFT, they do not pose a challenge for the linear response in the TD RS MC-DFT formalism. From the ab initio perspective, RSHs combining DFT either with long-range RPA or long-range MP2 correlation have been intensively developed due to their beneficial cost/accuracy ratio. Recent works have generalized this class of methods to a range-separated double-hybrid scheme\textsuperscript{179–181} of an improved performance for thermochemistry and noncovalent interactions. RS MC-DFT may also compete with multireference ab initio methods corrected for the dynamic correlation. Although the available RS MC-DFT approximations strive to reach the accuracy of the perturbatively corrected MCSCF methods, such as CASPT2, they recover the dynamic correlation at the marginal cost of the latter. It is noteworthy, though, that ab initio methods that provide dynamic correlation for multireference wavefunction based only on one- and two-electron reduced density matrices, cf. Ref. 120, 121, challenge the computational advantage of RS MC-DFT.

Further development of RS MC-DFT methods hinges upon the removal of fractional charge- and spin-errors, which short-range functionals inherit from the underlying semilocal approximations. Both errors hinder accurate description
of ground states and affect excited states of the mixed valence-Rydberg character. A promising route is to introduce the dependence on the correlated on-top pair density. This two-electron local function is a natural ingredient of the short-range functionals that appears in their exact large-$\mu$ asymptotic expansion. Next to minimization of the fractional charge and spin errors, the on-top pair density can be used to detect local spin-density, which would allow to correctly account for exchange and correlation in open-shell singlets or spin multiplets. Steps in these directions have recently been taken.\(^8\) In a broader perspective, the known small- and large-$\mu$ asymptotics of the exact eigenvalues and eigenfunctions of the range-separated Hamiltonian may lead to the emergence of systematically improvable RS approximations which abandon density functionals.\(^1\)\\n
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**CONFLICT OF INTEREST**

The authors have declared no conflicts of interest for this article.

**DATA AVAILABILITY STATEMENT**

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

**AUTHOR CONTRIBUTIONS**

**Katarzyna Pernal**: Conceptualization (lead); data curation (equal); formal analysis (equal); project administration (lead); writing - original draft (equal); writing-review & editing (equal). **Michal Hapka**: Data curation (equal); formal analysis (equal); validation (equal); writing - original draft (equal); writing-review & editing (equal).

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**RELATED WIREs ARTICLES**

- Long-range correction for density functional theory
- Double-hybrid density functionals
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**REFERENCES**

1. Hohenberg P, Kohn W. Inhomogeneous electron gas. Phys Rev. 1964;136:B864–71.
2. Mardirossian N, Head-Gordon M. Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals. Mol Phys. 2017;115:2315–72.
3. Jones RO. Density functional theory: its origins, rise to prominence, and future. Rev Mod Phys. 2015;87:897–923.
4. Peverati R, Truhlar DG. Quest for a universal density functional: the accuracy of density functionals across a broad spectrum of databases in chemistry and physics. Philos Trans R Soc A. 2014;372:20120476.
5. Savin A, Flad HJ. Density functionals for the Yukawa electron–electron interaction. Int J Quant Chem. 1995;56:327–32.
6. Savin A. On degeneracy, near-degeneracy and density functional theory. In: Seminario JM, editor. Recent developments and applications of modern density functional theory. Theoretical and computational chemistry. Volume 4. Amsterdam: Elsevier; 1996. p. 327–57 Available from: [https://www.sciencedirect.com/science/article/pii/S1380732396800914](https://www.sciencedirect.com/science/article/pii/S1380732396800914)
7. Perdew JP, Savin A, Burke K. Escaping the symmetry dilemma through a pair-density interpretation of spin-density functional theory. Phys Rev A. 1995;51:4531–41.
8. Stoll H, Savin A. Density functionals for correlation energies of atoms and molecules. In: Dreizler RM, da Providência J, editors. Density functional methods in physics. Boston, MA: Springer US; 1983. p. 177–207.
9. Savin A. Beyond the Kohn-Sham determinant. Singapore: World Scientific; 1995.
10. Levy M. Universal variational functionals of electron densities, first-order density matrices, and natural spin–orbitals and solution of the v-representability problem. Proc Natl Acad Sci U S A. 1979;76:6062–5.
11. Leininger T, Stoll H, Werner HJ, Savin A. Combining long-range configuration interaction with short-range density functionals. Chem Phys Lett. 1997;275:151–60.
12. Toulouse J. Review of approximations for the exchange-correlation energy in density-functional theory. arXiv preprint arXiv: 210302645; 2021.
13. Toulouse J, Colonna F, Savin A. Long-range–short-range separation of the electron–electron interaction in density-functional theory. Phys Rev A. 2004;70:062505.

14. Toulouse J, Savin A, Flad HJ. Short-range exchange-correlation energy of a uniform electron gas with modified electron–electron interaction. Int J Quantum Chem. 2004;100:1047–56.

15. Gill PM, Adamson RD. A family of attenuated Coulomb operators. Chem Phys Lett. 1996;261:105–10.

16. Song JW, Tokura S, Sato T, Watson MA, Hirao K. An improved long-range corrected hybrid exchange-correlation functional including a short-range Gaussian attenuation (LCgau-BOP). J Chem Phys. 2007;127:154109.

17. Toulouse J. Personal communication; 2021.

18. Goll E, Werner HJ, Stoll H. A short-range gradient-corrected density functional in long-range coupled-cluster calculations for rare gas dimers. Phys Chem Chem Phys. 2005;7:3917–23. https://doi.org/10.1039/B509242F

19. Pollet R, Savin A, Leininger T, Stoll H. Combining multideterminantal wave functions with density functionals to handle near-degeneracy in atoms and molecules. J Chem Phys. 2002;116:1250–8.

20. Toulouse J, Colonna F, Savin A. Short-range exchange and correlation energy density functionals: beyond the local-density approximation. J Chem Phys. 2005;122:014110.

21. Goll E, Werner HJ, Stoll H, Leininger T, Gori-Giorgi P, Savin A. A short-range gradient-corrected spin density functional in combination with long-range coupled-cluster methods: application to alkali-metal rare-gas dimers. Chem Phys. 2006;329:276–82.

22. Gerber IC, Angyán JG. Hybrid functional with separated range. Chem Phys Lett. 2005;415:100–5.

23. Curtiss LA, Raghavachari K, Redfern PC, Pople JA. Assessment of Gaussian-2 and density functional theories for the computation of enthalpies of formation. J Chem Phys. 1997;106:1063–79. https://doi.org/10.1063/1.473182

24. Fromager E, Toulouse J, Jensen HJA. On the universality of the long-/short-range separation in multiconfigurational density-functional theory. J Chem Phys. 2007;126:074111.

25. Fromager E, Réal F, Wählín P, Wahlgren U, Jensen HJA. On the universality of the long-/short-range separation in multiconfigurational density-functional theory. II. Investigating $\rho^2$ actinide species. J Chem Phys. 2009;131:054107.

26. Kananenka AA, Zgid D. Combining density functional theory and Green’s function theory: range-separated, nonlocal, dynamic, and orbital-dependent hybrid functional. J Chem Theory Comput. 2017;13:5317–31.

27. Franck O, Mussard B, Luppi E, Toulouse J. Basis convergence of range-separated density-functional theory. J Chem Phys. 2015;142:074107.

28. Pizziani S, Moroni S, Gori-Giorgi P, Bachelet GB. Local-spin-density functional for multideterminant density functional theory. Phys Rev B. 2006;73:155111.

29. Vosko SH, Wilk L, Nusair M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can J Phys. 1980;58:1200–11.

30. Gori-Giorgi P, Savin A. Properties of short-range and long-range correlation energy density functionals from electron-electron coalescence. Phys Rev A. 2006;73:032506.

31. Becke A, Savin A, Stoll H. Extension of the local-spin-density exchange-correlation approximation to multiplet states. Theor Chim Acta. 1995;91:147–56.

32. Freeman DL. Coupled-cluster expansion applied to the electron gas: inclusion of ring and exchange effects. Phys Rev B. 1977;15:5512–21.

33. Heyd J, Scuseria GE, Ernzerhof M. Hybrid functionals based on a screened Coulomb potential. J Chem Phys. 2003;118:8207–18.

34. Lieb EH, Oxford S. Improved lower bound on the indirect Coulomb energy. Int J Quantum Chem. 1981;19:427–39.

35. Goll E, Werner HJ, Stoll H, Leininger T, Gori-Giorgi P, Savin A. A short-range gradient-corrected spin density functional in combination with long-range coupled-cluster methods: application to alkali-metal rare-gas dimers. Chem Phys. 2006;329:276–82.

36. Gerber IC, Angyán JG. Hybrid functional with separated range. Chem Phys Lett. 2005;415:100–5.

37. Curtiss LA, Raghavachari K, Redfern PC, Pople JA. Assessment of Gaussian-2 and density functional theories for the computation of enthalpies of formation. J Chem Phys. 1997;106:1063–79. https://doi.org/10.1063/1.473182

38. Fromager E, Toulouse J, Jensen HJA. On the universality of the long-/short-range separation in multiconfigurational density-functional theory. J Chem Phys. 2007;126:074111.

39. Fromager E, Réal F, Wählín P, Wahlgren U, Jensen HJA. On the universality of the long-/short-range separation in multiconfigurational density-functional theory. II. Investigating $\rho^2$ actinide species. J Chem Phys. 2009;131:054107.

40. Kananenka AA, Zgid D. Combining density functional theory and Green’s function theory: range-separated, nonlocal, dynamic, and orbital-dependent hybrid functional. J Chem Theory Comput. 2017;13:5317–31.

41. Franck O, Mussard B, Luppi E, Toulouse J. Basis convergence of range-separated density-functional theory. J Chem Phys. 2015;142:074107.

42. Pizziani S, Moroni S, Gori-Giorgi P, Bachelet GB. Local-spin-density functional for multideterminant density functional theory. Phys Rev B. 2006;73:155111.

43. Vosko SH, Wilk L, Nusair M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can J Phys. 1980;58:1200–11.

44. Gori-Giorgi P, Savin A. Properties of short-range and long-range correlation energy density functionals from electron-electron coalescence. Phys Rev A. 2006;73:032506.

45. Becke A, Savin A, Stoll H. Extension of the local-spin-density exchange-correlation approximation to multiplet states. Theor Chim Acta. 1995;91:147–56.

46. Freeman DL. Coupled-cluster expansion applied to the electron gas: inclusion of ring and exchange effects. Phys Rev B. 1977;15:5512–21.

47. Heyd J, Scuseria GE, Ernzerhof M. Hybrid functionals based on a screened Coulomb potential. J Chem Phys. 2003;118:8207–15.

48. Lieb EH, Oxford S. Improved lower bound on the indirect Coulomb energy. Int J Quantum Chem. 1981;19:427–39.

49. Goll E, Ernst M, Moegle-Hofacker F, Stoll H. Development and assessment of a short-range meta-GGA functional. J Chem Phys. 2009;130:234112.

50. Tao J, Perdew JP, Staroverov VN, Scuseria GE. Climbing the density functional ladder: nonempirical meta-generalized gradient approximation designed for molecules and solids. Phys Rev Lett. 2003;91:1446401. https://doi.org/10.1103/PhysRevLett.91.1446401

51. Garza AJ, Bulik IW, Henderson TM, Scuseria GE. Range separated hybrids of pair coupled cluster doubles and density functionals. Phys Chem Chem Phys. 2015;17:22412–22.

52. Garza AJ, Bulik IW, Alencar AGS, Sun J, Perdew JP, Scuseria GE. Combinations of coupled cluster, density functionals, and the random phase approximation for describing static and dynamic correlation, and van der Waals interactions. Mol Phys. 2016;114:997–1018.

53. Mussard B, Toulouse J. Fractional-charge and fractional-spin errors in range-separated density-functional theory. Mol Phys. 2017;115:161–73.

54. Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. Phys Rev Lett. 1996;77:3865–8.

55. Toulouse J, Gori-Giorgi P, Savin A. A short-range correlation energy density functional with multi-determinantal reference. Theor Chem Acc. 2005;114:305–8.

56. Ferté A, Giner E, Toulouse J. Range-separated multideterminant density-functional theory with a short-range correlation functional of the on-top pair density. J Chem Phys. 2019;150:084103.

57. Stoyanova A, Teale AM, Toulouse J, Helgaker T, Fromager E. Alternative separation of exchange and correlation energies in multiconfiguration range-separated density-functional theory. J Chem Phys. 2013;139:134113.

58. Paquier J, Toulouse J. Four-component relativistic range-separated density-functional theory: short-range exchange local-density approximation. J Chem Phys. 2018;149:174110.
45. Paquier J, Toulouse J. Short-range correlation energy of the relativistic homogeneous electron gas. arXiv preprint arXiv:210207761 [Physics,chem-ph]; 2021.
46. Paquier J, Giner E, Toulouse J. Relativistic short-range exchange energy functionals beyond the local-density approximation. J Chem Phys. 2020;152:214106.
47. Toulouse J. Extension multidéterminantale de la méthode de Kohn-Sham en théorie de la fonctionnelle de la densité par décomposition de l'interaction électronique en contributions de longue portée et de courte portée [Theses]. Université Pierre et Marie Curie – Paris VI; 2005.
48. Kato T. On the eigenfunctions of many-particle systems in quantum mechanics. Commun Pure Appl Math. 1957;10:151–77.
49. Goll E, Stoll H, Thierfelder C, Schwerdtfeger P. Improved dipole moments by combining short-range gradient-corrected density-functional theory with long-range wave-function methods. Phys Rev A. 2007;76:032507.
50. Goll E, Werner HJ, Stoll H. Short-range density functionals in combination with local long-range ab initio methods: application to non-bonded complexes. Chem Phys. 2008;346:257–65.
51. Toulouse J, Zhu W, Ángyán JG, Savin A. Range-separated density-functional theory with the random-phase approximation: detailed formalism and illustrative applications. Phys Rev A. 2010;82:032502.
52. Ángyán JG, Gerber IC, Savin A, Toulouse J. van der Waals forces in density functional theory: Perturbational long-range electron-interaction corrections. Phys Rev A. 2005;72:012510.
53. Fromager E, Jensen HJA. Analysis of self-consistency effects in range-separated density-functional theory with Møller–Plesset perturbation theory. J Chem Phys. 2011;135:034116.
54. Heßelmann A, Ángyán J. Assessment of a range-separated orbital-optimised random-phase approximation electron correlation method. Theor Chem Acc. 2018;137:1–13.
55. Toulouse J, Gerber IC, Jansen G, Savin A, Ángyán JG. Adiabatic-connection fluctuation–dissipation density-functional theory based on range separation. Phys Rev Lett. 2009;102:096404.
56. Zhu W, Toulouse J, Savin A, Ángyán JG. Range-separated density-functional theory with random phase approximation applied to noncovalent intermolecular interactions. J Chem Phys. 2010;132:244108.
57. Iikura H, Tsuneda T, Yanai T, Hirao K. A long-range correction scheme for generalized-gradient-approximation exchange functionals. J Chem Phys. 2001;115:3540–4. https://doi.org/10.1063/1.1383587
58. Tsuneda T, Hirao K. Long-range correction for density functional theory. WIREs Comput Mol Sci. 2014;4:375–90.
59. Hédegård ED. Chapter 3. Multi-configurational density functional theory: progress and challenges. Hoboken, NJ: John Wiley & Sons, Ltd; 2020. p. 47–75.
60. Casanova D. Long-range density-functional correlation within the restricted active space CI method. J Chem Phys. 2018;148:124118.
61. Fromager E, Cimiraglia R, Jensen HJA. Merging multireference perturbation and density-functional theories by means of range separation: potential curves for Be2, Mg2, and Ca2. Phys Rev A. 2010;81:024502.
62. Hapka M, Pastorczak E, Krzeminski A, Pernal K. Long-range-corrected multiconfiguration density functional with the on-top pair density. J Chem Phys. 2020;152:094102.
63. Goll E, Leininger T, Manby FR, Mitrushchenkov A, Werner HJ, Stoll H. Local and density fitting approximations within the short-range/long-range hybrid scheme: application to large non-bonded complexes. Phys Chem Chem Phys. 2008;10:3353–7.
64. Pernal K. Long-range density-matrix-functional theory: application to a modified homogeneous electron gas. Phys Rev A. 2010;81:052511.
65. Rohr DR, Toulouse J, Pernal K. Combining density-functional theory and density-matrix-functional theory. Phys Rev A. 2010;82:052502.
66. Hédegård ED, Knecht S, Kielberg JS, Jensen HJA, Reiher M. Density matrix renormalization group with efficient dynamical electron correlation through range separation. J Chem Phys. 2015;142:24108.
67. Idasz K, Angeli C, Bak KL, Bakken V, Bast R, Boman L, et al. The Dalton quantum chemistry program system. WIREs Comput Mol Sci. 2014;4:269–84.
68. Olsen JMH, Reine S, Vahtras O, Kjellgren E, Reinholdt P, Hjorth Dundas KO, et al. Dalton project: a Python platform for molecular-and electronic-structure simulations of complex systems. J Chem Phys. 2020;152:214115. https://doi.org/10.1063/1.5144298
69. Werner HJ, Knowles PJ, Knizia G, Manby FR, Schütz M. Molpro: a general-purpose quantum chemistry program package. WIREs Comput Mol Sci. 2012;2:242–53.
70. Werner HJ, Knowles PJ, Manby FR, Black JA, Doll K, Heßelmann A, et al. The Molpro quantum chemistry package. J Chem Phys. 2020;152:144107.
71. Shao Y, Gan Z, Epifanovsky E, Gilbert ATB, Wormit M, Kussmann J, et al. Advances in molecular quantum chemistry contained in the Q-Chem 4 program package. Mol Phys. 2015;113:184–215.
72. Garniron Y, Applencourt T, Gasperich K, Benali A, Ferté A, Paquier J, et al. Quantum package 2.0: an open-source determinant-driven suite of programs. J Chem Theory Comput. 2019;15:3591–609.
73. Saue T, Bast R, Gomes ASP, Jensen HJA, Visscher L, Aucar IA, et al. The DIRAC code for relativistic molecular calculations. J Chem Phys. 2020;152:204104.
74. Ghosh S, Verma P, Cramer CJ, Gagliardi L, Truhlar DG. Combining wave function methods with density functional theory for excited states. Chem Rev. 2018;118:7249–92.
75. Marian CM, Heil A, Kleinschmidt M. The DFT/MRCI method. WIREs Comput Mol Sci. 2019;9:e1394.
100. Fast PL, Corchado J, Sanchez ML, Truhlar DG. Optimized parameters for scaling correlation energy. J Phys Chem A. 1999;103:3139.

101. Zheng J, Zhao Y, Truhlar DG. The DBH24/08 database and its use to assess electronic structure model chemistries for chemical reaction barrier heights. J Chem Theory Comput. 2009;5:808–21. https://doi.org/10.1021/ct800568m

102. Szabo A, Ostlund NS. The correlation energy in the random phase approximation: intermolecular forces between closed-shell systems. J Chem Phys. 1977;67:4351–60. https://doi.org/10.1063/1.434580
Ángyán JG, Liu RF, Toulouse J, Jansen G. Correlation energy expressions from the adiabatic-connection fluctuation–dissipation theorem approach. J Chem Theory Comput. 2011;7:3116–30. https://doi.org/10.1021/ct200501r

Goerigk L, Grimme S. A general database for main group thermochemistry, kinetics, and noncovalent interactions – assessment of common and reparameterized (meta-)GGA density functionals. J Chem Comput. 2010;6:107–26. https://doi.org/10.1021/ct090489g

Weymouth T, Couzinj EPA, Chen P, Reiher M. New benchmark set of transition-metal coordination reactions for the assessment of density functionals. J Chem Theory Comput. 2014;10:392–103.

Chabral S, Stoll H, Werner HJ, Leininger T. Analytic gradients for the combined sr-DFT/lr-MP2 method: application to weakly bound systems. Mol Phys. 2010;108:3373–82.

Mussard B, Szalay PG, Ángyán JG. Analytical energy gradients in range-separated hybrid density functional theory with random phase approximation. J Chem Theory Comput. 2014;10:1968–79.

Zhao Y, Truhlar DG. Benchmark databases for nonbonded interactions and their use to test density functional theory. J Chem Theory Comput. 2005;1:415–32. https://doi.org/10.1021/ct049851d

Chabral S, Jacquemin D, Adamo C, Stoll H, Leininger T. Communication: bond length alternation of conjugated oligomers: another step on the fifth rung of Perdew’s ladder of functional. J Chem Phys. 2010;133:151104.

Schwerdtfeger P, Pernpointner M, Laerdahl JK. The accuracy of current density functionals for the calculation of electric field gradients: a comparison with ab initio methods for HCl and CuCl. J Chem Phys. 1999;111:3357–64. https://doi.org/10.1063/1.479620

Sühnel T, Hermann H, Schwerdtfeger P. Solid state density functional calculations for the group 11 monohalides. J Phys Chem B. 2005;109:526–31. https://doi.org/10.1021/jp040685y

Giner E, Pradines B, Ferté A, Assaraf R, Savin A, Toulouse J. Curing basis-set convergence of wave-function theory using density-functional theory: a systematically improvable approach. J Chem Phys. 2018;149:194301.

Loos PP, Pradines B, Scemama A, Giner E, Toulouse J. Density-based basis-set incompleteness correction for GW methods. J Chem Theory Comput. 2020;16:1018–28.

Kohn W, Meir Y, Makarov DE. van der Waals energies in density functional theory. Phys Rev Lett. 1998;80:4153–6.

Chalasinski G, Szczęśniak MM. On the connection between the supermolecular Møller–Plesset treatment of the interaction energy and the perturbation theory of intermolecular forces. Mol Phys. 1988;63:205–24.

Gerber IC, Ángyán JG. London dispersion forces by range-separated hybrid density functional with second order perturbational corrections: the case of rare gas complexes. J Chem Phys. 2007;126:044103.

Dunning TH. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J Chem Phys. 1989;90:1007–23. https://doi.org/10.1063/1.456153

Woon DE, Dunning TH. Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon. J Chem Phys. 1993;98:1358–71. https://doi.org/10.1063/1.464303

Janesko BG, Henderson TM, Scuseria GE. Long-range-corrected hybrid density functionals including random phase approximation correlation: application to noncovalent interactions. J Chem Phys. 2009;131:034110.

Pernal K. Electron correlation from the adiabatic connection for multireference wave functions. Phys Rev Lett. 2018;120:013001. https://doi.org/10.1103/PhysRevLett.120.013001

Pastorczak E, Pernal K. Correlation energy from the adiabatic connection formalism for complete active space wave functions. J Chem Comput. 2010;5:1502–13. https://doi.org/10.1021/ct100489g

Goerigk L, Davidson ER. Studies in configuration interaction: the first-row diatomic hydrides. Phys Rev. 1969;183:23–30. https://doi.org/10.1103/PhysRev.183.23

Huron B, Malrieu JP, Rancurel P. Iterative perturbation calculations of ground and excited state energies from multiconfigurational zeroth-order wavefunctions. J Chem Phys. 1973;58:5745–59. https://doi.org/10.1063/1.1679199

Liu RF, Franzese CA, Malek R, Zuchowski PS, Ángyán JG, Szczęśniak MM, et al. Aurophilic interactions from wave function, symmetry-adapted perturbation theory, and rangehybrid approaches. J Chem Theory Comput. 2011;7:2399–407. https://doi.org/10.1021/ct1020243s

Pyykkö P. Strong closed-shell interactions in inorganic chemistry. Chem Rev. 1997;97:597–636. https://doi.org/10.1021/cr940396v

Schwerdtfeger P, Bruce AE, Bruce MRM. Theoretical studies on the photochemistry of the cis-to-trans conversion in dinuclear gold halide bis(diphenylphosphino)ethylene complexes. J Am Chem Soc. 1998;120:6587–97. https://doi.org/10.1021/ja973741h

Alam MM, Fromager E. Metallophilic interactions in A-frame molecules [S(MPH3)2] (M = Cu, Ag, Au) from range-separated density-functional perturbation theory. Chem Phys Lett. 2012;554:37–42.

Patkowski K. Chapter one – benchmark databases of intermolecular interaction energies: design, construction, and significance. In: Dixon DA, editor. Annu Rep Comput Chem. Volume 13. Amsterdam: Elsevier; 2017. p. 3–91.
162. Hedegård ED, Jensen HJA, Kongsted J. Polarizable embedding based on multiconfigurational methods: current developments and the road ahead. Int J Quant Chem. 2014;114:1102–7.
163. Schreiber M, Silva-Junior MR, Sauer SP, Thiel W. Benchmarks for electronically excited states: CASPT2, CC2, CCSD, and CC3. J Chem Phys. 2008;128:134110.
164. Hedegård ED. Assessment of oscillator strengths with multiconfigurational short-range density functional theory for electronic excitations in organic molecules. Mol Phys. 2017;115:26–38.
165. Kjellgren ER, Hedegård ED, Jensen HJA. Triplet excitation energies from multiconfigurational short-range density-functional theory response calculations. J Chem Phys. 2019;151:124113.
166. Rohrdanz MA, Martins KM, Herbert JM. A long-range-corrected density functional that performs well for both ground-state properties and time-dependent density functional theory excitation energies, including charge-transfer excited states. J Chem Phys. 2009;130:054112.
167. Laurent AD, Jacquemin D. TD-DFT benchmarks: a review. Int J Quant Chem. 2013;113:2019–39. https://doi.org/10.1002/qua.24438
168. Olsen JMH, Hedegård ED. Modeling the absorption spectrum of the permanganate ion in vacuum and in aqueous solution. Phys Chem Chem Phys. 2017;19:15870–5.
169. Van Gisbergen S, Groeneveld J, Rosa A, Snijders J, Baerends E. Excitation energies for transition metal compounds from time-dependent density functional theory. Applications to MnO$_4^-$, Ni(CO)$_4$, and Mn$_2$(CO)$_10$. J Phys Chem A. 1999;103:6835–44.
170. Rebolini E, Savin A, Toulouse J. Electronic excitations from a linear-response range-separated hybrid scheme. Mol Phys. 2013;111:1219–34.
171. Rebolini E, Toulouse J. Range-separated time-dependent density-functional theory with a frequency-dependent second-order Bethe-Salpeter correlation kernel. J Chem Phys. 2016;144:094107.
172. Rebolini E, Toulouse J, Teale AM, Helgaker T, Savin A. Excitation energies along a range-separated adiabatic connection. J Chem Phys. 2014;141:044123.
173. Rebolini E, Toulouse J, Teale AM, Helgaker T, Savin A. Excited states from range-separated density-functional perturbation theory. Mol Phys. 2015;113:1740–9.
174. Rebolini E, Teale AM, Helgaker T, Savin A, Toulouse J. Excitation energies from Görling-Levy perturbation theory along the range-separated adiabatic connection. Mol Phys. 2018;116:1443–51.
175. Hedegård ED, Toulouse J, Jensen HJA. Multiconfigurational short-range density-functional theory for open-shell systems. J Chem Phys. 2018;148:214103.
176. Rodríguez-Jiménez JA, Carreras A, Casanova D. Short-range DFT energy correction to multiconfigurational wave functions for open-shell systems. J Chem Phys. 2021;154:124116.
177. Franck O, Fromager E. Generalised adiabatic connection in ensemble density-functional theory for excited states: example of the H$_2$ molecule. Mol Phys. 2014;112:1684–701.
178. Senjean B, Knecht S, Jensen HJA, Fromager E. Linear interpolation method in ensemble Kohn–Sham and range-separated density-functional approximations for excited states. Phys Rev A. 2015;92:012518.
179. Goerigk L, Grimme S. Double-hybrid density functionals. WIREs Comput Mol Sci. 2014;4:576–600.
180. Kalai C, Toulouse J. A general range-separated double-hybrid density-functional theory. J Chem Phys. 2018;148:164105.
181. Kalai C, Mussard B, Toulouse J. Range-separated double-hybrid density-functional theory with coupled-cluster and random-phase approximations. J Chem Phys. 2019;151:074102.
182. Savin A. Models and corrections: range separation for electronic interaction-lessons from density functional theory. J Chem Phys. 2020;153:160901.

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