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A short-range gradient-corrected density functional in long-range coupled-cluster calculations for rare gas dimers

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A previously proposed scheme for coupling short-range (*sr*) density functionals with wavefunction-based long-range (*lr*) *ab initio* methods has been extended by (a) developing a new gradient-corrected *sr* functional of the Perdew–Burke–Ernzerhof (PBE) type and (b) introducing coupled-cluster (CC) approaches (CC with single and double excitations (CCSD), and with additional perturbative triples (CCSD(T))) at the *ab initio* side. The results show that mixing-in of *lr*-*ab initio* correlation helps to remove deficiencies of currently used density functionals for the treatment of van-der-Waals interactions. Compared to full *ab initio* calculations, the basis set dependence is weaker so that the accuracy of the mixed results surpasses that of the *ab initio* ones for basis sets of triple-zeta quality.

1. Introduction

Density functional (DFT) and wavefunction-based *ab initio* methods are to some extent complementary. DFT provides a very efficient (and yet reliable) treatment of dynamical correlation effects, in a formally independent-particle framework with modest basis sets. However, well-known shortcomings of DFT are the inability to treat near-degeneracy effects and long-range van-der-Waals (vdW) interactions correctly, and that there is no way of systematically checking or improving the results. On the other hand, *ab initio* methods allow an accurate treatment of static correlation and near-degeneracies as well as long-range correlation effects. There is a well established hierarchy of methods that allow one to approach the full configuration interaction (CI) and basis set limits systematically, but accurate calculations usually require large basis sets and are expensive. The question is whether it is possible to combine the merits (rather than the shortcomings) of both brands of methods.

The reason for the need of large basis sets and long configuration expansions in *ab initio* methods is the difficulty of explicitly describing the interelectronic cusp of the wavefunction. It has therefore been suggested[1–3] to relieve *ab initio* methods from the description of the cusp by splitting off the short-range (*sr*) part, containing the singularity at $r_{ij} = 0$, from the interelectronic interaction operator $1/r_{ij}$ of the Hamiltonian. The *sr* (exchange-)correlation contributions are then calculated by DFT, and *ab initio* methods are applied to the smooth long-range (*lr*) part only.

In this work we started with an already existing implementation of the short-range local density approximation to DFT (*sr*-LDA), coupled with long-range configuration interaction (*lr*-CI).[4–6] We added a new gradient-corrected short-range density functional, *cf.* section 2, in order to improve the performance of the method in the pure DFT limit, and extended the coupling to include Møller–Plesset second order perturbation theory (MP2), as well as the coupled-cluster method with single and double excitations (CCSD), and with additional perturbative triples (CCSD(T)), *cf.* section 3, in order to provide size-consistent methods on the *ab initio* side which faithfully describe long-range correlation effects. (In parallel to our work, *sr*-LDA/*lr*-MP2[7] and *sr*-LDA/*lr*-MCSCF[8] implementations have been developed very recently.) Our new *sr*-PBE/*lr*-CCSD(T) approach has been applied to the treatment of homo- and heteronuclear rare gas dimers, in order to get a consistent picture of its performance for van-der-Waals bound systems, *cf.* section 4. Some conclusions are given in section 5.

2. Functionals

The functionals to be described in this section refer to the following separation of the interelectronic interaction operator of the Hamiltonian into long- and short-range parts:

$$\begin{aligned} V_{\mathrm{ee}} &= V_{\mathrm{ee}}^{lr} + V_{\mathrm{ee}}^{sr}, \\ V_{\mathrm{ee}}^{lr} &= \sum_{i<j} \frac{\mathrm{erf}(\mu r_{ij})}{r_{ij}}, \\ V_{\mathrm{ee}}^{sr} &= \sum_{i<j} \frac{1-\mathrm{erf}(\mu r_{ij})}{r_{ij}}, \end{aligned} \tag{1}$$

where erf is the standard error function. The separation of the energy expression into a long-range part to be treated by wavefunction-based *ab initio* methods and a short-range part to be treated by DFT can readily be done using Levy's constrained-search formalism:[9]

$$E_0 = \min_{\rho}\left(\min_{\Psi\to\rho}\langle\Psi|T + V_{\mathrm{ne}} + V_{\mathrm{ee}}^{lr}|\Psi\rangle + E_0^{sr}[\rho]\right),$$

$$\begin{aligned} E_0^{sr}[\rho] &= \min_{\Psi\to\rho}\langle\Psi|T + V_{\mathrm{ee}}|\Psi\rangle - \min_{\Psi\to\rho}\langle\Psi|T + V_{\mathrm{ee}}^{lr}|\Psi\rangle \\ &= U_{\mathrm{H}}^{sr}[\rho] + E_{\mathrm{xc}}^{sr}[\rho]. \end{aligned} \tag{2}$$

Here, E_0 is the ground state energy, U_{H} is the Hartree energy, and E_{xc}^{sr} defines the functional to be approximated. Note that $E_{\mathrm{xc}}^{sr}[\rho]$ is no longer a functional of the electron density ρ alone, it also depends on the coupling parameter μ. For $\mu = 0$, its definition coincides with that of the usual density functional, but for $\mu > 0$ the dependence on ρ will change.

LDA approximations to $E_{\mathrm{xc}}^{sr}[\rho]$ are already available in the literature.[10,11] They rely on calculations for the homogeneous electron gas with long-range interelectronic interaction.

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According to eqn (2) differences have to be formed between the usual LDA exchange and correlation energies per particle and the corresponding μ-dependent functions for the homogeneous electron gas with long-range interaction. These quantities, $\varepsilon_x^{\mathrm{LDA}}(\mu,\rho)$ and $\varepsilon_c^{\mathrm{LDA}}(\mu,\rho)$, constitute the *sr*-LDA functional via $E_{xc}^{sr}[\rho] = \int d^3r\, \rho(\varepsilon_x^{\mathrm{LDA}}(\mu,\rho) + \varepsilon_c^{\mathrm{LDA}}(\mu,\rho))$.

Several strategies have been suggested for introducing a gradient correction to the *sr* exchange functional.[12–14] Here, we adopt (and modify) the PBE-like construction of ref. 14. The original functional of Perdew, Burke and Ernzerhof[15] reads

$$\begin{aligned} E_x^{\mathrm{PBE}} &= \int d^3r\, \rho \varepsilon_x^{\mathrm{LDA}}(\rho) F_x(s), \\ F_x(s) &= 1 + \kappa - \frac{\kappa}{1 + bs^2/\kappa}, \\ s &= \frac{|\nabla\rho|}{2k_F\rho}, \end{aligned} \tag{3}$$

where $k_F = (3\pi^2\rho)^{1/3}$. The parameters κ and b were derived from the Lieb–Oxford bound and from the requirement that the gradient coefficient for exchange cancels that for correlation. They have values of $\kappa^{\mathrm{PBE}} = 0.840$ and $b^{\mathrm{PBE}} = 0.219\,51$. In the short-range case, $\varepsilon_x^{\mathrm{LDA}}(\rho)$, as well as the constants κ and b in F_x should become μ-dependent, *i.e.* $\varepsilon_x^{\mathrm{LDA}}(\rho) \to \varepsilon_x^{\mathrm{LDA}}(\mu,\rho)$, $\kappa \to \kappa(\mu)$, $b \to b(\mu)$. In test calculations, we found that E_x^{PBE} is only weakly dependent on $\kappa(\mu)$, so we retained the original PBE value of κ for all μ. For $b(\mu)$, which is the gradient coefficient in the expansion $F_x = 1 + bs^2 + \ldots$, Toulouse *et al.*[14] inserted a function $b^{\mathrm{T}}(\tilde{\mu})$ ($\tilde{\mu} = \mu/(2k_F)$), analytically determined by expansion of the short-range exchange hole to second order in terms of the density gradient:

$$b^{\mathrm{T}}(\tilde{\mu}) = \frac{-c_1 + c_2 e^{1/(4\tilde{\mu}^2)}}{c_3 + 54c_4 e^{1/(4\tilde{\mu}^2)}}, \tag{4}$$

where $c_1 = 1 + 22\tilde{\mu}^2 + 144\tilde{\mu}^4$, $c_2 = 2\tilde{\mu}^2(-7 + 72\tilde{\mu}^2)$, $c_3 = -864\tilde{\mu}^4(-1 + 2\tilde{\mu}^2)$ and $c_4 = \tilde{\mu}^2\{-3 - 24\tilde{\mu}^2 + 32\tilde{\mu}^4 + 8\tilde{\mu}\sqrt{\pi}\ \mathrm{erf}[1/(2\tilde{\mu})]\}$. For $\mu = 0$, this function does not reduce to PBE's original value of b^{PBE}, since the latter was not derived from the gradient expansion of the exchange energy but rather was connected to the gradient expansion of the correlation energy. Thus, in order to make our new *sr*-PBE functional compatible with the original PBE one for $\mu = 0$, we multiply $b^{\mathrm{T}}(\tilde{\mu})$ by a scaling factor $b^{\mathrm{PBE}}/b^{\mathrm{T}}(0)$. Furthermore, test calculations show that no improvement over a simple LDA is obtained with $b^{\mathrm{T}}(\tilde{\mu})$ for large μ. We therefore introduce a cut-off function for $b^{\mathrm{T}}(\tilde{\mu})$ enhancing its damping for $\mu \to \infty$. This cut-off function has been fitted to the *sr* part of the non-local HF exchange energy of the He atom (as to one of the simplest systems with inhomogeneous density). It turns out that the μ-dependence of the He *sr* exchange energy (which we calculated pointwise with the aug-cc-pVQZ basis set[16]) can be well described with a simple Gaussian cut-off function, $\exp(-\alpha_x\tilde{\mu}^2)$, inserted in $b(\mu)$. An optimum value of $\alpha_x = 19.0$ was determined by minimising the integral $\int_0^{10} |E_x^{\mathrm{LDA}}(sr) - E_x^{\mathrm{HF}}(sr)| d\mu$. Accordingly, we suggest the use of

$$b(\mu) = \frac{b^{\mathrm{PBE}}}{b^{\mathrm{T}}(0)} b^{\mathrm{T}}(\tilde{\mu}) \exp(-\alpha_x\tilde{\mu}^2) \tag{5}$$

in eqn (3); with this one-parameter fit, we interpolate between the PBE value of b at $\mu = 0$ and $b = 0$ (*i.e.*, a purely LDA description of *sr*-exchange) in the limit $\mu \to \infty$.

For the *sr* correlation functional, we are aware of only two papers addressing the question of how to go beyond LDA.[3,14] The latter of these papers also gives a *sr*-GGA functional of the PBE type. The original PBE correlation functional[15] reads

$$\begin{aligned} E_c^{\mathrm{PBE}} &= \int d^3r\, \rho[\varepsilon_c^{\mathrm{LDA}}(\rho) + H(\rho,t)], \\ H(\rho,t) &= \gamma \ln\left\{1 + \frac{\beta t^2}{\gamma}\left[\frac{1 + At^2}{1 + At^2 + A^2t^4}\right]\right\}, \\ A &= \frac{\beta}{\gamma(\exp(-\varepsilon_c^{\mathrm{LDA}}/\gamma) - 1)}, \\ t &= \frac{|\nabla\rho|}{2k_s\rho}, \end{aligned} \tag{6}$$

where $k_s = \sqrt{4k_F/\pi}$. The parameters β and γ were determined from the gradient expansion of the correlation energy of the homogeneous electron gas and from the appropriate expression for the high-density limit. They have values of $\beta^{\mathrm{PBE}} = 0.066\,725$ and $\gamma^{\mathrm{PBE}} = 0.031\,091$. In the short-range case, $\varepsilon_c^{\mathrm{LDA}}(\rho)$ as well as the constants β, γ in H should become μ-dependent, *i.e.* $\varepsilon_c^{\mathrm{LDA}}(\rho) \to \varepsilon_c^{\mathrm{LDA}}(\mu,\rho)$, $\beta \to \beta(\mu)$, $\gamma \to \gamma(\mu)$. It has already been argued in ref. 14 that $\gamma(\mu)$ can be kept constant over μ. We therefore set $\gamma = \gamma^{\mathrm{PBE}}$. For $\beta(\mu)$, which is the gradient coefficient in the expansion $H = \beta t^2 + \ldots$, we first tried to redo the calculation of Ma and Brueckner[17] for the long-range Coulomb interaction. The calculation of ref. 17 is correct to order e^2. However, due to the absence of the singularity in the long-range interaction, the $O(e^2)$ contribution to β vanishes, *cf.*ref. 18. This would mean that for the short-range functional β becomes independent of μ. Unfortunately, this approximation is not optimum when applied to the calculation of the correlation energy of the He atom, *e.g.* Specifically, we calculated the *sr*-contribution to the correlation energy of He, in CI calculations with the aug-cc-pV5Z basis set,[16] as a function of μ. In order to fit this curve, we have to satisfy the condition $\beta(\mu) \to 0$ for $\mu \to \infty$. This means that a pure *sr*-LDA approximation without corrections is accurate for $\mu \to \infty$, which is in line with analytic results for this limit of ref. 3. Thus, as in the case of exchange, we have to find a function which interpolates between the standard PBE limit for $\mu = 0$ and zero for $\mu \to \infty$. However, we find that a simple Gaussian cut-off function does not lead to a satisfactory fit of the *ab initio* CI results for the *sr* correlation energy of He for intermediate values of μ; instead, a parametrisation according to

$$\beta(\mu) = \beta^{\mathrm{PBE}}\left(\frac{\varepsilon_c^{\mathrm{LDA}}(\mu,\rho)}{\varepsilon_c^{\mathrm{LDA}}(0,\rho)}\right)^{\alpha_c}, \tag{7}$$

gives much better results. An optimum value of $\alpha_c = 2.83$ was determined by minimising the integral $\int_0^{10} |E_c^{\mathrm{LDA}}(sr) - E_c^{\mathrm{CI}}(sr)| d\mu$. In summary, we generated PBE-like exchange and correlations functionals for use in *sr*-DFT/*lr*-*ab initio* calculations, which rely on data for the homogeneous electron gas and the He atom (with μ-dependent interelectronic interaction) and contain two parameters for fitting the cut-off of the gradient coefficients of exchange and correlations for large μ, α_x and α_c.

Let us now consider the performance of the various *sr* exchange functionals. Fig. 1 assesses the reliability of the *sr*-LDA approximation for the He atom. The quantity to be approximated is the non-local short-range exchange energy $E_x^{\mathrm{HF}}(sr)$ (solid curve, right scale); it is equal to the full HF exchange energy E_x^{HF}, at $\mu = 0$ (where the long-range part, $E_x^{\mathrm{HF}}(lr)$, vanishes) and gradually diminishes towards the $\mu \to \infty$ limit (where $E_x^{\mathrm{HF}}(lr) = E_x^{\mathrm{HF}}$). Ideally, the ratio of the LDA approximation for *sr*-exchange to the reference quantity, $E_x^{\mathrm{LDA}}(sr)/E_x^{\mathrm{HF}}(sr)$ (dashed curve, left scale), should be 1 for all μ. However, standard LDA underestimates the full HF exchange by 14% for He, and therefore the curve starts with 0.86 at $\mu = 0$. It is important to note that the quality of the

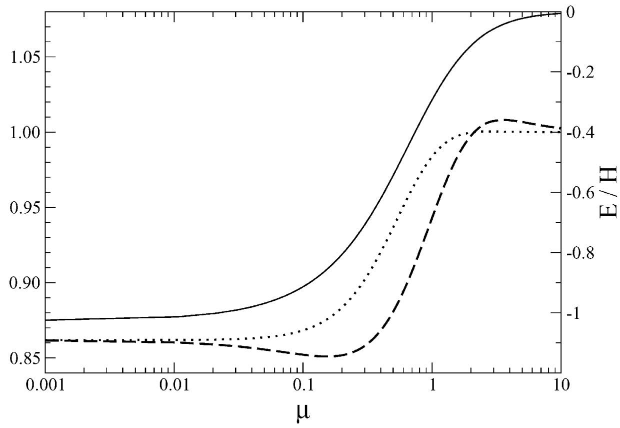

Fig. 1 Approximations for the exchange energy of He (aug-cc-pVQZ basis set), as a function of the coupling parameter μ: short-range HF exchange energy, $E_x^{HF}(sr)$ (solid curve, right scale), the ratio of the short-range LDA exchange energy, $E_x^{LDA}(sr)$, to $E_x^{HF}(sr)$ (dashed curve, left scale), and the ratio of the mixed *sr*-LDA/*lr*-HF approximation, $E_x^{LDA}(sr) + E_x^{HF}(lr)$, to the full HF exchange energy, E_x^{HF} (dotted curve, left scale).

approximation does not remain at this level for all μ, but gradually improves to 1, with a deviation of $<1\%$ for $\mu \geq 2$. This is in line with the findings of other workers:[3,19] it has been shown that LDA exchange becomes exact in the limit $\mu \to \infty$. It is to be noted, furthermore, that $E_x^{LDA}(sr)$ is coupled to $E_x^{HF}(lr)$ in our combined *sr*-DFT/*lr*-*ab initio* approach, and this mixing-in of the exact *lr*-HF exchange favourably affects the ratio of the approximation of full exchange to the reference value, $(E_x^{LDA}(sr) + E_x^{HF}(lr))/E_x^{HF}$ (dotted curve, left scale in Fig. 1). It starts again at the standard LDA value for He, of 0.86, at $\mu = 0$, but reaches the ideal value of unity even faster than $E_x^{LDA}(sr)/E_x^{HF}(sr)$, with a deviation of $<1\%$ already for $\mu \geq 1$. Fig. 2 shows, again for He, the μ-dependence of the exchange energy with the PBE-like functionals of ref. 14 (PBE^T) and of the present work (PBE). Again, we plot the ratio of the exchange energy in the combined *sr*-DFT/*lr*-HF approach to the HF reference value, $(E_x^{PBE}(sr) + E_x^{HF}(lr))/E_x^{HF}$, which ideally should be equal to unity over the whole range of μ. The results with the PBE-like functional of ref. 14 are seen to approximately halve the LDA errors, while our new modified PBE functional starts with the much smaller error of the standard PBE functional ($\approx 1\%$) at $\mu = 0$, and remains approximately constant over the whole range $0 \leq \mu < \infty$. Of course, the near-constancy with μ is due to the construction of our modified PBE functional, by fitting to the μ-dependence of $E_x^{HF}(sr)$ for the He atom. However, Fig. 3 shows that other systems like Ne^{8+} and Ne are also well described by our functional, with deviations of $\leq 2.5\%$ for $E_x^{PBE}(sr) + E_x^{HF}(lr)$ from the full non-local HF exchange, over the whole range of μ.

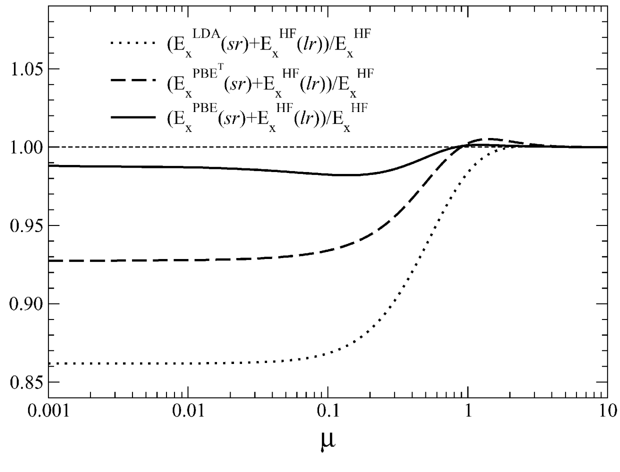

Fig. 2 Approximations for the exchange energy of He (aug-cc-pVQZ basis set), as a function of the coupling parameter μ: ratio of the mixed *sr*-DFT/*lr*-HF exchange approximation, $E_x^{DFT}(sr) + E_x^{HF}(lr)$, to the full HF exchange energy, E_x^{HF}, for DFT = LDA,[10] PBE^T,[14] and our modified PBE-like functional (PBE).

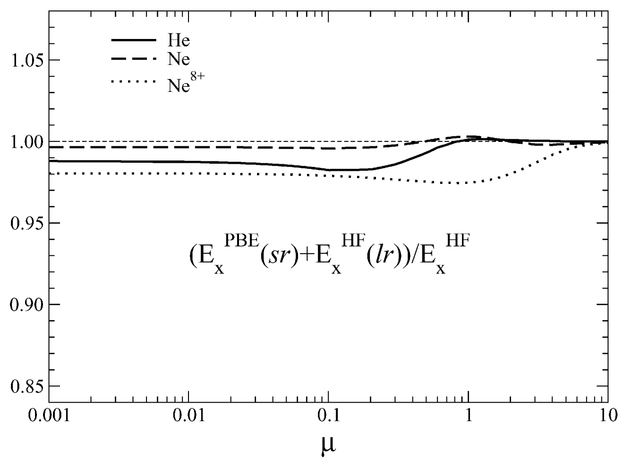

Fig. 3 Approximations for the exchange energy of He, Ne, Ne^{8+} (aug-cc-pVQZ basis sets), as a function of the coupling parameter μ: $(E_x^{PBE}(sr) + E_x^{HF}(lr))/E_x^{HF}$ is the ratio of the mixed *sr*-DFT/*lr*-HF exchange approximation, with our modified PBE-like functional, to the full HF exchange energy.

Let us finally consider the performance of the various *sr* correlation functionals. Fig. 4 assesses the reliability of the *sr*-LDA approximation for the He atom. The quantity to be approximated is the short-range correlation energy $E_c^{CI}(sr)$ (solid curve, right scale), which we calculated as the difference between the CI energy, E_c^{CI}, of the He atom with full interaction and the corresponding one for the long-range interaction, *cf.* above. It is equal to E_c^{CI} for $\mu = 0$ (where the *lr*-interaction vanishes) and approaches zero for $\mu \to \infty$ (where the *lr*-interaction takes over). Ideally, the *sr*-LDA approximation should reproduce $E_c^{CI}(sr)$, *i.e.* the ratio $E_c^{LDA}(sr)/E_c^{CI}(sr)$ (dashed curve, left scale) should be close to unity, for all μ. However, for $\mu = 0$ we observe the well-known overestimation of the exact He correlation energy by standard LDA, by nearly a factor of 3, but (as for exchange) a significant increase of the accuracy of the LDA approximation is found for $\mu > 0$: $E_c^{LDA}(sr)/E_c^{CI}(sr)$ approaches values of 1 ± 0.05 for $\mu \geq 2$. This improvement of LDA when applied to *sr* interaction only, has consequences also for the treatment of the full correlation energy in the *sr*-LDA/*lr*-*ab initio* approach, $E_c^{LDA}(sr) + E_c^{CI}(lr)$.

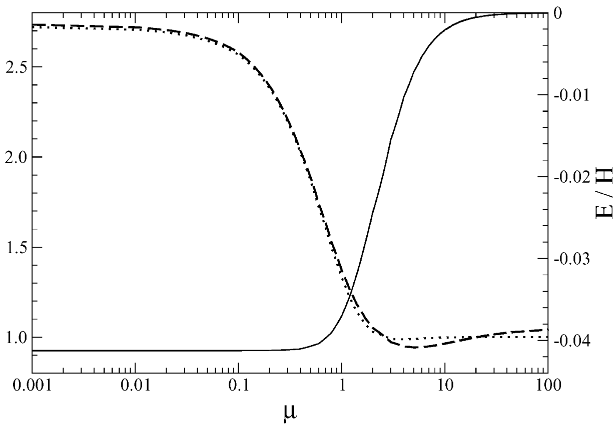

Fig. 4 Approximations for the correlation energy of He (aug-cc-pV5Z basis set), as a function of the coupling parameter μ: short-range correlation energy from CI calculations, $E_c^{CI}(sr)$ (solid curve, right scale), the ratio of the short-range LDA correlation energy, $E_c^{LDA}(sr)$, to $E_c^{CI}(sr)$ (dashed curve, left scale), and the ratio of the mixed *sr*-LDA/*lr*-CI approximation, $E_c^{LDA}(sr) + E_c^{CI}(sr)$, to the full CI correlation energy, E_c^{CI} (dotted curve, left scale).

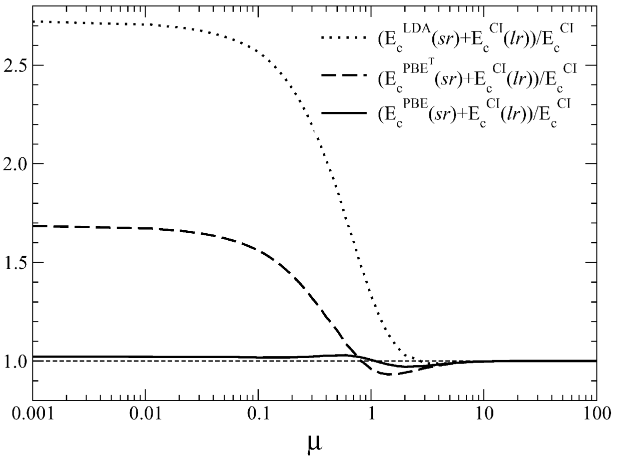

Fig. 5 Approximations for the correlation energy of He (aug-cc-pV5Z basis set), as a function of the coupling parameter μ: ratio of the mixed *sr*-DFT/*lr*-CI correlation approximation, $E_c^{\mathrm{DFT}}(sr) + E_c^{\mathrm{CI}}(lr)$, to the full CI correlation energy, E_c^{CI}, for DFT = LDA,[10] PBE$^{\mathrm{T}}$,[14] and our modified PBE-like functional (PBE).

The ratio of this quantity to E_c^{CI} (dotted curve, left scale), which should ideally be equal to unity, independent of μ, rapidly improves from the standard LDA value of ≈ 3 at $\mu = 0$, to values around 1 for $\mu > 0$, with deviations from the exact value of $<10\%$ for $\mu > 1.5$. Fig. 5 compares the *sr*-LDA functional with the *sr*-PBE functionals of ref. 14 and the present work. As for exchange, the *sr*-PBE functional of ref. 14 yields values half-way between LDA and the exact ones, when applied with *lr*-CI for the determination of the He correlation energy. Our own *sr*-PBE modification yields values within 3% of the exact He correlation energy for all values of μ. This accuracy somewhat deteriorates (to $\approx 10\%$) for other systems not used for fitting, like Ne^{8+} and Ne, *cf.* Fig. 6, but this is partly due to the fact that also the errors of the standard PBE functional (for $\mu = 0$) increase for these cases (to 5% for Ne, 9% for Ne^{8+}).

3. Implementation

We implemented the *sr*-DFT/*lr*-*ab initio* coupling within the MOLPRO 2002 *ab initio* suite of programs.[20] The implementation is currently restricted to the closed-shell case. (Extension to the open-shell case would require spin-polarised *sr* correlation functionals which are currently not available.) The available (non-spin-polarised) functionals are *sr*-LDA, in the parametrisation of Savin *et al.*,[10,11] and our own parametrisation of *sr*-PBE, the exchange part of which was obtained as a modification of the PBE-like GGA functional of ref. 14. These *sr* functionals can readily be used for orbital optimisation in a hybrid *sr*-DFT/*lr*-HF calculation. Based on the optimised orbitals, a *sr*-DFT/*lr*-*ab initio* calculation including *lr* correlation can be performed at the MP2, CCSD, CCSD(T),[21,22] or (internally contracted) MRCISD[23,24] levels. Usually, the resulting density is very similar to the input density from *sr*-DFT/*lr*-HF, and the influence of a density update on properties is negligible as shown in test calculations. However, this may be different in non-single-reference cases, and in these cases the calculation of *lr* correlation should be repeated with an updated density for the *sr*-DFT part. For single-reference cases without density update, the *sr*-DFT exchange can optionally be replaced by its non-local HF counterpart (the results with this option are denoted DFT(c) in section 4).

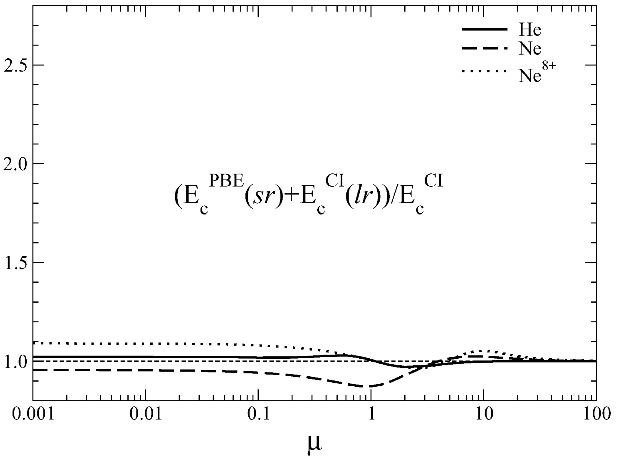

Fig. 6 Approximations for the correlation energy of He, Ne, Ne^{8+} (aug-cc-pVQZ basis sets, with additional functions for core-valence correlation in the case of Ne), as a function of the coupling parameter μ: $(E_c^{\mathrm{PBE}}(sr) + E_c^{\mathrm{CI}}(lr))/E_c^{\mathrm{CI}}$ is the ratio of the mixed *sr*-DFT/*lr*-CI correlation approximation (*lr*-CCSD(T) in the case of Ne), with our modified PBE-like functional, to the full CI or CCSD(T) correlation energy.

4. Results and discussion

The calculation of van-der-Waals (vdW) interactions is a notorious case where DFT with current local and semi-local density functionals fails and where a long-range *ab initio* correction may be of help. In order to systematically study the usefulness of our mixed *sr*-DFT/*lr*-*ab initio* approach for this case, we applied it to all homo- and heteronuclear rare gas dimers of the He, Ne, Ar, Kr, and Xe atoms. (These calculations supplement *sr*-LDA/*lr*-MP2 calculations for the homonuclear dimers He_2–Kr_2 which have been published during the course of our work.[7])

The first problem encountered is the question of how to choose the coupling parameter μ, within the *sr*-DFT/*lr*-*ab initio* calculations. This choice should follow from the general idea that intraatomic effects are treated by DFT, while the *ab initio* formalism is invoked for interatomic interactions only. As is apparent from eqn (1), the spatial coupling of DFT and *ab initio* is controlled by the cut-off function $\mathrm{erf}(\mu r_{ij})$. Hence, μ plays the role of an inverse distance, $\mu = 1/R_{ij}$, where interelectronic interactions with $r_{ij} < R_{ij}$ are in the DFT realm, while the *ab initio* treatment comes into play for $r_{ij} > R_{ij}$. (Of course, this is not a strict separation, since the transition is a gradual one; at $r_{ij} = R_{ij}$, $\approx 84\%$ of the interelectronic interaction is attributed to *lr*, but still a 11% *lr* contribution is obtained at $r_{ij} = R_{ij}/10$.)

For the homonuclear rare gas dimers, the length scales are set by the interatomic distances R_e; $R_{\mathrm{vdW}} = R_e/2$ can be defined as the van-der-Waals radii of the atoms. Thus, it seems natural to set $\mu = 1/R_{\mathrm{vdW}} = 2/R_e$. With this choice, $\approx 99\%$ of the truly interatomic interaction at $r_{ij} = R_e$ is treated at the *lr*-*ab initio* level. Note, however, that this does not mean that DFT has no chance to contribute to bonding any more: DFT contributions will certainly arise from the internuclear region where the densities of the two atoms start to overlap. Note also that the $\langle r \rangle$ expectation values of the *n*s and *n*p orbitals of the rare gas (Rg) atoms are considerably smaller than R_{vdW}, *e.g.* for Ar by factors of 2.5 and 2.1. At such distances, 60% and 50% of the interelectronic interaction are classified as *sr* when choosing $\mu = 1/R_{\mathrm{vdW}}$. It does not come as a surprise then that intraatomic properties of the Rg atoms are strongly influenced by DFT with this choice of μ. Even the atomic polarisabilities (which are on the average too high by 5%, in standard PBE calculations with aug-cc-pVTZ basis sets) remain more similar to pure DFT than to pure CCSD(T) when mixing-in *lr*-CCSD(T) with $\mu = 1/R_{\mathrm{vdW}}$.

For the heteronuclear dimers, two different vdW radii are involved, but a common μ is needed. For consistency reasons, we stick to the prescription $\mu = 2/R_e$ also in this case.

It might be argued that these choices of μ, although physically sensible, are not really uniquely fixed and not *a priori* better than other similar choices. Moreover, in a calculation with more than one vdW pair, we would have to choose a common μ anyway which necessarily cannot be optimum for both individual pairs (even if we would know this optimum). We therefore consider in the following also the use of an average μ value, with $\bar{\mu} = 2/\bar{R}_e = 0.290\,95$ (where $\bar{R}_e$ is averaged over the Rg_2 pairs (Rg = He,..., Xe)), for all RgRg′ dimers.

Results with the choice $\mu = 2/R_e$ are collected for bond lengths R_e, dissociation energies D_e, and harmonic wavenumbers ω_e, in Tables 1–3, respectively. These data were derived from seven points equally spaced with distances of 0.1 Å on the potential curve around the mininum, by means of a least-squares-fit to a function of the form $\sum_{i=-1}^{4} a_i R^i$. The results of Tables 1–3 have been obtained with the highest-level methods which we have at our disposal, *i.e.*, our new PBE-like functional at the short-range side, and the CCSD(T) method for long-range effects. In order to monitor the basis-set dependence of our results, we compare values obtained with two different basis sets, aug-cc-pVTZ and aug-cc-pVQZ.[16,25–27] We consider a triple-zeta quality of the basis set to be necessary for obtaining converged DFT results. Much larger basis sets are needed, on the other hand, for achieving basis set convergence in CCSD(T) calculations, but we cannot go beyond quadruple-zeta quality (*i.e.* include functions with $l > 4$) because of technical reasons in the DFT code we use.[20] These basis sets were used in all-electron calculations for He, Ne, Ar, while corresponding valence basis sets for the $(n-1)$spd $n$sp shells in connection with small-core ECPs[28] were used for Kr and Xe. Basis set superposition errors were dealt with using the counterpoise method.[29] All valence ns, np orbitals were correlated in CCSD(T). In each case, the results with the mixed method were compared to the limiting cases of pure PBE calculations ($\mu \to 0$) and standard CCSD(T) calculations ($\mu \to \infty$). Finally, comparison is also made to experimental data,[30,31] and mean absolute errors (MAE) from these data are given for R_e, D_e, and ω_e. Here, ω_e was determined from the zeroth-order coefficient of the Dunham expansion.

The following observations can be made from Tables 1–3. Firstly, the coupled *sr*-PBE/*lr*-CCSD(T) results are accurate to $\approx$0.04 Å for R_e, $\approx$15 μE_h for D_e, and 3 cm^{-1} for ω_e on the average, with maximum errors of 0.2 Å for $R_e(He_2)$, 38 μE_h for D_e(KrXe), and 11 cm^{-1} for $\omega_e(He_2)$. Secondly, the basis-set dependency of the results is very weak: the MAEs change by $\approx$0.003 Å for R_e, 3 μE_h for D_e, and 0.1 cm^{-1} for ω_e. (Additional calculations using aug-cc-pV5Z basis sets without h functions confirm these findings.) Thirdly, while the basis set dependency is similar as in pure PBE calculations, the mixed *sr*-PBE/*lr*-CCSD(T) method significantly outperforms the pure PBE one: bond-length errors are smaller by a factor of four, errors of binding energies by an order of magnitude. Moreover, the trends are much more consistent than in pure PBE calculations which strongly overestimate binding in He_2 and Ne_2 (by up to a factor of three), but underestimate it in Ar_2, Kr_2, and Xe_2 (also by up to a factor of three). Finally, the mixed *sr*-PBE/*lr*-CCSD(T) method also significantly outperforms the pure CCSD(T) method, which has a much stronger basis-set dependency, with errors in R_e and D_e changing by about a factor two when improving the basis quality from triple-zeta to quadruple-zeta. The MAEs with *sr*-PBE/*lr*-CCSD(T) are smaller by factors of four for R_e and six for D_e as compared to pure CCSD(T) calculations with triple-zeta basis; triple-zeta *sr*-PBE/*lr*-CCSD(T) even surpasses the accuracy of the pure CCSD(T) results with quadruple-zeta basis by a factor of two for R_e and three for D_e. Summarising, *sr*-PBE/*lr*-CCSD(T) seems to provide a means to accurately describe vdW bonds with moderate

Table 1 Bond lengths R_e (Å) of the Rg dimers from standard DFT calculations with PBE functional, standard CCSD(T) calculations and mixed *sr*-PBE/*lr*-CCSD(T) calculations. In each case, results with aug-cc-pVTZ and aug-cc-pVQZ basis sets are given in the form .../... Experimental data (Exp) are taken from ref. 30 and 31

	PBE	PBE/CCSD(T)	CCSD(T)	Exp
He_2	2.754/2.754	3.155/3.170	3.041/3.011	2.970
HeNe	2.928/2.912	3.097/3.101	3.122/3.074	3.031
HeAr	3.457/3.420	3.511/3.540	3.592/3.541	3.480
HeKr	3.631/3.634	3.722/3.726	3.815/3.748	3.693
HeXe	3.901/3.901	3.994/3.994	4.138/4.059	3.978
Ne_2	3.122/3.092	3.050/3.087	3.218/3.150	3.091
NeAr	3.557/3.541	3.417/3.437	3.615/3.547	3.489
NeKr	3.733/3.727	3.577/3.577	3.808/3.719	3.621
NeXe	3.958/3.950	3.782/3.773	4.087/3.981	3.861
Ar_2	4.021/4.000	3.738/3.745	3.894/3.827	3.756
ArKr	4.179/4.173	3.870/3.866	4.038/3.959	3.881
ArXe	4.406/4.396	4.060/4.059	4.261/4.178	4.067
Kr_2	4.330/4.336	3.993/3.975	4.169/4.076	4.008
KrXe	4.548/4.551	4.178/4.159	4.379/4.280	4.174
Xe_2	4.766/4.762	4.354/4.334	4.576/4.471	4.363
MAE	0.186/0.183	0.042/0.045	0.153/0.077	

Table 2 Dissociation energies D_e (μE_h) of the Rg dimers from standard DFT calculations with PBE functional, standard CCSD(T) calculations and mixed *sr*-PBE/*lr*-CCSD(T) calculations. In each case, results with aug-cc-pVTZ and aug-cc-pVQZ basis sets are given in the form .../... Experimental data (Exp) are taken from ref. 30 and 31

	PBE	PBE/CCSD(T)	CCSD(T)	Exp
He_2	116.1/119.9	21.4/21.7	27.1/29.6	34.7
HeNe	150.5/149.7	45.2/49.5	47.1/56.0	65.5
HeAr	136.1/146.9	80.5/78.5	71.0/81.1	91.6
HeKr	137.0/141.4	79.0/79.6	70.6/82.8	91.1
HeXe	131.2/135.5	73.4/74.9	64.8/77.0	86.6
Ne_2	177.4/180.4	100.7/115.8	81.7/105.9	133.8
NeAr	197.3/202.0	197.6/204.8	137.9/171.3	214.0
NeKr	215.2/208.9	207.9/229.0	143.3/184.0	226.7
NeXe	224.0/217.1	212.4/241.0	138.9/181.6	235.0
Ar_2	201.1/224.4	468.0/454.0	325.2/378.8	453.6
ArKr	222.1/235.3	540.8/542.0	375.8/449.2	575.4
ArXe	230.4/243.8	600.2/603.1	410.1/493.0	597.3
Kr_2	247.9/251.4	643.7/667.4	449.5/550.2	637.2
KrXe	260.0/263.8	744.9/776.9	508.6/624.8	739.4
Xe_2	273.8/278.4	860.0/899.8	595.7/734.7	894.0
MAE	189.7/187.9	17.3/14.3	108.6/58.4	

Table 3 Harmonic wavenumbers ω_e (cm^{-1}) of the Rg dimers from standard DFT calculations with PBE functional, standard CCSD(T) calculations and mixed *sr*-PBE/*lr*-CCSD(T) calculations. In each case, results with aug-cc-pVTZ and aug-cc-pVQZ basis sets are given in the form .../... Experimental data (Exp) are taken from ref. 30 and 31

	PBE	PBE/CCSD(T)	CCSD(T)	Exp
He_2	67.6/69.3	22.1/21.9	29.0/30.4	33.2
HeNe	53.3/54.4	25.9/27.3	29.1/32.2	35.0
HeAr	42.0/50.1	30.4/28.2	30.2/32.4	34.8
HeKr	41.7/41.9	27.0/26.5	27.6/30.4	32.0
HeXe	38.2/38.6	24.1/24.1	24.4/27.2	29.1
Ne_2	34.2/34.6	25.5/26.9	21.5/25.8	28.5
NeAr	28.8/29.6	29.0/27.5	22.1/25.1	28.2
NeKr	25.4/24.7	24.3/25.6	19.3/22.6	26.2
NeXe	23.3/23.0	22.8/24.7	17.2/20.4	24.3
Ar_2	21.2/22.5	30.8/29.2	25.8/27.9	30.9
ArKr	18.4/18.9	27.3/26.9	22.8/25.2	27.9
ArXe	16.8/17.4	26.1/25.8	21.3/23.7	27.1
Kr_2	15.2/14.9	22.9/23.6	19.3/21.8	23.6
KrXe	13.4/13.2	21.4/22.2	17.7/20.1	22.7
Xe_2	11.5/11.4	19.8/20.5	16.2/18.5	20.9
MAE	9.6/10.4	3.1/3.0	5.4/2.7	

Table 4 Bond lengths R_e (Å), dissociation energies D_e (μE_h) and harmonic wavenumbers ω_e (cm^{-1}) of the Rg dimers from *sr*-PBE/*lr*-CCSD(T) calculations with an average value of the coupling parameter, $\bar{\mu}$ = 0.290 95, *cf.* text. In each case, results with aug-cc-pVTZ and aug-ccpVQZ basis sets are given in the form …/…

	R_e	D_e	ω_e
He_2	3.085/3.124	17.5/17.0	21.4/19.7
HeNe	2.990/3.009	43.7/47.2	30.0/30.2
HeAr	3.496/3.529	78.5/75.6	30.5/27.9
HeKr	3.727/3.730	79.8/80.6	27.0/26.6
HeXe	4.025/4.021	77.6/80.3	24.3/24.6
Ne_2	2.970/3.023	106.5/118.6	32.0/30.3
NeAr	3.405/3.425	196.7/202.5	29.3/28.0
NeKr	3.575/3.575	207.7/228.9	24.3/25.7
NeXe	3.807/3.795	212.2/241.2	22.0/23.9
Ar_2	3.741/3.746	475.4/464.2	30.8/29.3
ArKr	3.875/3.869	557.5/564.3	27.3/27.1
ArXe	4.069/4.065	626.8/640.3	26.1/26.0
Kr_2	3.998/3.979	673.0/704.3	23.0/23.8
KrXe	4.183/4.163	776.1/818.3	21.5/22.3
Xe_2	4.363/4.340	912.3/970.7	19.8/20.7
MAE	0.040/0.042	21.3/26.1	3.0/2.8

Table 5 Bond lengths R_e (Å), dissociation energies D_e (μE_h) and harmonic wavenumbers ω_e (cm^{-1}) of the Rg dimers from *sr*-PBE/*lr-ab initio* calculations with aug-cc-pVTZ basis sets. In each case, results with *lr*-CCSD and *lr*-MP2 are given in the form …/…

	R_e	D_e	ω_e
He_2	3.155/3.218	21.4/15.4	22.1/18.7
HeNe	3.097/3.139	45.2/35.2	25.9/22.5
HeAr	3.511/3.546	80.3/64.6	30.3/27.7
HeKr	3.723/3.758	78.7/64.3	26.9/24.5
HeXe	3.995/4.028	73.0/61.0	24.0/22.1
Ne_2	3.051/3.074	100.6/84.1	25.5/23.3
NeAr	3.418/3.435	197.1/171.3	28.9/27.6
NeKr	3.578/3.596	207.1/182.4	24.2/23.0
NeXe	3.783/3.798	211.4/190.4	22.8/21.9
Ar_2	3.739/3.762	466.2/400.6	30.7/29.1
ArKr	3.871/3.894	538.1/466.4	27.2/25.8
ArXe	4.061/4.082	596.6/524.1	26.0/24.8
Kr_2	3.994/4.016	640.0/558.8	22.9/21.7
KrXe	4.179/4.200	739.1/653.5	21.4/20.4
Xe_2	4.355/4.374	853.3/760.0	19.7/18.9
MAE	0.041/0.052	17.2/56.3	3.2/4.8

basis sets and is, in that respect, superior to the pure PBE and CCSD(T) limits.

Let us now discuss how sensitive the *sr*-DFT/*lr-ab initio* results are with respect to the coupling parameter μ and the methods to be used for the DFT and the *ab initio* parts of the calculations. As to the first point, Table 4 shows results of *sr*-PBE/*lr*-CCSD(T) calculations with a common value $\bar{\mu}$ (*cf.* above) for all of the RgRg′ pairs. When comparing with the corresponding results in Tables 1–3, which were obtained with individual μ values for each RgRg′ pair, it is seen that there are only marginal changes for the MAEs of R_e and ω_e; only the D_e MAE deteriorates by $\approx 10\ \mu E_\mathrm{h}$ (to $\approx 25\ \mu E_\mathrm{h}$).

What about the effect of reducing the theoretical level at the *ab initio* side? Quite remarkably, triple excitations which are very important in pure CCSD(T) calculation (their omission enlarges the MAE values by ≈0.07 Å for R_e, $\approx 60\ \mu E_\mathrm{h}$ for D_e) do not play a significant role in the mixed *sr*-PBE/*lr*-CCSD(T) approach, *cf.* Table 5 – omitting them leaves the MAE values virtually unchanged, for the values of the coupling parameters used in Tables 1–3.

More important is a reduction of the theoretical level to MP2, *cf.* Table 5. Use of MP2 instead of CCSD(T) is seen to lead to a small, but significant increase of the MAEs for R_e and ω_e, and to a deterioration of the D_e MAE by $\approx 40\ \mu E_\mathrm{h}$. Note that pure MP2 overestimates correlation contributions to binding energies for the heavy Rg dimers, thus partly cancelling basis-set errors, while the mixed *sr*-PBE/*lr*-MP2 results are consistently poorer than the *sr*-PBE/*lr*-CCSD(T) ones for all the Rg dimers.

Interestingly, replacing PBE by LDA (*i.e.*, reducing the theoretical level at the DFT side) has a smaller effect than substituting CCSD(T) by MP2, *cf.* Table 6: the MAEs of R_e, D_e and ω_e are in-between the *sr*-PBE/*lr*-CCSD(T) and the *sr*-PBE/*lr*-MP2 errors; the D_e MAE is larger than the *sr*-PBE/*lr*-CCSD(T) one by $\approx 20\ \mu E_\mathrm{h}$ only. This is truly remarkable, since pure LDA (not shown in the tables) is much worse than pure PBE; bond lengths are underestimated by ≈0.4 Å, while dissociation energies are overestimated by factors of 2–10. This means that mixing-in of *lr*-CCSD(T) leads to a huge improvement, by factors 10 and 40 for R_e and D_e, respectively.

Finally, we consider the effect of replacing the short-range DFT exchange by the full non-local Hartree–Fock exchange, within *sr*-PBE/*lr*-CCSD(T). Here, the results are less good, about of the accuracy of the standard PBE ones (although the trends are better), *cf.* Table 6. Once more one observes that xc-DFT with a local description of both exchange and correlation is better than a combination of non-local HF exchange with local DFT correlation. In fact, the latter combination does not even produce potential curves with a minimum, for the Rg dimers, when applied in a pure DFT context.

How can we understand the success of *sr*-PBE/*lr*-CCSD(T) in reliably describing bonding in vdW molecules with moderate basis sets? Let us discuss this point at the example of Ar_2. Note that a simple mixing of PBE and CCSD(T) would not be successful, since both PBE and CCSD(T) considerably underestimate the bond strengths with moderate (*e.g.* triple-zeta) basis sets by factors of 2.3 and 1.4, respectively (*cf.* Tables 1 and 2). The key point is that the mixing is not done in an additive way but is connected with a short-range/long-range separation. Short-range DFT is more accurate than standard DFT (which is applied to the full interelectronic interaction), and long-range *ab initio* methods are less basis-set dependent than in the case where they have to describe the inner parts of the correlation cusp. This is illustrated in Table 7 for Ar_2 at the equilibrium bond length R_e, where we separated the CCSD correlation energy into pair contributions from atom-localised orbitals. In a standard CCSD calculation, the dominant

Table 6 Bond lengths R_e (Å), dissociation energies D_e (μE_h) and harmonic wavenumbers ω_e (cm^{-1}) of the Rg dimers from *sr*-DFT/*lr*-CCSD(T) calculations with aug-cc-pVTZ basis sets. In each case, results with *sr*-LDA and *sr*-PBE(c) are given in the form …/… For the definition of PBE(c), *cf.* text

	R_e	D_e	ω_e
He_2	3.181/3.195	22.1/14.4	22.2/18.6
HeNe	3.126/3.221	45.5/26.8	26.0/19.4
HeAr	3.534/3.726	81.7/43.4	30.3/20.9
HeKr	3.734/3.988	82.0/40.8	27.6/18.2
HeXe	4.000/4.347	77.4/35.6	24.9/15.4
Ne_2	3.099/3.256	94.0/50.5	23.2/14.8
NeAr	3.451/3.719	188.1/85.8	26.9/15.6
NeKr	3.615/3.949	199.9/84.9	23.1/12.8
NeXe	3.822/4.278	205.1/76.3	21.7/10.7
Ar_2	3.773/3.977	440.8/243.6	29.1/20.4
ArKr	3.906/4.134	508.5/274.9	25.7/17.6
ArXe	4.100/4.359	558.8/296.1	24.3/16.3
Kr_2	4.030/4.273	603.3/322.7	21.5/14.6
KrXe	4.222/4.460	687.9/384.8	19.9/13.9
Xe_2	4.402/4.656	784.2/434.0	18.1/12.5
MAE	0.047/0.272	33.1/177.4	4.0/12.2

Table 7 Breakdown of binding energies (μE_h) from *sr*-PBE/*lr*-CCSD and standard CCSD calculations for Ar_2, at two different internuclear distances, into explicitly treated intraatomic and interatomic correlation contributions. Additionally, we list *sr*-PBE/*lr*-HF and HF contributions to binding energies. In each case, results with aug-cc-pVTZ and aug-cc-pVQZ basis sets are given in the form .../...

		$R = R_e$	$R = 1.25R_e$
PBE/CCSD	Intraatomic	−25.7/−26.5	−10.3/−10.6
	Interatomic	474.2/490.7	202.1/210.4
	DFT/HF	17.4/−1.3	29.6/25.9
CCSD	Intraatomic	−209.3/−211.5	−38.8/−40.7
	Interatomic	841.4/902.7	186.9/196.5
	HF	−424.9/−430.8	−13.1/−13.0

attractive correlation contributions are seen to come from interatomic pairs, while intraatomic correlation is repulsive and smaller in magnitude by a factor of four. In the mixed *sr*-PBE/*lr*-CCSD calculation, a similar analysis shows that the explicitly treated intraatomic *sr* correlation is nearly completely damped off (*i.e.*, smaller by an order of magnitude than in the full CCSD calculation), but also the interatomic part is significantly reduced (by a factor of two). This is quite important because it is mainly the interatomic part of the correlation energy which is responsible for the basis-set dependency of the binding energy in the full CCSD calculation. With the restriction to *lr* interaction (with the coupling parameter μ chosen as described at the beginning of this section), not only the explicitly treated interatomic correlation contributions are reduced in magnitude but also the relative importance of the basis-set effects, *cf.* Table 7. Of course, this depends on a judicious choice of μ: μ should be thus small that DFT can contribute to interatomic bonding. On the other hand, for interatomic distances, where there is no significant interatomic overlap any more and where local and semi-local density functionals cannot contribute to bonding, *ab initio* should take over completely. This condition seems to be more or less satisfied with our choice of μ, *cf.* Table 7. For $R = 1.25R_e$, where HF repulsion is one order of magnitude smaller than interatomic correlation (it is only smaller by a factor of two at R_e!), the explicitly treated interatomic correlation contributions in the mixed *sr*-PBE/*lr*-CCSD calculation are very similar to those in the full CCSD calculation, and also the basis-set dependence is very similar.

5. Conclusions

The scheme for coupling short-range (*sr*) density functionals (DFT) with wavefunction-based long-range (*lr*) *ab initio* methods has been extended by (a) developing a new gradient-corrected *sr* functional of the Perdew–Burke–Ernzerhof (PBE) type and (b) introducing coupled-cluster (CC) approaches (CC with single and double excitations (CCSD), and with additional perturbative triples (CCSD(T))) at the *ab initio* side.

Test calculations of the rare gas dimers RgRg′ (Rg, Rg′ = He,..., Xe) show very encouraging results, when the coupling parameter μ is connected to the inverse bond length according to $\mu = 2/R_e$. At the highest level of approximation, *i.e.* *sr*-PBE/*lr*-CCSD(T) with aug-cc-pVQZ basis sets, mean absolute errors (MAE) of 0.045 Å and 14.3 μE_h are obtained for R_e and D_e, respectively. These errors are much smaller than those of standard PBE (and even smaller than those of standard CCSD(T)). They are also virtually unchanged, when reducing the basis-set quality to aug-cc-pVTZ and when leaving out triple excitations on the *ab initio* side (*i.e.*, using *lr*-CCSD).

Of course, further test calculations of other vdW systems and for more general intermolecular interactions are necessary to corroborate these findings. Moreover, use of efficient *ab initio* schemes (of the local correlation variety, *e.g.* ref. 32) is needed to make the method competitive in computational effort with standard DFT calculations. Finally, extension to the open-shell case is an important issue for the future. Work along these lines is in progress in our laboratory.

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