

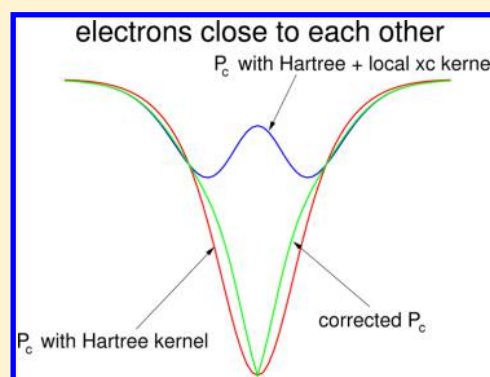
On the Short-Range Behavior of Correlated Pair Functions from the Adiabatic-Connection Fluctuation–Dissipation Theorem of Density-Functional Theory

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S Supporting Information

ABSTRACT: The short-range behavior of correlated pair functions from the adiabatic-connection fluctuation–dissipation theorem (ACFD) of density functional theory (DFT) employing local exchange–correlation kernels has been analyzed. It has been found that for large basis sets the pair function exhibits unphysical humps for small interelectronic distances if the adiabatic local density approximation kernel is used in the ACFD scheme (this method is termed ACFD/ALDA in this work). However, up to basis set sizes of quadruple- ζ type quality, the correlated pair function of ACFD/ALDA behaves physically correct and the method yields reasonable results for atomization energies, ionization potentials, and intermolecular interaction energies. In order to correct the deficiencies of the pair function of ACFD/ALDA for large basis sets, a short-range correction scheme has been devised on the basis of a combination of the ACFD/ALDA pair function for the large distance regime with a proper physically correctly behaving pair function at smaller distances. While this approach, termed as ACFD/ALDAcorr, practically yields results close to those of the ACFD/ALDA method for finite basis sets, it enables basis set extrapolation techniques and thus can take dynamic correlation effects fully into account in contrast to the ACFD/ALDA approach. This work also presents an efficient density-fitting algorithm to compute the ACFD correlation energies that enables the calculation of correlation energies of extended molecular systems.



1. INTRODUCTION

Random-phase approximation (RPA) electron correlation methods based on Kohn–Sham reference determinants were shown to represent accurate and parameter-free alternative approaches to standard density functional theory methods (DFT) for the description of electronic structure.^{1–5} Within the framework of the Kohn–Sham formalism, RPA methods can be derived from the adiabatic-connection fluctuation–dissipation (ACFD) theorem,^{6,7} which gives the correlation energy in terms of the dynamic Kohn–Sham response function and the frequency- and coupling-constant-dependent many-body response function. The latter is accessible within time-dependent DFT invoking approximations to the exchange–correlation kernel, the frequency-dependent functional derivative of the exchange–correlation potential with respect to the electron density. If the exchange–correlation kernel is completely neglected and only the Coulomb kernel is retained the RPA based on Kohn–Sham orbitals and eigenvalues results.

One of the most striking advantages of RPA methods over density functionals based on the local density approximation (LDA) or the generalized gradient approximation (GGA) is their ability to describe long-range electron correlation interactions² as well as static correlation effects^{1,8} correctly (more precisely, left–right static correlation effects for even electron systems, see refs 9 and 10). Moreover, Kohn–Sham RPA methods have been applied with some success both to molecular systems^{1,2} as well as

to bulk systems.^{11–14} The perhaps most severe disadvantage of RPA methods is, however, their inability to describe accurately the strength of covalent and ionic bonds, which are systematically underestimated.^{3,15} The reason for this is likely related to the self-correlation error of RPA methods that generally leads to a strong overestimation of electron correlation energies within the RPA. Thus, it seems to be desirable to go beyond the RPA level to improve the description of correlation effects that are affected by this self-correlation error.

A recent work by Scuseria et al. has demonstrated that the RPA method is identical to the so-called direct ring coupled-cluster doubles method, thus establishing a relation between the adiabatic-connection fluctuation–dissipation (ACFD) theorem and standard wave function methods¹⁶ (see also a recent related work by Jansen et al.¹⁷). In fact, the RPA method can be regarded as the first in a series of approximations to the full coupled-cluster doubles (CCD) method, neglecting certain contributions in the coupled-cluster amplitudes equation. A second step in this series of approximations would be to include also exchange type diagrams but exclude ladder diagrams, which leads to the ring coupled-cluster doubles (rCCD) method of McLachlan and Ball.^{18,19} Finally, also ladder contributions can be taken into account excluding, however, terms that are quadratic in the

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cluster amplitudes, leading to the linearized coupled cluster doubles^{20,21} or CC2 methods.²²

It is clear that with these augmentations one also abandons the favorite scaling behavior of RPA that was shown to be of the order of $N^4 \log(N)$ (with N being a measure of the molecular size) using a resolution-of-the-identity algorithm.²³ Furthermore, it is not clear whether the respective methods really improve upon the RPA method as they will also, to some extent, rely on the assumption that the correlation effects that are not accounted for are small or cancel out in a complete perturbation expansion. In fact, in ref 24, it has been shown that the rCCD method yields rather poor total energies and reaction energies for a range of molecular systems even though it corrects the self-correlation error of the RPA.

There exist, however, a number of alternative approaches to include higher order exchange contributions within RPA methods.^{25–31} Perhaps the most economic in a computational sense is the SOSEX (second order screened exchange) method in which the RPA doubles amplitudes are contracted with antisymmetrised integrals such that the method is exact through second order of perturbation theory. The method has been applied to both bulk systems²⁸ and molecules^{28,32} and yields improved total energies²⁸ and atomization energies³² compared to RPA. Another natural extension to the RPA that stays within the realm of the ACFD theorem is the EXX-RPA method^{29,33,34} in which the full nonadiabatic Kohn–Sham exchange kernel is taken into account. It has been shown that this method is competitive with higher level coupled cluster singles doubles methods for a number of molecular properties^{29,34,35} and is even, in contrast to standard DFT methods, capable to describe static correlation effects correctly.^{33,34} The method can also be applied to larger molecular systems by using a recent resolution-of-the-identity implementation.³⁴ Related to the EXX-RPA method, but derived from a modification of the RPA amplitude equation, is the recently developed RPAX2 method.³¹ This method is identical to the EXX-RPA for two-electron systems but differs from it for larger electronic systems. It was found that this method yields a remarkable accuracy for total energies as well as reaction and intermolecular interaction energies.³¹

As the above methods take into account (high-order) exchange interactions explicitly, it is clear that their scaling behavior will also increase at least by one order of magnitude compared to the RPA. Indeed, without the exploitation of local transformations, it is not possible to reduce the computational scaling of SOSEX, EXX-RPA and RPAX2 below N^5 . While this is of the same order as that of the MP2 method and still allows one to compute correlation energies for relatively large systems, one may ask whether there exist possibilities to describe exchange effects within the RPA more efficiently. Indeed, a recently developed ACFD method by Gould uses an approximate exchange kernel based on a radial exchange hole (RXH) that is derived from two constraints of the pair function and is thus almost free from empirical parameters.³⁶ It was shown in ref 36 that the RXH-RPA method clearly improves RPA correlation energies and van-der-Waals C_6 coefficients for a number of atoms. Whether this method performs that well also for molecular systems, however, has yet to be proven, and it has been argued that a modification of the kernel might be required in the molecular dissociation limit.³⁶ Other improvements over the RPA that do not attempt to directly describe exchange interactions are the single-excitation corrected RPA method by Ren et al.,³⁷ a nonlocal hybrid-functional-like correction to the RPA by Ruzsinszky et al.³⁸ and range-separated methods in which RPA electron correlation effects are described only for large interelec-

tronic distances while standard density-functional theory methods are used to describe the dynamic correlation effects.^{39–44} These latter approaches have the advantage that the strong basis set dependence of the RPA is much reduced since the interelectronic cusp of the correlated pair function needs not to be described explicitly.

While the short-range behavior of the correlated pair function of the RPA will reflect to some extent the behavior of standard correlation methods (indeed, it was observed in refs 1, 45, and 46 that RPA methods possess the same inverse cubed basis set dependence as standard correlation methods), in ref 47 it has been shown that extensions to the RPA supplementing the Coulomb kernel by adiabatic and local exchange-correlation kernels derived from standard LDA or GGA functionals will lead to pair functions that exhibit a $(r_{12})^{-1}$ divergence at small coupling strengths for short interelectronic distances and thus will potentially lead to a strong basis set dependence. Indeed, it was found that a theoretically derived inverse linear extrapolation method is not applicable for such methods if the correlation energies were calculated with basis sets of only up to hexuple- ζ quality so that, as a compromise, an inverse quadratic power law has been applied to estimate basis set extrapolated results.⁴⁷ While it has been shown that with these methods yield reasonable results for atomization energies and also intermolecular interactions,⁴⁷ it is clear that the unphysical behavior of the correlated pair function of local kernel extensions to the RPA prevents the determination of reliable results.

Recently Olsen and Thygesen have derived a nonlocal exchange-correlation (xc) kernel that is based on a renormalization of the homogeneous electron gas correlation hole.⁴⁸ The use of this kernel in ACFD calculations of the ground state correlation energy resolves the divergence problem of the pair function at short ranges, and it was found that an improved description of correlation energies and atomization energies compared to the RPA and also to the ACFD methods employing the ALDA xc kernel is obtained.⁴⁸

In this work, the behavior of the correlated pair function from ACFD calculations employing the ALDA xc kernel is analyzed. It is observed that indeed, in line with the analytical results of ref 47, the pair function exhibits an unphysical behavior for small interelectronic distances. This behavior, however, shows up only for very large basis sets of quintuple- ζ type quality and higher. Thus, ACFD/ALDA calculations may be performed in conjunction with smaller basis sets. It is known, however, that many molecular properties crucially depend on a proper description of dynamic correlation effects, which can only partially be captured with small basis sets due to the wrong description of the interelectronic cusp. Thus, in order to reduce the basis set error of electron correlation energies, it has become common to use basis set extrapolations using special correlation consistent atomic basis sets. Such basis set extrapolations, however, cannot be performed for the ACFD/ALDA method, since the dependence of the pair function on the basis set at short interelectronic distances leads in some cases even to spurious increases of the correlation energies if going from quadruple- to quintuple- ζ or hexuple- ζ type basis sets for some molecules, as will be shown in this work.

Therefore, in this work, an alternative approach to the one from Olsen et al.⁴⁸ is devised in order to correct the divergence problem of ACFD methods with local kernels. This method is based on a separation of the interelectronic distance into a short-range and a long-range region and is thus related to range-separation methods (see above). However, while in case of the

latter the idea is to reduce the basis set dependence of RPA by using a local functional description for the short interelectronic range, in this work the aim is to obtain an improved description of the correlated nonlocal pair function in the short-range region. This is achieved by combining the ACFD/ALDA pair function at long interelectronic distances with an RPA pair function using a scaled Coulomb kernel for the short interelectronic distance. This correction approach will be termed as ACFD/ALDAcorr in this work.

While the ACFD/ALDAcorr rectifies the unphysical behavior of the pair densities of ACFD/ALDA, both methods possess a formal steep scaling behavior of N^6 with respect to the molecular size, which makes them impractical for large molecular systems. Because of this, this work presents also a density-fitting algorithm for computing the ACFD/ALDA and ACFD/ALDAcorr correlation energies, which reduces the steep scaling behavior by 2 orders of magnitude. The effective computational speedups due to the density-fitting approach will be investigated numerically by some examples.

The organization of this work is as follows: section 2 presents the methods used in this work and also analyses the obedience of the normalization condition of the correlated pair function for the ACFD/ALDAcorr approach. Section 3 describes technical details of the calculations that were made. In section 4, results for atomization energies (section 4.2), ionization energies (section 4.3), and intermolecular interaction energies (section 4.4) of the corrected ACFD/ALDAcorr approach are shown. Section 5 summarizes the results.

2. METHOD

In this section, the convention is used that indices i,j,\dots label occupied and a,b,\dots label unoccupied orbitals. All equations are given for closed-shell electronic systems.

2.1. Correlation Energy within the Adiabatic-Connection Fluctuation–Dissipation Theorem Density Functional Theory. Following the formalism described in ref 29 (see also refs 1, 5, 24, and 47), the electron correlation energy can be written as a Coulomb type integral over the correlated pair function P_c

$$E_c = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{P_c(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (1)$$

which in turn can be obtained from a coupling-strength integration over the coupling strength-dependent pair function \tilde{P}_c^α :

$$P_c(\mathbf{r}_1, \mathbf{r}_2) = \int_0^1 d\alpha \tilde{P}_c^\alpha(\mathbf{r}_1, \mathbf{r}_2) \quad (2)$$

As has been shown in refs 6, 7, 24, 29, and 47, the coupling-strength-dependent correlated pair function can be calculated from a frequency integral over the difference between the coupled (χ_α) and uncoupled (χ_0) response functions at imaginary frequencies $i\omega$

$$\tilde{P}_c^\alpha(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{2\pi} \int_0^\infty d\omega (\chi_\alpha(\mathbf{r}_1, \mathbf{r}_2, i\omega) - \chi_0(\mathbf{r}_1, \mathbf{r}_2, i\omega)) \quad (3)$$

where the uncoupled response function is given in terms of the Kohn–Sham orbitals ϕ and eigenvalues ϵ

$$\chi_0(\mathbf{r}_1, \mathbf{r}_2, i\omega) = -\sum_{ia} \lambda_{ia,ia}(i\omega) \phi_i(\mathbf{r}_1) \phi_a(\mathbf{r}_1) \phi_i(\mathbf{r}_2) \phi_a(\mathbf{r}_2) \quad (4)$$

with

$$\lambda_{ia,i'a'}(i\omega) = \frac{4(\epsilon_a - \epsilon_i)}{(\epsilon_a - \epsilon_i)^2 + \omega^2} \delta_{ia,i'a'} \quad (5)$$

The coupled response function can be written in terms of the excitation energies ω_p and the corresponding functions $v_p(\mathbf{r})$

$$\chi_\alpha(\mathbf{r}_1, \mathbf{r}_2, i\omega) = -\sum_p \frac{4\omega_p^\alpha}{\omega_p^\alpha + \omega^2} v_p^\alpha(\mathbf{r}_1) v_p^\alpha(\mathbf{r}_2) \quad (6)$$

where the latter are obtained from a contraction of vectors \mathbf{U}_p^α with the occupied-virtual orbital products

$$v_p^\alpha(\mathbf{r}) = \sum_{ia} U_{p,ia}^\alpha \phi_i(\mathbf{r}) \phi_a(\mathbf{r}) \quad (7)$$

The vectors \mathbf{U}_p^α are related to the solutions of a reduced eigenvalue equation, termed Casida's equation^{49,50}

$$[\epsilon^2 + 4\epsilon^{1/2} \mathbf{K}_{\text{Hxc}}^\alpha \epsilon^{1/2}] \mathbf{V}_p^\alpha = (\omega_p^\alpha)^2 \mathbf{V}_p^\alpha \quad (8)$$

via the transformation $\mathbf{U}_p^\alpha = (\omega_p^\alpha)^{-1/2} \epsilon^{1/2} \mathbf{V}_p^\alpha$. In eq 8, the matrix ϵ is a diagonal matrix defined as $\epsilon_{ia,jb} = \delta_{ia,jb}(\epsilon_a - \epsilon_i)$. The matrix \mathbf{K}_{Hxc} in eq 8 is defined by the integral

$$(\mathbf{K}_{\text{Hxc}}^\alpha)_{ia,jb} = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_i(\mathbf{r}_1) \phi_a(\mathbf{r}_1) k_{\text{Hxc}}^\alpha(\mathbf{r}_1, \mathbf{r}_2) \phi_j(\mathbf{r}_2) \phi_b(\mathbf{r}_2) \quad (9)$$

where the function k_{Hxc}^α in the integrand denotes the sum of the α -dependent Coulomb- and exchange-correlation kernel f_{xc}^α

$$k_{\text{Hxc}}^\alpha(\mathbf{r}_1, \mathbf{r}_2) = \frac{\alpha}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{\text{xc}}^\alpha(\mathbf{r}_1, \mathbf{r}_2) \quad (10)$$

While, in general, this quantity is both frequency dependent and nonlocal, in this work, f_{xc} is approximated by the adiabatic and local density approximation kernel f_{ALDA}

$$f_{\text{xc}}^\alpha(\mathbf{r}_1, \mathbf{r}_2) \approx f_{\text{ALDA}}^\alpha(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \quad (11)$$

that is the second functional derivative of the LDA exchange-correlation energy. Because the nonadiabaticity of the kernel implies that also the eigenfunctions \mathbf{V}_p^α of the Casida eq 8 do not depend on the frequency, the integration in eq 3 can be done analytically, and one arrives at a simplified equation for the correlation energy (see eq 12 in ref 29). On the other hand, the correlation part of the ALDA exchange-correlation kernel (in this work the VWN5 functional is used⁵¹) depends nonlinearly on the coupling strength α ^{47,52,53}

$$f_{\text{AVWN}}^\alpha(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\alpha} f_{\text{AVWN}} \left[\frac{1}{\alpha^3} \rho(\mathbf{r}_1) \right] \delta(\mathbf{r}_1 - \mathbf{r}_2) \quad (12)$$

Thus, a numerical integration over α in eq 2 is required in general.

2.2. Density Fitting Method for the Calculation of ACFD/ALDA Correlation Energies. In section 2.1, it has been shown that the correlated pair function \tilde{P}_c^α can be obtained from the uncoupled and coupled Kohn–Sham response functions (eq 3). It was shown in previous works^{54–56} that the latter can efficiently be calculated by employing density fitting of the occupied-virtual orbital products. Here, we follow closely the formalism used in ref 54 and introduce an auxiliary basis set with functions $g_p(\mathbf{r})$ (auxiliary functions labeled as P, Q, R, \dots). While in the following equations these might be replaced by any set of functions that can be used to fit $\phi_i(\mathbf{r}) \phi_a(\mathbf{r})$ products, in this work a set of (nonorthogonal) Gaussian functions has been used with the size of N_{aux} . The uncoupled response function can then be approximated as

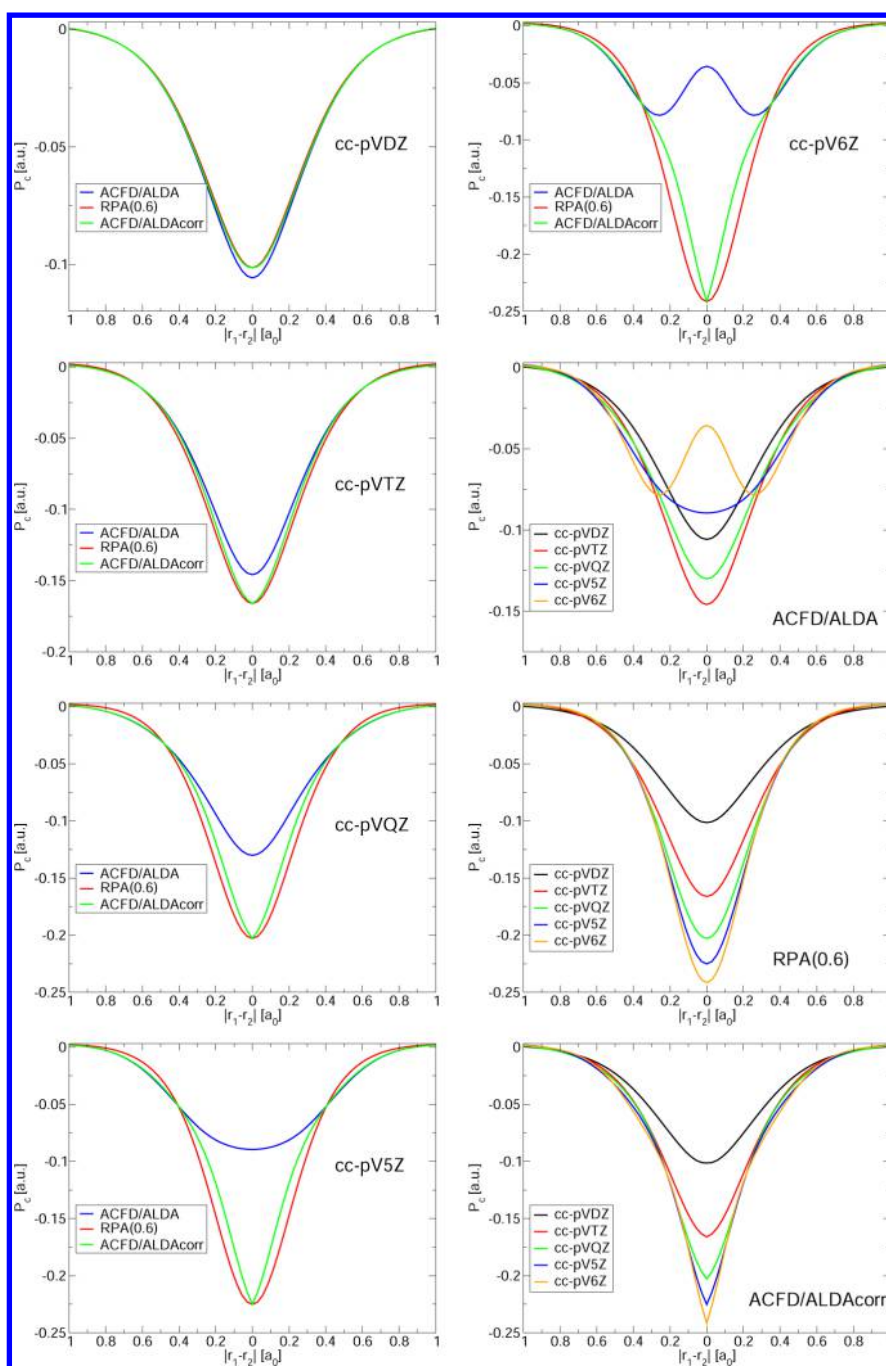


Figure 1. Helium atom: correlated pair function P_c . The reference electron is located at a distance of $0.25 a_0$ from the nucleus. P_c is plotted on a line through the reference electron, which is perpendicular to the connection between the nucleus and the reference electron. The diagrams shown in the first column and the first diagram at the top in the second column present the form of the pair functions of the three methods ACFD/ALDA, RPA(0.6), and ACFD/ALDAcorr using the Dunning basis sets cc-pVXZ with $X = D, T, Q, 5$, and 6 . The second to fourth diagram from the top of the second column show the same P_c curves, this time, however, grouped together according to methods and not basis sets. That is, for each method, separately, the dependence of the form of the pair function on the basis set is shown.

$$\begin{aligned}\tilde{\chi}_0(\mathbf{r}_1, \mathbf{r}_2, i\omega) &= \sum_{PQ} \sum_{RS} \sum_{ia} g_P(\mathbf{r}_1) S_{PR}^{-1} N_{ia, R} \chi_{ia, ia}^{aux}(i\omega) N_{ia, S} S_{SQ}^{-1} g_Q(\mathbf{r}_2) \\ &= \sum_{PQ} \sum_{RS} g_P(\mathbf{r}_1) S_{PR}^{-1} (\chi_0^{aux}(i\omega))_{RS} S_{SQ}^{-1} g_Q(\mathbf{r}_2)\end{aligned}\quad (13)$$

with the three index integrals $N_{ia, P} = (ia|\eta|P)$ over the product $\phi_i(\mathbf{r}_1)\phi_a(\mathbf{r}_2)$ and an auxiliary function $g_P(\mathbf{r}_2)$ and the metric integrals $S_{PQ} = (P|\eta|Q)$ over two auxiliary functions $g_P(\mathbf{r}_1)$ and $g_Q(\mathbf{r}_2)$. For the fitting norm η , in this work, the Coulomb norm

$\eta = (1/r_{12})$ was chosen.^{56,57} The matrix χ_0^{aux} in eq 13 can be regarded as a representation of the uncoupled response function in the auxiliary basis set and is of the dimension $N_{aux} \times N_{aux}$. In an analogue way, the coupled response function can be written as

$$\tilde{\chi}_\alpha(\mathbf{r}_1, \mathbf{r}_2, i\omega) = \sum_{PQ} \sum_{RS} g_P(\mathbf{r}_1) S_{PR}^{-1} (\chi_\alpha^{aux}(i\omega))_{RS} S_{SQ}^{-1} g_Q(\mathbf{r}_2)\quad (14)$$

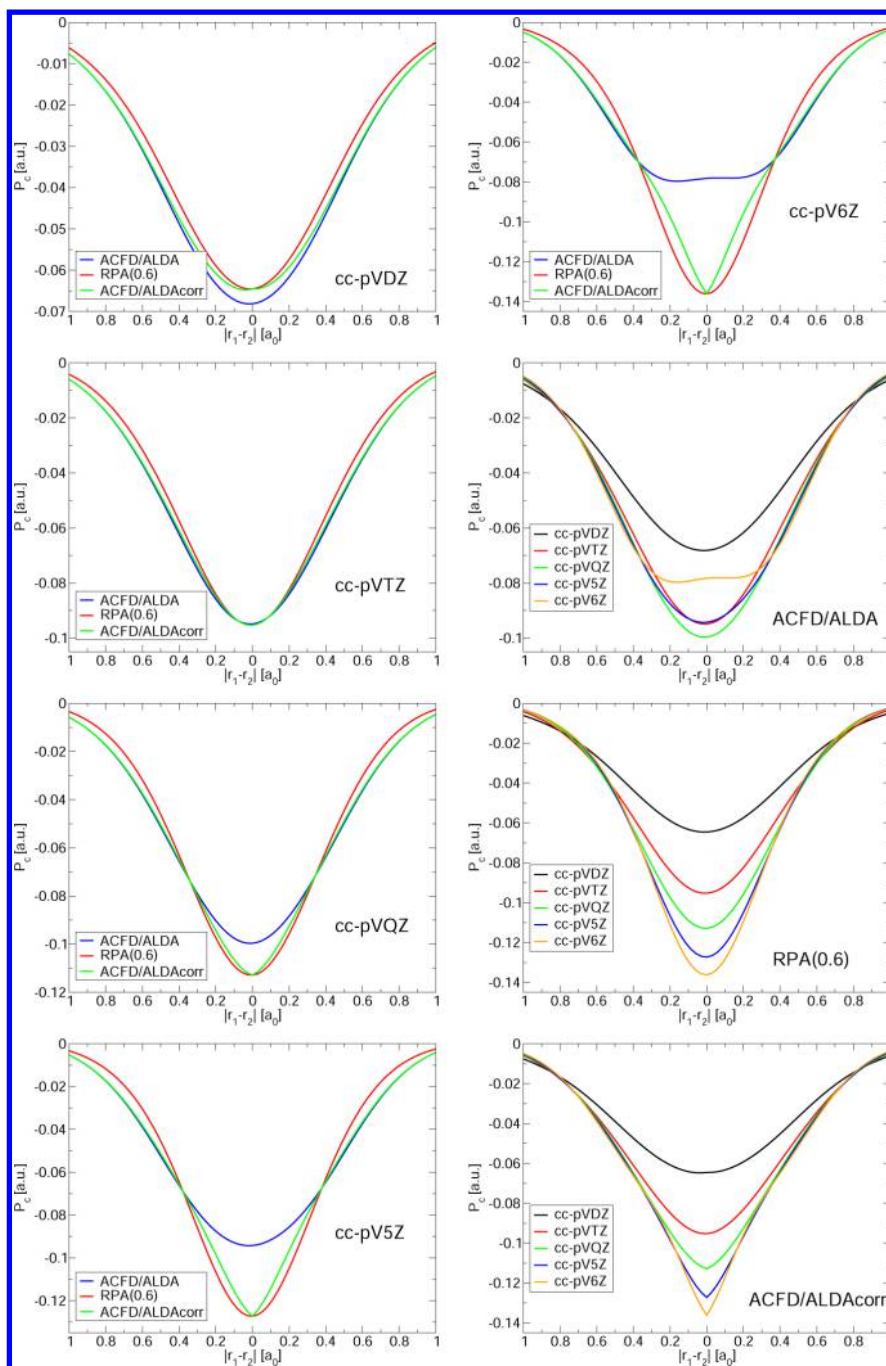


Figure 2. Water molecule: correlated pair function P_c . The reference electron is located on the O–H bond at a distance of $0.5 a_0$ from the oxygen nucleus. P_c is plotted on a line through the reference electron, which is perpendicular to the connection from the position of the oxygen nucleus and the reference electron and which lies in the molecular plane. The diagrams shown in the first column and the first diagram at the top in the second column present the form of the pair functions of the three methods ACFD/ALDA, RPA(0.6), and ACFD/ALDAcorr using the Dunning basis sets cc-pVXZ with $X = D, T, Q, S$, and 6. The second to fourth diagram from the top of the second column show the same P_c curves, this time, however, grouped together according to methods and not basis sets. That is, for each method, separately, the dependence of the form of the pair function on the basis set is shown.

where the auxiliary basis set representation χ_0^{aux} can be obtained from^{54,58}

$$\begin{aligned}\chi_\alpha^{\text{aux}}(i\omega) &= \chi_0^{\text{aux}}(i\omega) + \mathbf{N}^T \lambda(i\omega) \mathbf{F}^\alpha (\mathbf{S} - \mathbf{N}^T \lambda(i\omega) \mathbf{F}^\alpha)^{-1} \chi_0^{\text{aux}}(i\omega) \\ &= \mathbf{S} (\mathbf{S} - \mathbf{N}^T \lambda(i\omega) \mathbf{F}^\alpha)^{-1} \chi_0^{\text{aux}}(i\omega)\end{aligned}\quad (15)$$

with the three-index kernel integrals

$$F_{ia,P}^\alpha = \left(ia \left| \frac{\alpha}{r_{12}} \right| P \right) + (ia f_{xc}^\alpha | P) \quad (16)$$

It may be seen that the computation of χ_0^{aux} requires only contractions of three-index quantities of the size of $N_{\text{occ}} \times N_{\text{virt}} \times N_{\text{aux}}$ and two-index quantities of the dimension $N_{\text{aux}} \times N_{\text{aux}}$ and a relatively inexpensive inversion of a matrix of the dimension $N_{\text{aux}} \times N_{\text{aux}}$. One can observe that, with this, the computation of the density fitted coupled and uncoupled response functions (under the condition that local xc kernels are used to compute the latter) require computational steps that do not scale higher than \mathcal{N}^4 with the molecular size, thus significantly reducing the

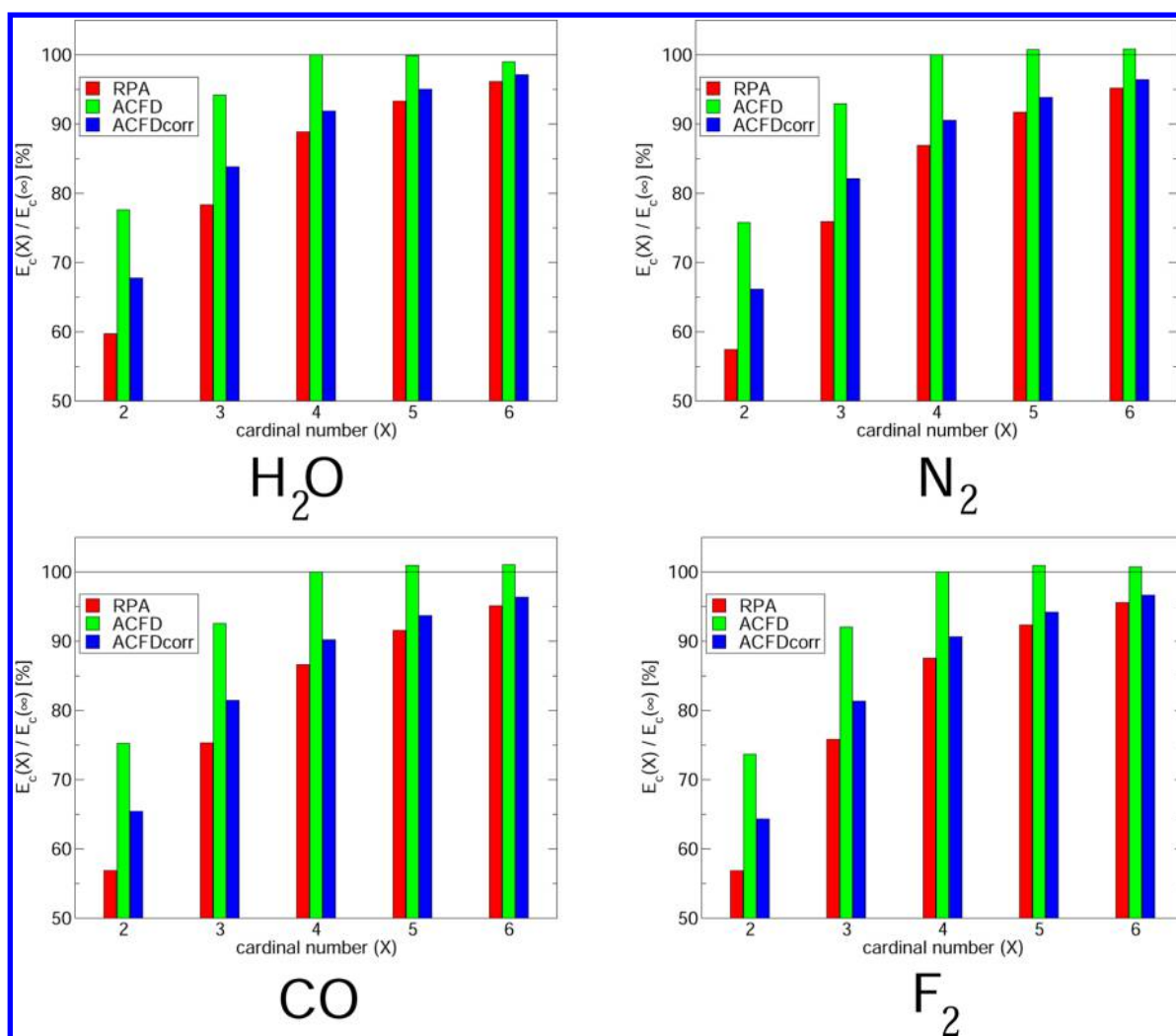


Figure 3. Basis set convergence (displayed by the ratio of the correlation energies calculated with finite basis sets and the basis set extrapolated correlation energy) of correlation energies of the methods RPA (red bars), ACFD/ALDA (green bars), and ACFD/ALDAcorr (blue bars) (the acronyms for the latter two methods were abbreviated to ACFD and ACFDcorr in the diagrams). In the case of the ACFD/ALDA method for which no extrapolation method is possible, the estimate for the basis set limit was set to $E_c(X = 4)$.

computational cost of the approach described in section 2.1. Note that in ref 58 a similar and even more efficient method has been used in which a double density-fitting of the xc kernel matrix was applied. While that approach was shown to yield, with a reasonable accuracy, dispersion energies, in the current work it was found that total correlation energies could not be calculated accurately enough with this method because of the numerical problems arising due to the numerical integration over two auxiliary functions and the ALDA xc kernel that has large values in small density regions. For the calculation of the three-index integrals (i.e. $|f_{xc}^\alpha| P$) this problem was found to be much less severe. Using eqs 13 and 14, the correlation energy, in analogy to eqs 1–3, can then be calculated as

$$E_c = -\frac{1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \mathbf{J} \mathbf{S}^{-1} (\chi_0^{\text{aux}}(i\omega) - \chi_\alpha^{\text{aux}}(i\omega)) \mathbf{S}^{-1} \quad (17)$$

with the Coulomb matrix \mathbf{J} in the auxiliary basis set defined as $J_{PQ} = (P | 1/r_{12} | Q)$. Note that for $\eta = (1/r_{12})$ eq 17 simplifies further, since then $\mathbf{S} = \mathbf{J}$. Equation 17 shows that the calculation of the correlation energy requires integrations over both the coupling strength and the frequency. In the density fitting

algorithm described in this section, both integrations are done numerically. While the coupling strength integration was observed to be highly accurate already for a small number of quadrature points, in ref 23 it was found in case of a related resolution-of-identity RPA method that the quadrature error for integrations over ω increases linearly with the system size but decreases exponentially with the number of quadrature points. It should hold true that the same is also true for the current approach; thus, the overall scaling behavior of the density fitting method described here is given by $N^4 \times \log(N)$ where the logarithmic factor stems from the cost of the frequency integration in eq 17. Note also that in the case of RPA ($f_{xc}^\alpha = 0$) the coupling-strength integration may be done analytically by performing a calculation of the logarithm of a matrix of the dimension of the auxiliary basis set.²³

2.3. Analysis of the Short-Range Behavior of ACFD Pair Functions. It was shown in ref 47 that at weak coupling strengths the correlated pair function \tilde{P}_c^α obtained from the ACFD method described in section 2.1 exhibits a $(1/r_{12})$ divergence if an adiabatic LDA kernel and an even more severe $(1/r_{12}^2)$ divergence if an adiabatic GGA kernel is employed in eq 10. Numerical results for a range of molecules have shown that

this leads to a poor basis set convergence of the electron correlation energies that only decrease with the linear inverse power of the cardinal number instead of the decreasing with the cubed inverse power that is obtained with conventional correlation methods (including the RPA method).

In this section, the short-range behavior ($|r_1 - r_2| \rightarrow 0$) of the correlated pair function $P_c(\mathbf{r}_1, \mathbf{r}_2)$ (eqs 2–7) is analyzed for a range of molecules and different basis sets. For this, here and throughout this work, the ALDA xc kernel is used in eq 10 and the orbitals and orbital energies were obtained from a preceding Kohn–Sham calculation using the PBE xc functional.⁵⁹

Two examples, namely for the He atom and the H₂O molecule, of this analysis are presented in Figures 1 and 2 (more may be found in the Supporting Information). In the case of the He atom, the reference electron was located at a distance of 0.25 a_0 from the nucleus, and in the case of H₂O, the reference electron was located on the O–H bond at a distance of 0.5 a_0 away from the oxygen atom. The pair function in Figures 1 and 2 is plotted on a line through the reference electron, which is perpendicular to the connection line through the positions of the respective helium/oxygen nucleus and the reference electron. In the case of the H₂O molecule, this line was set in the molecular plane (thus explaining the slightly asymmetric shape of the pair function in this case). Both in the case of the He atom and in case of the H₂O molecule, one can see that the ACFD pair function indeed shows an unphysical behavior at short distances, see the second diagrams from top on the right-hand sides in Figures 1 and 2. This, however, is only observed if large basis sets with cardinal numbers $X \geq 4$ are used. Up to this basis set size, the shapes of the pair functions are similar to those of the RPA method, see the second diagrams from bottom on the right-hand sides in Figures 1 and 2 (note that these diagrams actually show the pair functions for an RPA method using a scaled Coulomb kernel, see below). Generally, it is found that the ACFD/ALDA pair function decreases in magnitude for cardinal numbers X going from 2 to 4, faking a fast convergence, but exhibits an irregular behavior for cardinal numbers $X \geq 5$, often showing unphysical humps, see Figure 1 and the Supporting Information.

This behavior is also reflected in the correlation energies obtained with the ACFD method which often decrease in magnitude when switching from $X = 5$ to $X = 6$ basis sets (see Supporting Information). This can, for example, be seen for the H₂O molecule in Figure 3, which shows the percentual contribution to the basis set limit of the respective correlation energies for four molecules. Due to the incorrect behavior of the ACFD/ALDA pair function at short ranges and for $X > 4$, the basis set limit for this method was set to the $X = 4$ results in this case.

2.4. Short Range Correction Approach to the ACFD Pair Function. Due to the wrong behavior of the ACFD pair function at short ranges in this work the following correction approach is proposed:

$$P_c(\mathbf{r}_1, \mathbf{r}_2) = (1 - s(r_{12}))P_c^{\text{sr}}(\mathbf{r}_1, \mathbf{r}_2) + s(r_{12})P_c^{\text{ACFD/ALDA}}(\mathbf{r}_1, \mathbf{r}_2) \quad (18)$$

where P_c^{sr} is a proper short-range approximation to the correlated pair function and $s(r_{12})$ is a switching function depending on the interelectronic distance $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ having the property that $s(r_{12})_{r_{12} \rightarrow 0} \rightarrow 0$ and $s(r_{12})_{r_{12} \rightarrow \infty} \rightarrow 1$. While P_c^{sr} might be taken from any correlation method that yields finite pair functions for $r_{12} \rightarrow 0$, a natural choice would be to use the pair function from an RPA calculation. It was observed, however, that the RPA pair function is generally much lower at small distances than the

ACFD/ALDA pair function, preventing a seamless interpolation between the two functions. Because of this, the RPA pair function was calculated with a modified RPA method in which the Coulomb kernel was scaled with a prefactor of 0.6, leading to shapes of the pair functions shown in the respective diagrams in Figures 1 and 2 (the acronym RPA(0.6) is used in the diagrams to distinguish it from the standard RPA method). Note that this scaling of the RPA kernel also makes sense physically as it reduces the self-correlation error present in the RPA method (for two-electron systems the self-correlation would cancel exactly if a scaling of one-half was used^{8,33}). A physical argument for the choice of the scaling factor of the RPA kernel is given in section 2.5, which analyses whether the approach of eq 18 fulfills the sum rule for the pair correlation function.

For the switching function $s(r_{12})$, we use

$$s(r_{12}) = \text{erf}(cr_{12}) \quad (19)$$

which is widely used in range-separated methods combining DFT and wave function methods. The parameter c in eq 19 determines the interpolation range and was set to a value of 2 in this work; that is, the switching between the ACFD/ALDA and RPA(0.6) pair functions occurs basically in the range $r_{12} \leq 1 a_0$. On inspection of the ACFD/ALDA pair functions for several systems and locations of the reference electron, this range appears to be sufficient to truncate the unphysical behavior of the ACFD/ALDA pair function for $r_{12} \rightarrow 0$. It should be noted that the connection scheme of eq 19 requires only minor modifications of the implementations described in sections 2.1 and 2.2; namely, the respective pair function simply needs to be contracted with two-center (exploiting the Gaussian product theorem in the standard case) integrals of the type $(\text{Pl erf}(cr_{12})/r_{12}|Q)$, which can be obtained by a simple modification of standard electron repulsion integral routines.⁶⁰

In Figures 1 and 2, the results of the interpolation method of eq 18 is shown for basis sets of the cardinal number range $X = 2 - 6$. One can see that for $X = 2$ the ACFD/ALDA and the RPA(0.6) pair functions are very close to each other while for larger values of X the RPA(0.6) pair functions decrease much more strongly at small distances than the ACFD/ALDA pair function. The corrected pair functions, denoted as ACFD/ALDAcorr in the diagrams and in the following, are given by the green curves in the respective diagrams in Figures 1 and 2. One can observe that with the choice of $c = 2$ in eq 19 a rather seamless interpolation between $P_c^{\text{ACFD/ALDA}}$ and $P_c^{\text{RPA(0.6)}}$ is obtained and the basis set convergence of the corrected pair function is illustrated in the first diagrams from the bottom on the right-hand side in Figures 1 and 2. While it can be seen that the basis set convergence, by construction, is now the same as that of RPA(0.6) at short ranges, the ACFD/ALDAcorr pair functions even exhibit a cusp for $r_{12} \rightarrow 0$. While this behavior is shared in common with the exact pair function (in an infinite basis set), in the current case this has to be attributed, however, to the choice of the switching function in eq 18 and can be regarded as an artifact. It should also be noted that some cases have been found where the interpolation between the short- and long-range pair functions is not as smooth as in the examples presented in Figures 1 and 2 and the corrected pair function oscillates somewhat in the interpolation region. These cases, however, were only observed in regions where the magnitude of the pair function is small, see Supporting Information, so that this behavior has a marginal effect on the correlation energies.

In the diagrams in Figure 3, the basis set convergence of the correlation energies of RPA, ACFD/ALDA, and the ACFD/ALDAcorr method is analyzed for the four molecules H₂O, N₂, CO, and F₂. Due to the unphysical behavior of the ACFD/ALDA

pair function at short interelectronic distances, it is concluded that an estimate for the basis set limit for this method is not possible using standard techniques, more precisely, it is likely that ACFD/ALDA correlation energies are divergent upon increase of the cardinal number X to infinity. Because of this, here and in the following, the energies and energy differences calculated by the ACFD/ALDA method are shown for the largest basis set for which the ACFD/ALDA pair function still behaves physical, that is, for quadruple- ζ type basis sets. This means that the green bars in the diagrams in Figure 3 are shown relative to ACFD/ALDA correlation energies calculated with quadruple- ζ type basis sets rather than extrapolated ones. With this, one can see in Figure 3 that the ACFD/ALDA method shows an unusual (fake) fast convergence toward the basis set limit, while in the case of RPA and ACFD/ALDAcorr the convergence is much slower and one can observe that it is very similar to each other for larger cardinal numbers (for smaller values of X the ACFD/ALDAcorr are closer to the extrapolated correlation energies than the RPA ones). Therefore, both for the RPA and for the ACFD/ALDAcorr correlation energies, the standard extrapolation formula

$$E_c(X) = E_c(\infty) + \frac{A}{X^3} \quad (20)$$

was used employing the results from the aug-cc-pV5Z and aug-cc-pV6Z basis sets.^{1,45,46} It can be concluded that with the correction scheme of eq 18 the ACFD/ALDA correlation energies can now safely be extrapolated to the complete basis set limit, necessary to fully account for dynamic electron correlation effects.

2.5. Obedience of the Normalization Condition of the Correlated Pair Function. The exact total pair function $P(\mathbf{r}_1, \mathbf{r}_2)$ fulfills the normalization condition

$$\int d\mathbf{r}_1 d\mathbf{r}_2 P(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \quad (21)$$

where N corresponds to the number of electrons of the system. The total pair function can be split up into a classical part that does not describe any electron correlation and is given by $P_{\text{classical}}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)$ and an exchange-correlation part P_{xc} that accounts for the change of the pair function due to exchange and correlation effects. P_{xc} itself can be separated into an exchange P_x and correlation P_c part where the latter corresponds to the coupling strength integrated pair correlation function of eq 1. For each contribution to the total pair function individual normalization conditions hold true:

$$\int d\mathbf{r}_1 d\mathbf{r}_2 P_{\text{classical}}(\mathbf{r}_1, \mathbf{r}_2) = N^2 \quad (22)$$

$$\int d\mathbf{r}_1 d\mathbf{r}_2 P_x(\mathbf{r}_1, \mathbf{r}_2) = -N \quad (23)$$

$$\int d\mathbf{r}_1 d\mathbf{r}_2 P_c(\mathbf{r}_1, \mathbf{r}_2) = 0 \quad (24)$$

Condition 24 is trivially fulfilled by standard RPA methods, since both the coupled and uncoupled response functions (eqs 4 and 6), and thus, the correlated pair functions are expanded in products of occupied \times unoccupied orbitals. In contrast to this, this does not hold true for the modified pair function of eq 18. Therefore, we analyze errors to the norm integral of eq 24 due to the ansatz of section 2.4. For this, eq 24 is rewritten in the form

$$\begin{aligned} P_c(\mathbf{r}_1, \mathbf{r}_2) &= P_c^{\text{sr}}(\mathbf{r}_1, \mathbf{r}_2) + s(r_{12})(-P_c^{\text{sr}}(\mathbf{r}_1, \mathbf{r}_2) + P_c^{\text{ACFD/ALDA}}(\mathbf{r}_1, \mathbf{r}_2)) \\ &= P_c^{\text{sr}}(\mathbf{r}_1, \mathbf{r}_2) + s(r_{12})\Delta P_c(\mathbf{r}_1, \mathbf{r}_2) \end{aligned} \quad (25)$$

where it can now easily be seen that the normalization condition is fulfilled by the first part of eq 25 but not, in general, for the second part, since the difference of the pair functions ΔP_c is not equal to zero, of course.

In order to analyze how strongly the integrals $\int d\mathbf{r}_1 d\mathbf{r}_2 s(r_{12})\Delta P_c(\mathbf{r}_1, \mathbf{r}_2)$ deviate from zero, they were calculated for the three systems Ne, H₂O, and CO using double- to hextuple- ζ type Dunning basis sets and various scaling factors of the Coulomb kernel used in the RPA calculations for generating the short-range part P_c^{sr} of the pair function. The results are shown in Table 1. It can be observed that most values in the table are below

Table 1. Errors of the Norm Integral of Equation 24 for Correlated Pair Functions of the Form of Equations 18 and 25, Respectively, Using Double to Hextuple- ζ Dunning Basis Sets^a

system	kernel scaling	VDZ	VTZ	VQZ	VSZ	V6Z
Ne	0.4	0.020	0.027	0.027	0.025	0.024
	0.5	0.014	0.018	0.016	0.014	0.012
	0.6	0.008	0.009	0.006	0.003	0.001
	0.7	0.003	0.001	-0.004	-0.008	-0.010
	0.8	-0.002	-0.008	-0.014	-0.018	-0.021
	0.9	-0.007	-0.015	-0.023	-0.028	-0.031
	1.0	-0.011	-0.023	-0.032	-0.038	-0.041
H ₂ O	0.4	0.012	0.014	0.012	0.010	0.007
	0.5	0.008	0.007	0.004	0.001	-0.002
	0.6	0.003	0.001	-0.004	-0.008	-0.011
	0.7	-0.001	-0.006	-0.012	-0.016	-0.019
	0.8	-0.005	-0.012	-0.019	-0.024	-0.028
	0.9	-0.008	-0.018	-0.027	-0.032	-0.036
	1.0	-0.012	-0.024	-0.034	-0.040	-0.044
CO	0.4	0.015	0.019	0.018	0.015	0.012
	0.5	0.010	0.010	0.007	0.003	0.000
	0.6	0.005	0.002	-0.003	-0.008	-0.012
	0.7	-0.001	-0.006	-0.013	-0.019	-0.024
	0.8	-0.005	-0.013	-0.023	-0.030	-0.035
	0.9	-0.009	-0.021	-0.032	-0.040	-0.045
	1.0	-0.014	-0.028	-0.041	-0.050	-0.056

^aThe errors are shown for several scaling factors of the Coulomb kernel used in the RPA calculations from which the short-range pair function $P_c^{\text{sr}}(\mathbf{r}_1, \mathbf{r}_2)$ is constructed. The respective smallest values for a given basis set and system are marked in bold.

0.02 on magnitude, which indicates that the short- and long-range part to the integral $\int d\mathbf{r}_1 d\mathbf{r}_2 s(r_{12})\Delta P_c(\mathbf{r}_1, \mathbf{r}_2)$ largely compensate each other. Indeed, it was observed that the separate short- and long-range contributions to the norm over the pair function are one order of magnitude larger and amount to 0.08 (Ne), 0.05 (H₂O), and 0.07 (CO) for the long-range ACFD/ALDA part (cc-pV6Z basis set). On an absolute scale, the individual short- and long-range contributions to the pair function themselves can be considered as quite small, and it can be concluded that the approach of eq 18 only to a small degree violates the normalization constraint of eq 24.

In Table 1, also, the dependence of the error of the norm integral on the scaling factor of the Coulomb kernel used in the RPA calculation is highlighted. While one can observe that the optimal choice of the scaling factor varies with respect to the basis set (for small basis sets, a value of 0.7 yields the smallest errors to the norm integral, while for large basis sets a scaling factor of

0.5 gives the smallest errors), it appears that the value of 0.6 that was chosen by adapting the short-range RPA pair function to the long-range ACFD/ALDA pair function in the connection scheme of eq 18 (see section 2.4) also gives the smallest errors of the norm integral if medium sized triple- or quadruple- ζ type basis sets are used, see Table 1. Much larger errors are obtained, for example, if the RPA pair function (with a kernel scaling of 1.0) is used in the correction approach of eq 18. This shows that the choice of the scaling parameter for the Coulomb kernel that enters as an empirical parameter in the correction approach of section 2.4 is physically motivated both by the size of the pair function at short interelectronic distances and by the normalization constraint of eq 24.

3. TECHNICAL DETAILS

The ACFD/ALDA and the corrected ACFD/ALDAcorr methods described in section 2 have been tested for atomization energies, ionization potentials, and intermolecular interaction energies. In all calculations, the total electron–electron interaction energy was calculated as the sum of the (first-order) exact exchange energy and the ACFD/ALDA correlation energies defined in eqs 1 and 17, employing the orbitals and orbital eigenvalues from a standard Kohn–Sham calculation using the PBE xc potential.⁵⁹ The xc kernel, however, was approximated by the ALDA xc kernel (eq 11). While in ref 47 it has been argued that a nonconsistent choice of potential and kernel might lead to artificial instabilities in the solution of the TDDFT eigenvalue equation, in this work no such instabilities were encountered for any studied system. Note also that the combination of a GGA potential and the ALDA kernel is often employed for the calculation of response properties^{61–64} or intermolecular interaction contributions.^{54,65,66}

The atomization energies were calculated for the molecules from the HEAT database^{67,68} using the geometries published in ref 67. As reference values, the theoretical CCSD(T)/CBS values from ref 68 were used, excluding vibrational and spin–orbit corrections. The RPA and ACFD/ALDAcorr results were obtained by a quintuple–hexuple extrapolation (eq 20) of the correlation energies using the corresponding aug-cc-pV(5,6)Z basis sets of Dunning.^{69–72} In contrast to this, the zeroth- and first-order energies were not extrapolated, but the respective results for the aug-cc-pV6Z basis sets were taken. In the case of the uncorrected ACFD/ALDA method, no extrapolation was made for the correlation energies, but the results from the aug-cc-pVQZ basis set were used for comparison, see section 2.3. Moreover, results from standard PBE and RPA methods were considered for comparison, the former calculated using the aug-cc-pV6Z basis set and the latter, too, extrapolated with the scheme mentioned above. Note that a table containing correlation energies for all molecules from the HEAT database for the (aug-)cc-pVXZ basis sets ($X = 2 - 6$) is presented in the Supporting Information. In this table, it can also be seen that the RPA and ACFD/ALDA methods yield nonvanishing correlation energies for the H atom. This unphysical self-correlation effect is largely reduced by 1 order of magnitude in the ACFD/ALDA and ACFD/ALDAcorr methods compared to RPA, where the correlation energy of the H atom amounts to about -0.02 hartree.

The ionization potentials were calculated for the systems from the IP13 database from Minnesota.⁷³ Here, due to the relatively weak basis set dependence of the ionization energies, the calculations were done using the aug-cc-pVQZ basis set only. Note that the reference values for this database are partially

experimental and partially theoretical using the QCISD/MG3 method; see ref 73. The cation calculations were performed using relaxed geometries; that is, the ionization energies refer to nonvertical ones.

For testing the ACFD/ALDA and ACFD/ALDAcorr methods for intermolecular interaction energies, the S22 database of Hobza et al. was used,⁷⁴ which contains seven dimers dominated by electrostatic interactions, 8 dimers dominated by dispersion interactions, and 7 dimers in which both electrostatic and dispersion interactions contribute to a similar extent to the total stabilization of the complex. Here, the calculations were done using basis sets with up to aug-cc-pVQZ quality, so that for RPA and the ACFD/ALDAcorr methods the triple to quadruple- ζ two point extrapolation of Bak et al.⁷⁵ was performed for the intermolecular correlation contribution to approximate the basis set limit while the remaining interaction energy contributions were estimated on the aug-cc-pVQZ basis set level. In the case of the uncorrected ACFD/ALDA method, no extrapolation of the $X = 3, 4$ results was made; see section 2.3. Due to the comparatively higher computational cost, all calculations for the S22 systems were done using density fitting, both for the Kohn–Sham calculations and for the calculation of the correlation energies using the method of section 2.2. For this, the corresponding aug-cc-pVXZ-JKfit⁷⁶ and aug-cc-pVXZ-MP2fit⁷⁷ auxiliary basis sets were used. The accuracy of the density fitting approach of section 2.2 is analyzed in Table 2, which shows unfitted and fitted

Table 2. Accuracy of the Density Fitting Implementation (Energies in hartree)^a

molecule	basis	ACFD/ALDA	ACFD/ALDA(dfit)
H ₂ O	aVDZ	−0.25989629	−0.25985553
	aVTZ	−0.31545416	−0.31547937
	aVQZ	−0.33493018	−0.33492090
N ₂	aVDZ	−0.37885717	−0.37882464
	aVTZ	−0.46455924	−0.46453440
	aVQZ	−0.49990725	−0.49994473
CO	aVDZ	−0.36680917	−0.36678879
	aVTZ	−0.45123846	−0.45121800
	aVQZ	−0.48743892	−0.48744375
F ₂	aVDZ	−0.52179649	−0.52174645
	aVTZ	−0.65169006	−0.65169892
	aVQZ	−0.70821047	−0.70823199
MAE	aVDZ		3.6.10 ^{−5}
	aVTZ		2.0.10 ^{−5}
	aVQZ		1.8.10 ^{−5}

^aMean absolute errors (MAE) for each basis set are shown in the last three lines of the table.

correlation energies for four molecules for the aug-cc-pV(2,3,4)Z(-MP2fit) basis sets. One can observe that for all molecules the density fitting error lies in the range of $2 - 4 \times 10^{-5}$ Hartree so that it can be expected that the errors for energy differences do not exceed 0.01–0.02 kcal/mol. If the fitting errors are systematic, the latter may be even lower in praxis. In the intermolecular interaction calculations, the Boys–Bernardi counterpoise correction was used to reduce the basis-set superposition error.⁷⁸

The integrations over the coupling strength in eq 2 was performed numerically using a 7-point Gauss–Legendre

quadrature. The same type of quadrature but with 20 quadrature points was also used for the frequency integration in case of the density fitting method, see eq 3 (see also ref 79). In both cases, it was found that the quadrature error did not exceed about 10^{-6} hartree, which is in line with the findings of previous works.^{29,34,47}

In all calculations, except of those for the S22 dimer systems, core electrons were correlated. The grid accuracy for the calculation of the xc potential and xc kernel integrals was set to a value of 10^{-8} that was found to reduce the quadrature error to the range of 10^{-8} hartree and below. Open shell systems treated in this work were calculated with a spin unrestricted reference state to enable full symmetry breaking. All calculations were done using the Molpro quantum chemistry program.⁸⁰

4. RESULTS

In this section, the performances of the following approximations to the ACFD (adiabatic-connection fluctuation dissipation theorem) correlation method (see section 2) are analyzed for various properties:

- RPA, the exchange-correlation kernel is completely neglected in eq 10 and the Coulomb kernel is fully taken into account;
- RPA(0.6), the exchange-correlation kernel is completely neglected in eq 10 and the Coulomb kernel is scaled by a prefactor of 0.6;
- ACFD/ALDA, the exchange-correlation kernel is approximated by the ALDA (adiabatic local density approximation) kernel (eq 11);
- ACFD/ALDAcorr, the total correlated pair function is constructed by using eq 18 where the short-range part is approximated by the RPA(0.6) pair function and the long-range part is approximated by the ACFD/ALDA pair function.

All ACFD methods were used in conjunction with orbitals and orbital energies from preceding PBE (Perdew–Burke–Ernzerhof) DFT calculations.

All calculations were done using augmented and non-augmented correlation-consistent Dunning basis sets^{69–72} for which the acronyms aVXZ and VXZ will be used in the following (with $X = D, T, Q, 5$, and 6).

4.1. Computational Efficiency of the Density Fitting ACFD/ALDA Method. The computational efficiency of the density-fitting (DF) implementation of the ACFD/ALDA method (see section 2.2) has been tested for the molecules acetylene and benzene using aVDZ and aVTZ basis sets. The CPU times are compiled in Table 3 and were obtained by performing all-electron calculations of the correlation energies of the two molecules with the respective methods. These calculations have been done on one core/thread on a Intel(R) Xeon E5-2650 CPU (Sandybridge) clocked at 2.0 GHz. Note that no point group symmetries were exploited in the calculations.

It can be seen in Table 3 that for the C_2H_2 molecule the timings for ACFD/ALDA and DF-ACFD/ALDA (ACFD/ALDA with density fitting) are comparable, for the aVTZ basis set the speedup due to DF is only about 1.8. On the other hand, in the case of C_6H_6 , the DF-ACFD/ALDA method is about 4 times and 10 times faster than the unfitted ACFD/ALDA method using the aVDZ and aVTZ basis sets, respectively. The last two lines in the table display the approximate scaling exponents α with respect to an assumed power law scaling behavior of N_{sys}^α with N_{sys} denoting the system size (note that

Table 3. CPU Time in Seconds for the Calculation of the ACFD/ALDA (Section 2.1) and Density-Fitted ACFD/ALDA (DF-ACFD/ALDA) (Section 2.2) Correlation Energies for the Molecules C_2H_2 and C_6H_6 Using aVDZ and aVTZ Basis Sets^a

system	basis	ACFD/ALDA	DF-ACFD/ALDA		DF-ACFD/ALDAcorr	
			$f_{xc}^\alpha = \alpha f_{xc}$	$f_{xc}^\alpha = \alpha f_{xc}$	$f_{xc}^\alpha = \alpha f_{xc}$	$f_{xc}^\alpha = \alpha f_{xc}$
C_2H_2	aVDZ	6.6	6.6	1.9	7.3	2.2
C_6H_6		1024.5	244.0	64.0	254.7	73.2
C_2H_2	aVTZ	33.3	18.5	5.9	20.0	7.4
C_6H_6		10167.8	913.6	273.8	945.4	309.9
N_{sys}^α	aVDZ	4.8	3.3	3.2	3.2	3.2
N_{sys}^α	aVTZ	5.6	3.6	3.5	3.5	3.4

^aAlso shown in the table are corresponding timings for the density-fitted ACFD/ALDAcorr method (DF-ACFD/ALDAcorr) as well as for both DF-ACFD/ALDA and DF-ACFD/ALDAcorr the CPU times if the approximation $f_{xc}^\alpha = \alpha f_{xc}$ is employed (5th and 7th column, see text). The last two lines in the table display the exponents α of the system size (N_{sys}) scaling derived from the CPU times if the simple power law N_{sys}^α is assumed. Calculations were done in serial mode on a Intel(R) Xeon E5-2650 CPU (Sandybridge) clocked at 2.0 GHz.

$N_{\text{sys}}(C_6H_6) = 3N_{\text{sys}}(C_2H_2)$ has been used). It can be observed that, as expected, the scaling behavior of ACFD/ALDA is of the order of N_{sys}^{5-6} while for DF-ACFD/ALDA a scaling of N_{sys}^{3-4} is measured, thus significantly reducing the computational expense of the ACFD/ALDA method especially for larger systems.

The fifth column in Table 3 also shows the timings for an approximate DF-ACFD/ALDA method in which the coupling-strength dependent xc kernel is assumed to be linearly dependent on the coupling strength α . With this approximation, the xc kernel integrals have to be calculated only once and not for each coupling strength quadrature point (a Gauss–Legendre quadrature with seven quadrature points was used in the calculation). While it will be shown in section 4.4 how accurate this approach is compared to the ACFD/ALDA method, the performance gains with a factor of about 3.3 (see Table 3) indicate that, in fact, most of the computation time in the DF-ACFD/ALDA method is spent for calculating the xc kernel integrals (note that in the calculations tight integration grids were used as described in section 3).

Columns 6 and 7 in Table 3 show the CPU times for the DF-ACFD/ALDAcorr method with and without the approximation $f_{xc}^\alpha = \alpha f_{xc}$. As can be seen, compared to the timings for the DF-ACFD/ALDA method, the additional time needed to compute the RPA(0.6) pair function and the range-separated integrals is negligible even for C_6H_6 in the aVTZ basis set. The reason for this is that the most time-consuming parts in the calculations of the DF-ACFD/ALDA and DF-ACFD/ALDAcorr correlation energies are shared in common. These are (1) calculation and transformation of integrals to the MO basis and (2) calculation of the uncoupled response functions. Because of this, it can be concluded that the additional computational effort needed to calculate DF-ACFD/ALDAcorr correlation energies is marginal compared to the gain of a physically correctly behaving pair function in the short distance regime.

4.2. Atomization Energies. Table 4 displays the atomization energies for the different methods for the molecules from the HEAT database. It can be observed that the PBE functional yields a mean absolute error (MAE) of about 11 kcal/mol, which

Table 4. Atomization Energies (in kcal/mol)^a

molecule	PBE	RPA	ACFD/ ALDA	ACFD/ ALDAcorr	reference
N ₂	243.93	226.02	225.90	224.89	228.15
H ₂	104.62	108.77	103.34	104.76	109.49
F ₂	52.95	31.03	43.85	36.05	38.45
CO	269.10	247.68	261.02	257.31	259.72
O ₂	143.93	114.76	125.73	120.54	120.27
C ₂ H ₂	415.04	388.61	398.65	399.79	405.45
CCH	277.20	250.16	261.06	261.37	265.21
CF	145.17	122.13	133.65	129.52	132.67
CH ₂	194.53	182.52	184.83	186.46	190.71
CH	84.66	82.28	81.59	82.26	84.07
CH ₂	310.00	298.25	297.98	300.82	307.84
CN	197.68	175.47	180.84	179.98	179.38
CO ₂	416.30	371.29	392.32	386.44	390.20
H ₂ O ₂	282.35	258.11	266.55	261.92	268.96
H ₂ O	234.34	224.81	227.74	226.27	233.04
HCN	326.48	303.95	308.85	308.99	313.21
HCO	295.38	267.87	277.93	275.78	279.23
HF	142.03	133.43	139.32	136.18	141.72
HNO	223.64	201.51	204.57	201.76	205.54
HO ₂	195.36	167.77	176.48	171.79	175.05
NH ₂	188.75	180.85	175.23	177.07	182.44
NH ₃	302.12	293.20	287.14	289.60	298.00
NH	88.54	83.17	79.47	80.51	82.97
NO	172.40	150.01	153.60	150.86	152.25
OF	72.12	47.08	56.80	51.09	52.20
OH	109.93	104.17	105.04	104.21	107.17
MAE	11.34	7.27	3.93	3.80	

^aMean absolute errors to the reference values from ref 68 are shown in the last line of the table.

is similar or even better than that reported in other recent benchmarks.⁸¹ The strongest deviations of the PBE atomization energies to the CCSD(T) reference values are found for the NO and OF molecules where the PBE values differ by about 20 kcal/mol from the reference values. Compared to this, the RPA atomization energies are often more accurate than the PBE ones and deviate by about 7 kcal/mol from the reference values on average. This better performance of RPA over the PBE method is especially observed for electron-rich cases such as N₂, O₂, F₂, or CO₂, see Table 4 and ref 1. However, in total, it can well be seen in Table 4 that the RPA atomization energies, with only few exceptions, systematically underestimate the reference values. While one may wonder whether this is due to an inaccurate description of short-range electron correlation effects, in ref 1 it was shown that an additional local short-range correlation functional, leading to the so-called RPA+ approximation,⁸² did not lead to any improvement of this behavior.

In contrast to this, Table 4 shows that both the ACFD/ALDA and ACFD/ALDAcorr atomization energies yield significantly better atomization energies on average than the RPA method. Both the ACFD/ALDA and the ACFD/ALDAcorr method have MAEs of about 4 kcal/mol only, which is of the same magnitude or even slightly better than with standard hybrid or meta GGA functionals.⁸¹ It can be seen in Table 4 that also the individual ACFD/ALDA and ACFD/ALDAcorr atomization energies are close to each other, indicating that the short-range correction in the ACFD/ALDAcorr method has no significant influence on the calculation of atomization energies.

The Supporting Information also contains a table showing the atomization energies for different basis sets ranging from (aug)-

cc-pVDZ to (aug-)cc-pV6Z. Here, it can be observed that the use of diffuse functions for the calculation of the RPA and ACFD/ALDAcorr correlation energies can affect the atomization energies by 1 kcal/mol or even more. In addition, calculations of at least quadruple- ζ basis set quality are required to reduce the basis set error for the atomization energies to 3 kcal/mol or less on average.

A comparison of the results of the ACFD/ALDA method of this work to those of Furche et al.⁴⁷ shows significant differences in the atomization energies; for example, for the CO molecule, we obtain a value of about 260 kcal/mol while Furche et al. report a value of 287 kcal/mol⁴⁷ (using either the LDA or PBE functional for the reference state calculation). In contrast, the RPA results are in a much better agreement with each other (a difference of 3 kcal/mol is observed in case of CO). For the most part, the reason for this discrepancy probably lies in the fact that the values of ref 47 are obtained by basis set extrapolation techniques while in this work no such extrapolation has been attempted. However, even a comparison of raw correlation energies shows clear differences: for the NH₃ molecule, we obtain a decrease in the correlation energy from −148.4 to −158.5 kcal/mol (PBE potential and ALDA kernel) using the cc-pVTZ and cc-pV6Z Dunning basis sets (see Supporting Information) while in the work of Furche et al. an increase from −148.6 to −106.7 kcal/mol (PBE potential and kernel) with the same basis sets is observed.⁴⁷ It is likely that this difference stems from the use of different xc kernels in both cases because compared to ACFD/ALDA pair functions the pair functions from ACFD/adiabaticGGA methods exhibit an even stronger divergence of $1/r_{12}^2$ for small interelectronic distances; see ref 47. Compared to this, both the ACFD/ALDA and the ACFD/ALDAcorr results for the atomization energies are close to the results of Olsen et al. who have used a renormalized ALDA kernel to correct the short-range behavior of the pair function (see ref 48), and though a different set of molecules is used in this work and in ref 48, the mean absolute errors to the accurate reference results are almost identical (3.9 kcal/mol (this work) and 3.7 kcal/mol (ref 48)).

4.3. Ionization Energies. The accuracy of ionization energies obtained by the different methods compared to the reference values from the IP13 database is presented in Table 5. In comparison to the RPA method, for which a MAE of about 6.1 kcal/mol is obtained, now the PBE functional as well as the ACFD/ALDA and ACFD/ALDAcorr methods yield ionization energies that are closer to the reference values. In case of the ACFD/ALDA and ACFD/ALDAcorr methods, which again (see section 4.2) give very similar results for the considered systems, the error is even only of the order of 1–2 kcal/mol and thus is significantly better than those obtained with a range of different density functionals.⁸¹ The largest errors of about 4 kcal/mol for the ACFD/ALDA and ACFD/ALDAcorr ionization energies are found for the Cl₂ molecule; that is, however, much better than with the PBE functional for which an error of even 8 kcal/mol is found in this case (see Table 4).

The closeness between the ACFD/ALDA and ACFD/ALDAcorr ionization energies again indicates that the short-range correction to the ACFD/ALDA pair function has only a little influence on the considered property.

4.4. Intermolecular Interaction Energies. The accuracy of the ACFD/ALDA and ACFD/ALDAcorr method for predicting intermolecular interaction energies was tested for the S22 database of Hobza et al.⁷⁴ This benchmark set is a challenging test for electron correlation methods, since the dimer systems contained in this database are not only of different types but also

Table 5. Ionization Potentials (in kcal/mol)^a

system	PBE	RPA	ACFD/ ALDA	ACFD/ ALDAcorr	reference
C	266.08	265.81	260.05	259.91	259.74
S	240.53	248.68	235.96	236.33	238.34
SH	239.44	247.62	237.67	237.90	238.36
Cl	299.15	304.36	297.61	297.15	299.31
Cl ₂	257.00	266.74	261.42	261.22	265.30
OH	304.22	309.14	298.48	298.33	298.90
O	324.40	325.58	310.71	311.47	313.67
O ₂	281.90	283.71	277.23	277.47	278.90
P	241.92	242.23	240.04	239.91	242.80
PH	236.24	237.52	232.36	232.75	234.10
PH ₂	230.05	231.82	223.57	224.46	226.30
S ₂	217.56	221.38	214.74	215.18	216.00
Si	189.06	194.11	187.24	187.56	188.05
MAE	3.57	6.16	1.79	1.57	

^aThe aug-cc-pVQZ basis set was used. Mean absolute errors to the reference values from ref 73 are shown in the last line of the table.

of different sizes ranging from systems with 20 electrons to systems with up to 136 electrons.

The extrapolated interaction energies for the S22 data set are compiled in Table 6. The last two lines in the table show the mean absolute errors and the percentual deviations for each method to the CCSD(T)/CBS reference values from Takatani et al.⁸³ presented in the last column. One can observe that a relatively large average error of 0.81 kcal/mol is obtained for the RPA method that especially underestimates the interaction energies of the complexes with strong hydrogen bridges (e.g., the (HCCOH)₂ dimer) as well as the interaction energies of the π - π stacking complexes (Bz₂ (C_{2h}) and AT (stacked)). It should be noted, however, that the performance of RPA for the S22 benchmark complexes can strongly be improved by calculating the Kohn–Sham orbitals and eigenvalues using a different xc potential (e.g., the TPSS potential) for which the MAE reduces to 0.4 kcal/mol.² This quite large dependence of the RPA interaction energies on the reference determinant indicates that a self-consistent RPA method is desirable.

A remarkable improvement over the RPA interaction energies is obtained both using the ACFD/ALDA and the ACFD/ALDAcorr methods, see columns 3 and 5 in Table 6. Indeed, the very small error of 0.13–0.12 kcal/mol for both methods clearly outperforms results achieved with other recently developed RPA variants^{34,41} and also other DFT methods that are corrected to describe weak intermolecular interaction energies.^{84–86} Compared to the findings made for the atomization and ionization energies (see sections 4.2 and 4), this fact can now, however, be attributed to the much stronger importance of the behavior of the pair function at larger interelectronic distances, for which both the ACFD/ALDA and ACFD/ALDAcorr methods resemble each other, of course.

In the case of the ACFD/ALDA method, for which again only results for the aug-cc-pVQZ basis set are shown, it has also been analyzed to which extent the approximation $f_{xc}^{\alpha} = \alpha f_{xc}$, that is, the assumption that the xc kernel depends linearly on the coupling strength, can reproduce the results for a correctly scaled ALDA xc kernel; see eq 12. The results for this approximation are shown in column 4 in Table 6. A comparison of the interaction energies with the ones from column 3 shows a very good agreement between the two approaches, and it is found that the approximation $f_{xc}^{\alpha} = \alpha f_{xc}$ yields even slightly more accurate interaction energies than the standard ACFD/ALDA method. This result may be of importance in

Table 6. Intermolecular Interaction Energies for the S22 Complexes (in kcal/mol)^a

dimer	RPA	ACFD/ ALDA	ACFD/ ALDA	ACFD/ ALDAcorr	CCSD(T)
	aVTZ → aVQZ	aVQZ	aVQZ $f_{xc}^{\alpha} = \alpha f_{xc}$	aVTZ → aVQZ	CBS
(NH ₃) ₂ (C _{2h})	−2.63	−3.05	−3.08	−3.03	−3.17
(H ₂ O) ₂ (C _s)	−4.26	−4.85	−4.89	−4.81	−5.02
(HCOOH) ₂ (C _{2h})	−17.41	−18.91	−19.01	−18.92	−18.80
(CHONH ₂) ₂	−15.07	−16.26	−16.35	−16.28	−16.12
uracil–uracil (C _{2h})	−18.99	−20.33	−20.42	−20.34	−20.69
2-pyridoxine-2-aminopyridine	−15.78	−17.10	−17.19	−17.09	−17.00
AT (WC)	−15.50	−16.80	−16.90	−16.81	−16.74
(CH ₄) ₂ (D _{3d})	−0.40	−0.53	−0.54	−0.54	−0.53
(C ₂ H ₄) ₂ (D _{2d})	−1.15	−1.49	−1.51	−1.50	−1.50
Bz–CH ₄ (C ₃)	−1.14	−1.44	−1.46	−1.45	−1.45
Bz–Bz (C _{2h})	−1.89	−2.41	−2.45	−2.45	−2.62
pyrazine–pyrazine (C _s)	−3.32	−3.93	−3.98	−3.98	−4.20
uracil–uracil (C ₂)	−8.69	−9.61	−9.61	−9.68	−9.74
indole–Bz (stacked)	−3.40	−4.15	−4.20	−4.19	−4.59
AT (stacked)	−10.04	−11.27	−11.36	−11.35	−11.66
C ₂ H ₄ –C ₂ H ₂ (C _{2v})	−1.26	−1.49	−1.51	−1.49	−1.51
Bz–H ₂ O (C _s)	−2.87	−3.27	−3.30	−3.28	−3.29
Bz–NH ₃ (C _s)	−1.98	−2.31	−2.33	−2.32	−2.32
Bz–HCN (C _s)	−3.95	−4.45	−4.48	−4.47	−4.55
Bz–Bz (C _{2v})	−2.23	−2.65	−2.68	−2.67	−2.71
indole–Bz (T-shaped)	−4.99	−5.58	−5.62	−5.61	−5.62
phenole–phenole	−6.18	−6.93	−6.98	−6.93	−7.09
MAE	0.81	0.13	0.12	0.12	
Δ [%]	15.31	2.35	2.01	2.04	

^aThe mean absolute errors and relative deviations (|Δ|) to the CCSD(T) reference values are shown in the last two lines of the table.

the calculation of large molecular systems where a linearly scaled xc kernel would significantly reduce the computation time, since the three-index integrals ($ialf_{xc}^{\alpha}|P$) in eq 16 would have to be calculated only once, see section 4.1.

5. SUMMARY

The short-range behavior of correlated pair functions from the adiabatic-connection fluctuation dissipation theorem employing adiabatic local density approximation kernels (ACFD/ALDA) has been studied for a range of atomic and molecular systems. It has been found that, in line with the analytical results of ref 47, ACFD/ALDA are unphysical in regions of small interelectronic distances indicated by spurious humps of the pair functions. However, this behavior only shows up with relatively large basis sets of quintuple- ζ type and larger while for smaller basis sets, for the systems that were studied, the ACFD/ALDA pair function has a regular shape. This short-range behavior of the ACFD/ALDA pair function is also reflected in the correlation energies obtained therefrom: with basis sets from double- to quadruple- ζ quality the correlation energies generally increase on magnitude while with larger basis sets the correlation energies either increase only slightly (indicating a fake convergence) or even decrease on magnitude. Because of this, with the ACFD/ALDA

method, it is not possible to reliably estimate the complete basis set limit by, for example, basis set extrapolation techniques. This, however, is of crucial importance in order to fully account for dynamic electron correlation effects.

The results presented in this work apparently contradict to the findings of Furche et al.⁴⁷ in which a much worse dependence of the ACFD/(local xc kernel) correlation energy on the size of the basis set was observed. However, the study in ref 47 was done by using adiabatic generalized-gradient corrected (AGGA) kernels for which the divergency of the pair function for $r_{12} \rightarrow 0$ is even stronger than with ALDA kernels. In fact, one result of this work is that the ACFD/ALDA method can yield reasonable results for atomization energies, ionization potentials, and intermolecular interaction energies if medium sized triple- or quadruple basis sets are used. In particular, for intermolecular interaction energies, it was found that the ACFD/ALDA shows a high accuracy. This has been shown for the S22 benchmark set containing 22 intermolecular complexes (with average interaction energies of 7.3 kcal/mol) for which the mean absolute error of the ACFD/ALDA method is only 0.13 kcal/mol, which is clearly better than with many recently developed DFT^{84–86} and wave function methods^{58,83,87} that were tested for this benchmark set.

In order to rectify the unphysical behavior of the ACFD/ALDA pair function at short interelectronic ranges, a short-range correction method has been developed and tested, which is based on a seamless connection between a correctly behaving pair function of a modified RPA method for the short interelectronic range and the ACFD/ALDA pair function for larger distances. While this scheme requires two parameters to adapt the switching range and the size of the short-range pair function for $r_{12} \rightarrow 0$, these can be obtained by physical means. Namely, the parameter determining the interpolation range was chosen such that unphysical contributions to the pair function, occurring for larger basis sets, are cut off. Second, the parameter that adapts the size of the short-range pair function is chosen such that it resembles the ACFD/ALDA pair function for small basis sets where the latter still behaves physically correct. It turns out that with this choice also the error to the norm integral ($\int \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 P_c(\mathbf{r}_1, \mathbf{r}_2)$), which is zero for the exact correlated pair function but generally nonzero for pair functions derived from the correction approach of this work, is minimized.

It has been found that the correlation energies obtained by the corrected ACFD/ALDAcorr method possess a regular dependence on the basis set size that is qualitatively identical to the one of the RPA method and other (standard) wave function correlation methods. Thus, the correction approach to the ACFD/ALDA pair function enables the use of standard basis set extrapolation techniques so that the basis set errors, which plague common ab initio methods, can effectively be reduced. Numerical results for atomization energies, ionization potentials, and intermolecular interaction energies obtained by the ACFD/ALDAcorr resemble closely large basis set results of the ACFD/ALDA method and show a high accuracy.

A density fitting implementation of the ACFD/ALDA method, termed as DF-ACFD/ALDA, was shown to reproduce the nonfitted correlation energies with a good accuracy if standard MP2-fitting basis sets are employed. Due to the significantly lower scaling behavior of this approach compared to the standard ACFD/ALDA method, that (in the approach described in section 2.1) requires the calculation of all TDDFT eigenvectors in a given basis set, the method can also be applied to large molecular systems. Indeed, it was found that the effective scaling behavior of the ACFD/ALDA with respect to the system

size is reduced by two orders of magnitude using the DF approximation. This means that the DF-ACFD/ALDA method is not much more computationally expensive than corresponding Kohn–Sham reference calculations. A comparison of the CPU timings for the DF-ACFD/ALDA and DF-ACFD/ALDAcorr method has shown that the additional computational effort needed to compute ACFD/ALDAcorr correlation energies is marginal compared to the overall computation cost. This, in addition to the physically correctly behaving pair function at small interelectronic distances, more than justifies to use the ACFD/ALDAcorr instead of the ACFD/ALDA method in molecular calculations.

■ ASSOCIATED CONTENT

Supporting Information

Tables containing correlation energies, atomization energies, ionization energies, and intermolecular interaction energies, as well as figures showing the short-range behavior of the pair function for He, Ne, H₂, H₂O, and CO for various positions of the reference electron. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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