



Power Series Approximation for the Correlation Kernel Leading to Kohn-Sham Methods Combining Accuracy, Computational Efficiency, and General Applicability

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A power series approximation for the correlation kernel of time-dependent density-functional theory is presented. Using this approximation in the adiabatic-connection fluctuation-dissipation (ACFD) theorem leads to a new family of Kohn-Sham methods. The new methods yield reaction energies and barriers of unprecedented accuracy and enable a treatment of static (strong) correlation with an accuracy of high-level multireference configuration interaction methods but are single-reference methods allowing for a black-box-like handling of static correlation. The new methods exhibit a better scaling of the computational effort with the system size than rivaling wave-function-based electronic structure methods. Moreover, the new methods do not suffer from the problem of singularities in response functions plaguing previous ACFD methods and therefore are applicable to any type of electronic system.

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A long-standing goal in density-functional theory (DFT) and electronic structure theory in general is the development of methods that can treat any type of electronic system including those characterized by noncovalent interactions or by static (strong) correlation with high accuracy yet manageable computational effort. Here, we present a family of Kohn-Sham (KS) methods that reaches this goal. The methods exhibit for reaction energies and barriers of molecules an accuracy that is unprecedented in DFT and rivals that of computationally more demanding high-level quantum chemistry methods. Furthermore, the new methods describe well noncovalent interactions, like van der Waals interactions. Concerning static correlation, the KS formalism of DFT, in principle, enables its efficient treatment on the basis of a single-reference wave function, the KS determinant, despite the fact that the real physical wave function in cases of static correlation is of multireference character. So far, no KS method could live up to this promise. The methods presented here, however, enable exactly this.

KS methods treating the correlation energy via the adiabatic-connection fluctuation-dissipation (ACFD) theorem [1,2] in recent years have proven to represent a highly promising novel generation of DFT methods [3–12]. In ACFD methods, all parts of the electronic energy except the correlation energy are calculated exactly. This is a characteristic ACFD methods share with wave-function-based electronic structure methods like the hierarchy of coupled-cluster methods [13,14]. The KS correlation energy is calculated via the ACFD theorem according to

$$E_c = \frac{-1}{2\pi} \int_0^\infty d\omega \int_0^1 d\alpha \text{Tr}\{[\mathbf{X}_\alpha(i\omega) - \mathbf{X}_0(i\omega)]\mathbf{F}_H\}. \quad (1)$$

In Eq. (1), \mathbf{X}_0 denotes the dynamic, i.e., frequency-dependent, density-density (potential-density) KS response

matrix that is the basis set representation of the response function of the KS model system of hypothetical non-interacting electrons. \mathbf{X}_α stands for the dynamic density-density response matrix of a corresponding electronic system with electrons interacting via an electron-electron interaction scaled by the coupling constant $0 \leq \alpha \leq 1$. The matrix \mathbf{X}_α turns into the KS response matrix \mathbf{X}_0 for $\alpha = 0$ and into the response function of the real electron system with fully interacting electrons for $\alpha = 1$. The electronic systems for all values of the coupling constant are uniquely defined via the Hohenberg-Kohn theorem by the requirement to have the same ground state electron density. All response matrices are evaluated for complex frequencies $i\omega$.

The matrix \mathbf{F}_H represents the Coulomb interaction in the same auxiliary basis set that is used for the construction of \mathbf{X}_0 and \mathbf{X}_α . This auxiliary basis set is required in addition to the basis set to represent one-electron states, i.e., orbitals. For notational simplicity, the auxiliary basis set is assumed to be orthonormal here; for nonorthonormal auxiliary basis sets, additional overlap matrices occur. The introduction and construction of auxiliary basis sets is described in detail in the Supplemental Material (SM) [15] and in Ref. [8].

While the KS response matrix \mathbf{X}_0 can be straightforwardly constructed from the KS orbitals and eigenvalues (see the SM), the response matrices \mathbf{X}_α are accessible via time-dependent density-functional theory in the response regime [33–35] according to

$$\mathbf{X}_\alpha(i\omega) = [\mathbf{1} - \mathbf{X}_0(i\omega)\mathbf{F}_{Hxc}^\alpha(i\omega)]^{-1}\mathbf{X}_0(i\omega). \quad (2)$$

In Eq. (2), \mathbf{F}_{Hxc}^α represents the sum of the Hartree kernel plus the dynamic exchange-correlation kernel, the frequency-dependent functional derivative of the exchange-correlation potential with respect to the electron density.

Equations (1) and (2) are exact. However, the exchange-correlation kernel is not known exactly, except for special situations [36]. Therefore, at this point, approximations have to be invoked. In most ACFD methods, the exchange-correlation kernel is completely neglected; this amounts to the direct random phase approximation (dRPA). The dRPA, in contrast to conventional DFT methods employing functionals within the local density or generalized gradient approximation, is able to describe van der Waals interactions; for reaction energies, however, results typically are only moderately better than those of conventional DFT methods, and atomization and total energies are very poor [7,8,37]. Moreover, the dRPA suffers from the fundamental problem that it is not self-interaction free and, e.g., yields an unphysical correlation energy in one-electron systems.

An ACFD method completely free of self-interactions results if the frequency-dependent exchange kernel is fully taken into account in addition to the Hartree kernel [8,9,12,38–41]. The exchange kernel itself is not known. However, the sum \mathbf{F}_{Hx} of the Hartree plus the exchange kernel obeys an integral equation, which turns into the matrix equation

$$\mathbf{X}_0 \mathbf{F}_{Hx} \mathbf{X}_0 = \mathbf{H}_{Hx} \quad (3)$$

in a basis set representation. Starting with Eq. (3), we suppress the frequency argument $i\omega$ for notational clarity unless it is indispensable. The matrix \mathbf{H}_{Hx} represents a function $h_{Hx}(i\omega; \mathbf{r}, \mathbf{r}')$ which is known explicitly in terms of KS orbitals and eigenvalues and thus is accessible; see Refs. [39–41].

Multiplication of Eq. (3) from the right and from the left with $\mathbf{L}^{-1} = (-\mathbf{X}_0)^{-1/2}$, the inverse of the KS response matrix, yields

$$\mathbf{L} \mathbf{F}_{Hx} \mathbf{L} = \mathbf{L}^{-1} \mathbf{H}_{Hx} \mathbf{L}^{-1}. \quad (4)$$

Because all response functions occurring here are Hermitian and negative definite, the square root \mathbf{L} of $-\mathbf{X}_0$ is well defined. Inserting Eq. (4) into Eq. (2) yields

$$\begin{aligned} \mathbf{X}_\alpha &= \mathbf{L} [-\mathbf{1} - \alpha \mathbf{L}^{-1} \mathbf{H}_{Hx} \mathbf{L}^{-1}]^{-1} \mathbf{L} \\ &= \mathbf{L} \mathbf{U} [-\mathbf{1} - \alpha \boldsymbol{\tau}]^{-1} \mathbf{U}^\dagger \mathbf{L}; \end{aligned} \quad (5)$$

see the SM for details. In the second line of Eq. (5), the spectral representation

$$\mathbf{L}^{-1} \mathbf{H}_{Hx} \mathbf{L}^{-1} = \mathbf{U} \boldsymbol{\tau} \mathbf{U}^\dagger \quad (6)$$

was used with the diagonal matrix $\boldsymbol{\tau}$ containing the eigenvalues and with the unitary matrix \mathbf{U} containing the eigenvectors of $\mathbf{L}^{-1} \mathbf{H}_{Hx} \mathbf{L}^{-1}$.

If expression (5) for the response matrix \mathbf{X}_α is inserted into the ACFD theorem (7), then the correlation energy assumes the form [8]

$$\begin{aligned} E_c &= \frac{-1}{2\pi} \int_0^\infty d\omega \int_0^1 d\alpha \text{Tr} \{ [\mathbf{L}(i\omega) \mathbf{U}(i\omega) \\ &\times [(-\mathbf{1} - \alpha \boldsymbol{\tau}(i\omega))^{-1} + \mathbf{1}] \mathbf{U}^\dagger(i\omega) \mathbf{L}(i\omega)] \mathbf{F}_H \}. \end{aligned} \quad (7)$$

Expression (7) can be readily evaluated for any given set of KS orbitals and eigenvalues. The resulting ACFD method [8] is denoted as ACFD[Hx]. In this notation, the kernel employed in the ACFD theorem is abbreviated in square brackets. The dRPA in this notation reads as ACFD[H]. The ACFD[Hx] approach not only is free of unphysical self-interactions, but it furthermore describes reaction energies and van der Waals interactions more accurately compared to the dRPA [8]. Moreover, the ACFD[Hx] approach yields a qualitatively correct, although not highly accurate, dissociation limit when breaking bonds including multiple bonds without the necessity to artificially break spin symmetry [38]; see Fig. 1 for the example of the dissociation of the N_2 molecule.

The ACFD[Hx] dissociation curve of N_2 (see Fig. 1) at medium bond lengths from 3.0–4.5 Bohr exhibits unphysical features pointing to a fundamental shortcoming of the ACFD[Hx] approach, which becomes apparent when analyzing expression (5) for the response matrix \mathbf{X}_α [42]. The eigenvalues τ of $\mathbf{L}^{-1} \mathbf{H}_{Hx} \mathbf{L}^{-1}$ can assume negative numbers below -1 . For equilibrium geometries, this seems not to happen; however, when stretching bonds, it does. If $\tau < -1$, then $-1 - \alpha\tau = 0$ for a certain value of $0 \leq \alpha \leq 1$, and $-1 - \alpha\tau > 0$ if α is larger than this value. For $-1 - \alpha\tau = 0$, the diagonal matrix $[-\mathbf{1} - \alpha\boldsymbol{\tau}]^{-1}$ and thus the response matrix \mathbf{X}_α become singular; whenever $-1 - \alpha\tau > 0$, an eigenvalue of $[-\mathbf{1} - \alpha\boldsymbol{\tau}]^{-1}$ becomes positive, and subsequently, the response matrix \mathbf{X}_α is no longer negative definite, which is unphysical; see Fig. 2. This means the ACFD[Hx] approach is not applicable to some electronic structures. This shortcoming has to be caused by the neglect of the correlation kernel in the construction of

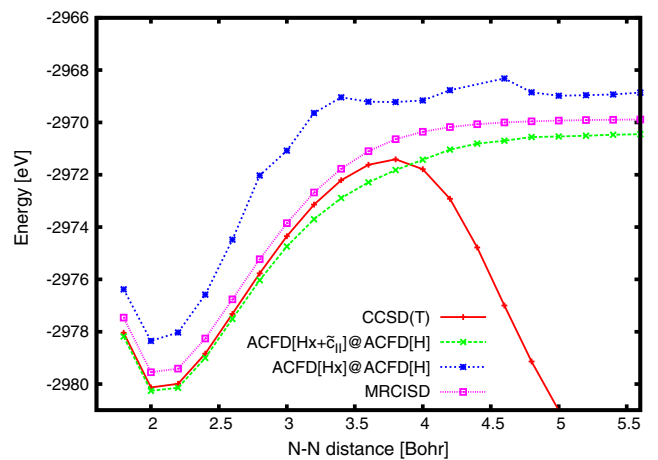


FIG. 1. Dissociation curves of N_2 for different methods; for the nomenclature, see the text later on.

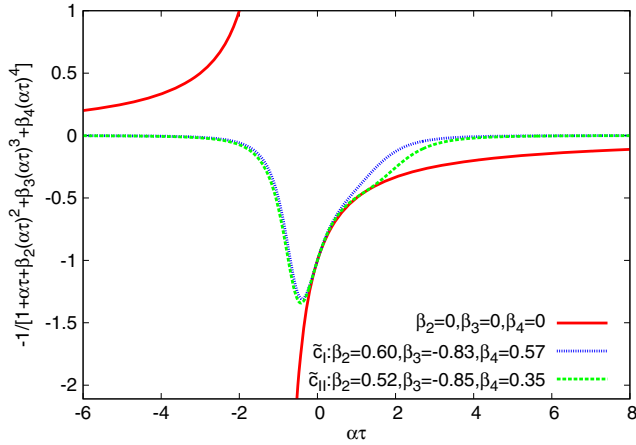


FIG. 2. $1/[-1 - \alpha\tau - \beta_2\alpha^2\tau^2 - \beta_3\alpha^3\tau^3 - \beta_4\alpha^4\tau^4]$ for different β parameters.

the response matrix \mathbf{X}_α [see Eq. (5)] because this is the only approximation invoked in the approach.

In this work, we present a power series approximation (PSA) for the correlation kernel that guarantees that all involved response matrices are negative definite. In this way, a generally applicable method is obtained. Taking into account the correlation kernel via the PSA introduced here, moreover, leads to much higher accuracies while not increasing the computational effort significantly.

In perturbation theory along the adiabatic connection, the correlation energy and potential are expanded in Taylor series with respect to the coupling constant α [43,44]. It was shown that the leading term in these Taylor series is of quadratic order in α . The Taylor series in the correlation energy and potential implies a corresponding Taylor series for the correlation kernel

$$\mathbf{F}_c^\alpha = \sum_{n=2}^{\infty} \alpha^n \mathbf{F}_c^{(n)}. \quad (8)$$

Next, we define a matrix $\mathbf{H}_c^\alpha = \mathbf{X}_0 \mathbf{F}_c^\alpha \mathbf{X}_0$. With the Taylor series (8), we obtain

$$\mathbf{L}^{-1} \mathbf{H}_c^\alpha \mathbf{L}^{-1} = \sum_{n=2}^{\infty} \alpha^n \mathbf{L}^{-1} \mathbf{H}_c^{(n)} \mathbf{L}^{-1} \quad (9)$$

with the matrices $\mathbf{H}_c^{(n)} = \mathbf{X}_0 \mathbf{F}_c^{(n)} \mathbf{X}_0$.

The matrices $\mathbf{H}_c^{(n)}$ are not known exactly; we therefore invoke the approximation

$$\mathbf{L}^{-1} \mathbf{H}_c^{(n)} \mathbf{L}^{-1} \approx \beta_n [\mathbf{L}^{-1} \mathbf{H}_{H_x} \mathbf{L}^{-1}]^n, \quad (10)$$

the PSA. With the spectral representation (6) of $\mathbf{L}^{-1} \mathbf{H}_{H_x} \mathbf{L}^{-1}$, we obtain the expression

$$\mathbf{X}_\alpha \approx \mathbf{L} \mathbf{U} \left[-\mathbf{1} - \alpha\tau - \sum_n \beta_n \alpha^n \tau^n \right]^{-1} \mathbf{U}^\dagger \mathbf{L} \quad (11)$$

for the response matrix \mathbf{X}_α . In Eq. (11), the correlation kernel, more precisely, $\mathbf{L} \mathbf{F}_c^\alpha \mathbf{L} = \mathbf{L}^{-1} \mathbf{H}_c^\alpha \mathbf{L}^{-1}$, is approximated by the power series $\mathbf{U} [\sum_n \beta_n \alpha^n \tau^n] \mathbf{U}^\dagger$. Inserting Eq. (11) in the ACFD theorem (1) yields an expression for the correlation energy that has the same basic form as the ACFD[H_x] expression (7) and can be evaluated with only negligible additional computational effort. The only difference is that the diagonal matrix $[-\mathbf{1} - \alpha\tau]^{-1}$ in Eq. (7) is replaced by $[-\mathbf{1} - \alpha\tau - \sum_n \beta_n \alpha^n \tau^n]^{-1}$. The factors β_n in Eqs. (10) and (11) are parameters that are undetermined so far. As a first step, we here reduce the PSA to the leading three terms and have determined the three parameters β_2 , β_3 , and β_4 such that the error in the reaction energies for a training set of 24 reactions of small molecules (see Table 1 of the SM) is minimized.

As is common for ACFD methods, we carried out non-self-consistent calculations; i.e., we determined the orbitals and eigenvalues by some self-consistent Kohn-Sham procedures and then evaluated the total electronic energy with the exact exchange energy and the correlation energy from the ACFD theorem. We here use exact exchange-only (EXX) calculations [45–49] or self-consistent dRPA calculations to determine the KS orbitals and eigenvalues. Self-consistent dRPA calculations can be carried out in several ways [37,50,51]; we used the method of Ref. [37]. The resulting approaches are denoted as ACFD[$H_x + \tilde{c}_I$]@EXX and ACFD[$H_x + \tilde{c}_{II}$]@ACFD[H]. In this notation, the second entry in the acronyms points to the methods used to obtain the KS orbitals and eigenvalues. In the square brackets of the first entry, as before, the kernel used in the ACFD theorem is specified; the correlation kernel in the PSA introduced here is indicated by \tilde{c}_I and \tilde{c}_{II} . The indices I and II refer to the two different sets of parameters β_2 , β_3 , and β_4 that are listed in Fig. 2 and that were obtained by minimizing the reaction energies of the training set of Table 1 of the SM for the approaches ACFD[$H_x + \tilde{c}_I$]@EXX and ACFD[$H_x + \tilde{c}_{II}$]@ACFD[H], respectively. In Fig. 2, the function $1/[-1 - \alpha\tau - \beta_2\alpha^2\tau^2 - \beta_3\alpha^3\tau^3 - \beta_4\alpha^4\tau^4]$ is displayed for the two sets of β parameters. For the β parameters \tilde{c}_I and \tilde{c}_{II} , this function, in contrast to the function $1/[-1 - \alpha\tau]$ of the ACFD[H_x] method, never becomes singular or positive, i.e., leads to physically reasonable response matrices \mathbf{X}_α for any electronic system. Note that in the optimization of the β parameters, it was not enforced to obtain nonsingular or negative functions $1/[-1 - \alpha\tau - \beta_2\alpha^2\tau^2 - \beta_3\alpha^3\tau^3 - \beta_4\alpha^4\tau^4]$. The minimization of the reaction energies of the training set by itself resulted in physically reasonable functions, which indicates that the PSA for the correlation kernel is a reasonable ansatz.

All calculations were carried out with the development version of the program package Molpro [52]; see the SM for technical details.

Figure 3 shows that the new approaches ACFD[$H_x + \tilde{c}_I$]@EXX and ACFD[$H_x + \tilde{c}_{II}$]@ACFD[H] lead to much more

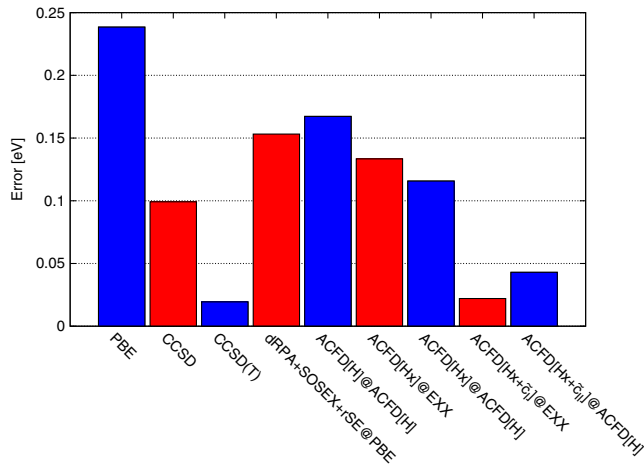


FIG. 3. Root mean squared error of the reaction energies of the training set.

accurate reaction energies than any other density-functional method, including other ACFD methods. (By dRPA+SOSEX+rSE@PBE an approach is designated that combines the dRPA with a second order screened exchange (SOSEX) and a correction due to renormalized singles excitations (rSE); see Refs. [53,54].) Furthermore, the new approaches are more accurate than the coupled-cluster singles-doubles (CCSD) method [55] and are approaching the accuracy of the coupled-cluster singles doubles perturbative triples [CCSD(T)] method [13,56,57], which is often considered the gold standard for reactions of the type considered here. Indeed, the accuracy of ACFD[$Hx + \tilde{c}_I$]@EXX as well as ACFD[$Hx + \tilde{c}_{II}$]@ACFD[H] is better than 1 kcal/mol (0.043 eV), which is considered as chemical accuracy, i.e., the accuracy required to reliably describe chemical processes.

Somewhat surprisingly, the ACFD[$Hx + \tilde{c}_I$]@EXX results are more accurate than the ACFD[$Hx + \tilde{c}_{II}$]@ACFD[H] ones, despite the fact that in the generation of the orbitals and eigenvalues for the latter approach, the correlation potential is not neglected but taken into account at the dRPA level. Correlation potentials from self-consistent dRPA (ACFD[H]) calculations have been shown to be of good quality in most cases [37,58]. However, in a lot of reactions of the training set of Table 1 of the SM, the hydrogen molecule H_2 is involved. For a two-electron system like H_2 , the dRPA self-interaction error is particularly important. This may compromise the quality of the orbitals and eigenvalues used as input in the ACFD[$Hx + \tilde{c}_{II}$]@ACFD[H] approach and might be the reason for the somewhat lower accuracy compared to the ACFD[$Hx + \tilde{c}_I$]@EXX approach. (Of course, the ACFD[$Hx + \tilde{c}_{II}$] energy itself is completely free of self-interactions; see above.)

In order to check whether the new methods also perform well for reactions not contained in the training set, we considered another set of reactions. Again, the new

methods performed with chemical accuracy; see the SM for details. Furthermore, we optimized the β parameters of the PSA for the correlation kernel, taking into account only half the reactions contained in the training set, and obtained very similar results; see the SM.

Next, we considered a standard example for static (strong) correlation, the dissociation of the nitrogen molecule N_2 . Figure 1 shows that the ACFD[$Hx + \tilde{c}_{II}$]@ACFD[H] method yields a smooth dissociation curve without the unphysical features of the ACFD[Hx] method. Moreover, the resulting dissociation energy with 9.724 eV compares very well with the corresponding value from experiment of 9.787 eV [59] and is even slightly more accurate than that of 9.674 eV of a multireference configuration interaction calculation taking into account single and double excitations (MRCISD [60,61]) from a reference configuration space containing all valence configurations. The single-reference CCSD(T) method, on the other hand, is not able to describe the dissociation of N_2 correctly [13,62]. Around the equilibrium bond distance, however, the CCSD(T) energies can be assumed to be highly accurate. In this region, the ACFD[$Hx + \tilde{c}_{II}$]@ACFD[H] and the CCSD(T) curves are almost on top of each other. It is important to point out that neither the N_2 molecule nor bond dissociation is included in the training set of Table 1 of the SM. This means that even though the parameters β_2 , β_3 , and β_4 were optimized with reaction energies, the ACFD[$Hx + \tilde{c}_{II}$]@ACFD[H] method accurately describes bond dissociation and thus static correlation. This shows that the basic ansatz, i.e., the PSA for the correlation kernel, is quite robust.

We then calculated 12 reaction barriers from a test set in Ref. [63]. The root mean square error of 0.027 eV for both the ACFD[$Hx + \tilde{c}_I$]@EXX and the ACFD[$Hx + \tilde{c}_{II}$]@ACFD[H] methods, compared to 0.105 eV for CCSD, underlines the accuracy of our method for systems in nonequilibrium geometries; see the SM for details.

Finally, the ability of the new methods to describe noncovalent interactions was checked with a test set of 24 noncovalently bounded dimers; see the SM for details. For this test set, the new methods yield more accurate results than CCSD and self-consistent dRPA, i.e., ACFD[H]@ACFD[H], calculations. The training set of Table 1 of the SM for determining the β parameters does not contain the van der Waals bonded system. The fact that nevertheless such systems can be described more accurately than with the CCSD method again is an argument for the PSA for the correlation kernel.

In summary, we have introduced with the PSA the possibility to take into account a correlation kernel in ACFD methods. Together with the exact treatment of the Hartree and exchange kernel, this leads to a new family of KS methods with unprecedented accuracy. Moreover, the new methods represent the first single-reference methods that can treat static (strong) correlation as accurate as high-level multireference methods (MRCISD) in a black-box

manner, i.e., without the need to specify a space of reference configurations to be taken into account. This means the new methods are generally applicable to any type of electronic structure. While the new methods show accuracies of high-level quantum chemistry approaches, they are computationally more efficient. The ACFD[$Hx + \tilde{c}$] methods exhibit a formal N^5 scaling with the system size N while CCSD and CCSD(T) exhibit an N^6 or N^7 scaling, respectively, and multireference configuration interaction methods even scale factorially. For the small molecules considered here for the reaction energies and barriers, ACFD[$Hx + \tilde{c}_I$]@EXX and ACFD[$Hx + \tilde{c}_{II}$]@ACFD[H] calculations require about 2 and 10 times more time than conventional KS calculations with the exchange-correlation functional due to Perdew, Burke, and Ernzerhof [64], respectively, while CCSD and CCSD(T) calculations require about 20 and 80 times more. Finally, we emphasize that the ACFD[$Hx + \tilde{c}_I$]@EXX and the ACFD[$Hx + \tilde{c}_{II}$]@ACFD[H] approaches are just the two first members of this new family of KS methods using the PSA for the correlation kernel. By taking into account more terms in the Taylor series (9) and by possibly better determined parameters β_n , probably even more accurate results may be attainable without increasing the computational effort.

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