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Third-order corrections to random-phase approximation correlation energies

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Several random-phase approximation (RPA) correlation methods were compared in third order of perturbation theory. While all of the considered approaches are exact in second order of perturbation theory, it is found that their corresponding third-order correlation energy contributions strongly differ from the exact third-order correlation energy contribution due to missing interactions of the particle-particle-hole-hole type. Thus a simple correction method is derived which makes the different RPA methods also exact to third-order of perturbation theory. By studying the reaction energies of 16 chemical reactions for 21 small organic molecules and intermolecular interaction energies of 23 intermolecular complexes comprising weakly bound and hydrogen-bridged systems, it is found that the third-order correlation energy correction considerably improves the accuracy of RPA methods if compared to coupled-cluster singles doubles with perturbative triples as a reference. © 2011 American Institute of Physics. [doi:10.1063/1.3590916]

I. INTRODUCTION

The description of electron correlation plays an important role in the theoretical study of molecular systems. This perhaps becomes most obvious when one considers molecular systems that are far from their ground-state equilibrium or in case of weakly bound molecular complexes where the Hartree-Fock method completely fails. However, even for nonproblematic systems Hartree-Fock theory fails to deliver the chemical accuracy of 1 kcal/mol for binding energies, 0.01 Å for bond distances, or 10 cm⁻¹ for vibrational frequencies. Because of this the electron correlation effects missing in Hartree-Fock theory have to be accounted for. Usually this is done using standard *ab initio* correlation methods like configuration interaction, Møller-Plesset perturbation theory, or coupled-cluster theory.¹⁻⁶ Since these methods are conventionally much more computationally expensive than Hartree-Fock, Kohn-Sham density-functional methods (DFT)⁷⁻⁹ have become very popular as a compromise between accuracy and cheapness since they are commonly even cheaper than Hartree-Fock methods but usually less accurate than standard *ab initio* correlation methods.

However, the development of new computational algorithms like density fitting¹⁰⁻¹⁸ and Cholesky decomposition¹⁹⁻²⁴ (see also Refs. 25 and 26 for singular value decomposition approaches in coupled-cluster theory), the transformation into local basis functions,^{14,15,27-38} or the exploitation of parallel computer architectures^{18,39-42} has led to an increase of the feasibility of standard *ab initio* methods also for extended molecular systems so that electron correlation effects can nowadays also accurately be accounted for quite large systems that formally could be described only on the density functional theory level. However, though in contrast to DFT common *ab initio* correlation methods have

the advantage that they can systematically be improved, one usually has to restrict oneself to those methods that have the lowest scaling behaviour with respect to the molecular size N , that is, second-order Møller-Plesset perturbation theory (MP2) scaling as N^5 or coupled-cluster singles-doubles (CCSD) which has a scaling behaviour of N^6 .

Among these methods one can also classify random-phase approximation (RPA) correlation methods^{2,43-51} which, as was recently shown by Scuseria *et al.*,⁵² are related to coupled cluster doubles theory in which one only keeps terms of the particle-hole type (see also Ref. 2; in fact, it has been shown that the dispersion interaction energy on the coupled-cluster doubles level is identical to the dispersion energy described by RPA response propagators of the monomers, see Ref. 53). Because of this they are generally computationally less expensive than corresponding coupled-cluster methods restricted to doubles excitations but have in comparison with, e.g., Møller-Plesset perturbation theory methods the advantage that certain types of correlation energy diagrams, namely, those with a ring structure,^{2,48,54} are summed up to infinity. In spite of this feature of RPA methods one may now ask why they have rarely been used in the past to calculate the electron correlation energy for molecular ground states. In Sec. II it will be shown that the extraction of the correlation energy from the RPA is by far not unique and a number of RPA methods were developed that are exact in second order of perturbation theory, but differ in third-order. We here refer to these methods as “normal” RPA (NRPA) methods^{46,55} in order to point out the difference to so called higher RPA methods^{45,47,55-61} (like SOPPA, second-order polarisation propagator approximation^{47,62}) in which the wave function that enters the RPA equations also contains double excitations.

In recent years RPA methods have become more popular in the framework of density functional theory.⁶³⁻⁷⁶ The use of

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the Kohn-Sham determinant instead of the Hartree-Fock determinant as the reference determinant in RPA methods might be advantageous in order to account implicitly for single excitations that are commonly absent in Hartree-Fock based RPA methods. It has been shown for some small molecules that, depending however on the underlying exchange-correlation potential, Kohn-Sham orbitals are closer to Brueckner orbitals than Hartree-Fock orbitals⁷⁷ (see, however, Ref. 78) and therefore might be closer to variationally optimised orbitals in RPA approaches. It has also been demonstrated recently that an adiabatic-connection RPA method based on exact Kohn-Sham exchange is superior for the description of bond dissociation than the corresponding Hartree-Fock based approach.⁷⁹ RPA correlation functionals also appear to be attractive candidates in range-separated DFT methods in which the short-range electron correlation is described by standard DFT methods and the long-range correlation, that is poorly described on the standard DFT level, is described with RPA.^{68,69,71,73,80–82} The advantage of such range-separated methods is that they are less basis set dependent than common *ab initio* correlation methods since the interelectronic cusp problem is screened out by using a DFT description for small interelectronic distances.

In this work several random-phase approximation correlation methods based on the Hartree-Fock reference determinant will be considered. In Sec. II the explicit expressions for the correlation energies of the different RPA methods will be presented. In Sec. III the third-order contributions to the correlation energy for these RPA methods will be investigated numerically and a simple correction approach will be derived that enforces correctness in third order for the different RPA methods. Section IV shows the performance for the RPA methods for total correlation energies (Subsection IV A), reaction energies (Subsection IV B), and intermolecular interactions (Subsection IV C). It will be shown that the third-order correction to RPA correlation energies considerably improves their accuracy if compared to coupled-cluster singles doubles with perturbative triples (CCSD(T)) reference values. Finally, Sec. V discusses the results and concludes.

II. CORRELATION ENERGY IN THE RANDOM PHASE APPROXIMATION

The RPA equations determining the excitation energies ω_n and the amplitudes X_n, Y_n are given by^{3,46,83,84}

$$\begin{pmatrix} \epsilon + \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\epsilon - \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \lambda & \mathbf{0} \\ \mathbf{0} & \lambda \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}, \quad (1)$$

where the matrices \mathbf{A} , \mathbf{B} , \mathbf{X} , and \mathbf{Y} have the dimension $n_{\text{occ}} \times n_{\text{virt}}$ with n_{occ} and n_{virt} being the number of occupied and unoccupied spin orbitals, respectively. The matrix ω collects the positive eigenvalues of the Hessian matrix in its diagonal. Here and in the following the orbitals are assumed to be real-valued. Note that Eq. (1) has the complementary solution $\begin{pmatrix} \mathbf{Y} \\ \mathbf{X} \end{pmatrix}_n$ corresponding to an eigenvalue $-\omega_n$. The Hessian and overlap matrices occurring in Eq. (1) are defined as

$$(\epsilon + A)_{ia,jb} = \langle \Psi_i^a | \hat{H} - E_0 | \Psi_j^b \rangle, \quad (2)$$

$$B_{ia,jb} = \langle \Psi_{ij}^{ab} | \hat{H} - E_0 | \Psi \rangle = \langle \Psi | \hat{H} - E_0 | \Psi_{ij}^{ab} \rangle, \quad (3)$$

$$\lambda_{ia,jb} = \langle \Psi_i^a | \Psi_j^b \rangle. \quad (4)$$

\hat{H} is the electronic hamiltonian, E_0 the Hartree-Fock ground-state energy, and Ψ_i^a, Ψ_{ij}^{ab} are singly and doubly excited wave functions, respectively. Indices i, j, k, \dots label occupied and a, b, c, \dots label unoccupied orbitals. If the wave function Ψ in Eqs. (2)–(4) is approximated by the Hartree-Fock wave function, then the NRPA approach^{46,55} is obtained and the Hessian and overlap matrices are given by

$$(\epsilon + A)_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + \langle ij|ab \rangle - \langle ia|jb \rangle, \quad (5)$$

$$B_{ia,jb} = \langle ij|ab \rangle - \langle ij|ba \rangle, \quad (6)$$

$$\lambda_{ia,jb} = \delta_{ij} \delta_{ab}, \quad (7)$$

with ϵ_i and ϵ_a being occupied and virtual orbital energies and $\langle rs|tu \rangle$ defines a two-electron repulsion integral in physicist's notation.

Originally correlation energies within the RPA were obtained for infinite systems like the homogeneous gas.^{48,51,54,85–87} For finite systems, however, it was found that the RPA correlation energy is wrong by a prefactor of two in second order. Because of this several “normal” RPA approaches exist which enforce the correct behaviour in second order.

McLachlan and Ball derived an expression for the RPA correlation energy by multiplying the corresponding expression from the RPA correlation energy for the homogeneous electron gas by a factor of one half.^{43,88} The RPA correlation energy, which will be termed as NRPA1 correlation energy in the following and which is identical to the ring coupled-cluster doubles correlation energy (rCCD),⁵² is then given by

$$E_c^{\text{NRPA1}} = \frac{1}{4} \text{Tr}(\mathbf{B}\mathbf{T}) = \frac{1}{4} \text{Tr}({}^1\mathbf{B}^1\mathbf{T} + {}^3\mathbf{B}^3\mathbf{T}). \quad (8)$$

In Eq. (8) the final expression on the right-hand side is written in spatial orbitals. The amplitudes \mathbf{T} are given by $\mathbf{T} = \mathbf{Y}\mathbf{X}^{-1}$ and the matrices ${}^1\mathbf{B}, {}^1\mathbf{T}$ and ${}^3\mathbf{B}, {}^3\mathbf{T}$ define singlet and triplet Hessian matrices and amplitudes, respectively.

In the RPA correlation energy expression from Fukuda *et al.*,⁸⁹ termed as NRPA2 here, the correct second-order behaviour is enforced by subtracting the second-order energy from the electron-gas formula:

$$E_c^{\text{NRPA2}} = \frac{1}{2} \text{Tr}(\mathbf{B}\mathbf{T}) - E_c^{(2)}. \quad (9)$$

Since the Hartree-Fock determinant is used as the reference determinant here, $E_c^{(2)}$ is identical to the second-order Møller-Plesset (MP2) correlation energy.

It has been shown by Oddershede and Jørgensen^{47,59} that if the Hartree-Fock wave function is used to solve the RPA Eq. (1), then there is an inconsistency in the corresponding two-particle density matrix since the Hartree-Fock ground state is not the ground state for the RPA excitation operators.^{90–92} Namely, the condition that ${}^1\mathbf{Y}^1\mathbf{X}^T = -{}^3\mathbf{Y}^3\mathbf{X}^T$, which arises from the condition that the wave function is an eigenfunction of the spin-squared operator \mathbf{S}^2 with eigenvalue zero, is not

fulfilled.⁴⁷ Because of this triplet excitation energies, in contrast to singlet excitation energies, within the NRPA (time-dependent Hartree-Fock) are often poor^{93–96} and it has been stated by Chambaud *et al.* that in fact triplet instabilities occur in any π -electronic system like ethylene or benzene.⁹⁷ While one possibility to overcome this deficiency is to use higher-order RPA approaches^{45,47,55–61} [like SOPPA (Refs. 47 and 62)], Oddershede proposed to enforce the condition ${}^1\mathbf{Y}^1\mathbf{X}^T = -{}^3\mathbf{Y}^3\mathbf{X}^T$ in the RPA correlation energy and arrives at^{46,47}

$$\begin{aligned} E_c^{\text{NRPA3}} &= \frac{1}{2}\text{Tr}[({}^1\mathbf{B} - {}^3\mathbf{B})^1\mathbf{Y}^1\mathbf{X}^T] \\ &\approx \frac{1}{2}\text{Tr}[({}^1\mathbf{B} - {}^3\mathbf{B})^1\mathbf{Y}^1\mathbf{X}^{-1}], \end{aligned} \quad (10)$$

where it has been used that $\mathbf{Y}\mathbf{X}^T \approx \mathbf{Y}\mathbf{X}^{-1}$ since the two expressions differ only in second order in the small vector component \mathbf{Y} .^{47,98}

Szabo and Ostlund have shown that none of the above given expressions for the RPA correlation energy fulfill the desired criterion that the long-range behaviour of the dispersive part of the interaction energy between two separate closed-shell molecules is described on the coupled Hartree-Fock level, i.e., the interaction contribution does not reduce to the dispersion energy on the time-dependent Hartree-Fock level for the methods NRPA1, NRPA2, and NRPA3.^{46,99} Because of this Szabo and Ostlund proposed the following expression for the RPA correlation energy:

$$E_c^{\text{NRPA4}} = \frac{1}{2}\text{Tr}({}^1\mathbf{B}[{}^1\mathbf{Y}^1\mathbf{X}^{-1} + {}^3\mathbf{Y}^3\mathbf{X}^{-1}]) \quad (11)$$

which again is exact to second order and describes the long-range correlation energy on the coupled Hartree-Fock level.⁴⁶

It can be shown that the desired long-range behaviour of the RPA correlation energy as well as correctness in second order can also be obtained by using an adiabatic connection approach.^{85,100,101} In the adiabatic connection method the electron-electron interactions (here all interactions that are not described on the Hartree-Fock level) are switched on by multiplication with a coupling-strength parameter α which varies between 0 (interaction turned off) and 1 (interaction fully turned on). The electron correlation energy is then obtained by an integral over the coupling strength and is given by^{47,74,102}

$$\begin{aligned} E_c^{\text{AC-RPA}} &= \frac{1}{2} \int_0^1 d\alpha \text{Tr}(\mathbf{C}[(\mathbf{X}_\alpha + \mathbf{Y}_\alpha)(\mathbf{X}_\alpha + \mathbf{Y}_\alpha)^T - \mathbf{1}]) \\ &= \frac{1}{2} \int_0^1 d\alpha \text{Tr}(\mathbf{C}\mathbf{P}_\alpha^c), \end{aligned} \quad (12)$$

where $C_{ia,jb} = \langle ij|ab \rangle$ and \mathbf{P}^c is the correlation part of the pair density within the RPA. The RPA eigenvector components \mathbf{X}_α and \mathbf{Y}_α at the coupling strength α are the solutions of a modified RPA Eq. (1) in which the matrices \mathbf{A} and \mathbf{B} are scaled by the coupling strength α .

Recently Kresse *et al.* have derived another RPA variant which requires only the solution vectors \mathbf{X} and \mathbf{Y} of the direct RPA (dRPA) equation which has the same form as Eq. (1) but in which all exchange integrals in Eqs. (5) and (6) are neglected.⁷⁰ While dRPA misses the exchange part of the second order correlation energy (diagram (1b) in Figure 1), it can

be obtained if the dRPA amplitudes $\mathbf{T}^{\text{dRPA}} = \mathbf{Y}_{\text{dRPA}}\mathbf{X}_{\text{dRPA}}^{-1}$ are contracted with antisymmetrised two-electron integrals. The method is termed as second order screened exchange (SOSEX) and the correlation energy reads⁷⁰

$$E_c^{\text{SOSEX}} = \frac{1}{2}\text{Tr}(\mathbf{B}\mathbf{T}^{\text{dRPA}}). \quad (13)$$

The advantage of the SOSEX method over the other RPA methods discussed in this section is that the amplitudes \mathbf{T}^{dRPA} can be obtained with a lower computational cost, see, e.g., Refs. 67, 103, and 104.

III. THIRD-ORDER CORRECTIONS TO NORMAL RANDOM-PHASE APPROXIMATION CORRELATION ENERGIES

While all RPA approaches discussed in Sec. II, namely, NRPA1 (rCCD), NRPA2, NRPA3, NRPA4, AC-RPA, and SOSEX are exact to second-order of perturbation theory, they differ in third order. A corresponding third order analysis of RPA correlation energies has already been made by Szabo and Ostlund,⁴⁶ Oddershede,⁴⁷ and very recently by Jansen *et al.*¹⁰² (see also Ref. 105). The third order correlation energy is given in diagrammatical form^{2,46,54} in Figure 1, more precisely it is given by the sum of the diagrams (2a)–(2l) in Figure 1. The corresponding algebraic expressions can be looked up in Ref. 1. All normal RPA methods (including SOSEX and AC-RPA) contain only those third order contributions that are of the particle-hole (ph) type, i.e., diagrams (2a)–(2h). The individual prefactors for each perturbation theory diagram for the different RPA methods are displayed in Table I. It can be seen that the NRPA1 method accounts for all third order ph contributions, but with a wrong prefactor of one half. This is corrected by the NRPA2 method which includes all ph diagrams with the correct prefactor of one. In contrast to this all other RPA methods displayed in Table I only contain fractions of the total ph correlation contribution. For example, the NRPA4 method from Szabo and Ostlund excludes the diagrams (2g) and (2h) from Figure 1 and the NRPA3 method contains even less third order correlation contributions than NRPA4. The SOSEX method contains, in addition to the direct RPA diagram (2a), only one further exchange type contribution, namely, diagram (2e). The AC-RPA method misses only one ph third-order contribution, but has wrong prefactors of $\frac{1}{3}$ and $\frac{2}{3}$ for the other ph diagrams, as can be seen in Table I.

In order to investigate the importance of the third-order correlation contributions numerically, the individual third order contributions from Figure 1 were calculated for a range of small molecules (see Sec. IV A for details). In Figure 2 the correlation energy contributions are shown for the three molecules H₂O, CO, and HCOOCH₃. It can be seen that in spite of quantitative differences for all three cases the relative magnitudes of the individual contributions are very similar and this observation also transfers to all other systems studied in this work. It is apparent from Figures 2(a), 2(c), and 2(e) that diagrams (2d) and (2g) as well as (2e) and (2f) are identical, which is due to the fact that real valued orbitals were used. The direct third-order ring diagram (2a) always gives a strong positive contribution to the third-order correlation

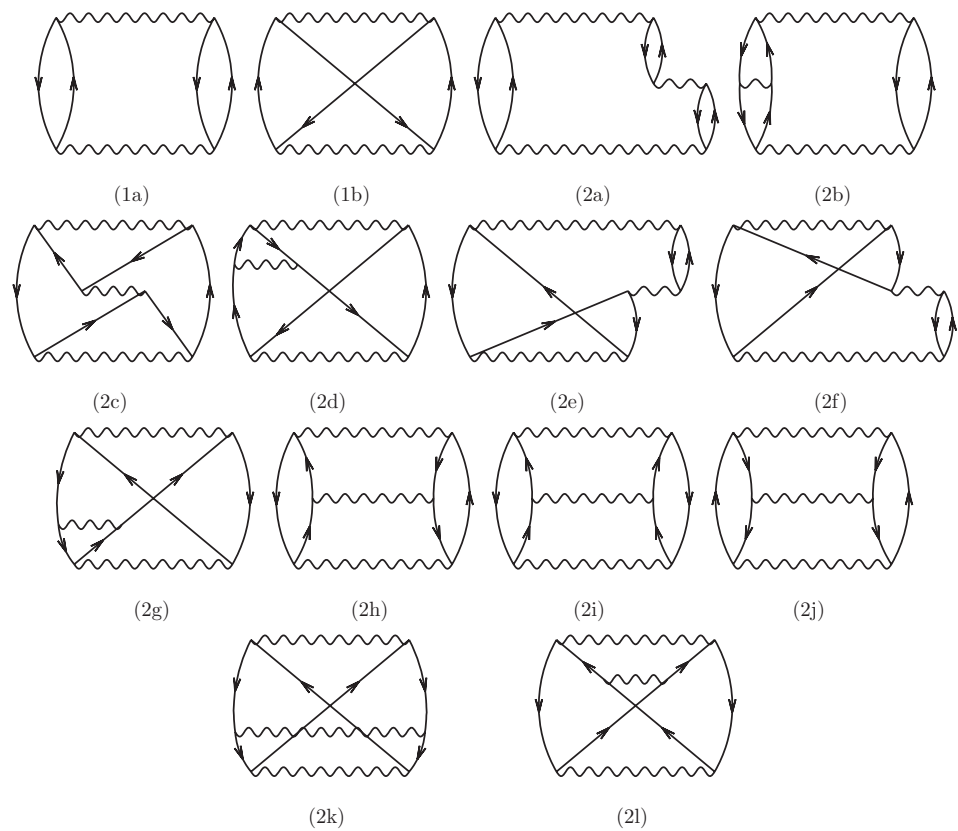


FIG. 1. Second- and third-order Goldstone diagrams. Diagrams (1a) and (1b) correspond to the direct and exchange term of the second order correlation energy, diagrams (2a)–(2h) are particle-hole diagrams and diagrams (2i)–(2l) are particle-particle and hole-hole diagrams. Note that only particle-hole diagrams of the type (2a)–(2h) are contained in conventional RPA correlation methods, see Table I.

energy, but it is more than compensated by the ph-exchange diagrams (2b) and (2h). The sum of all other ph-exchange diagrams leads to a small positive correlation energy contribution, so that the total third order ph-correlation energy is always a significant negative contribution, as shown by the green bars in Figure 2. In contrast to this the pp-hh-correlation contributions that are missing in the NRPA methods, displayed by the blue bars in Figures 2(a), 2(c), and 2(e), always sum up to a positive correlation contribution, see orange bars in Figure 2. As a consequence, the ph and pp-hh correlation diagrams of third order always cancel each other to a large extent and so the total third order correlation contribution is

TABLE I. Comparison of the third order expansions of various RPA correlation methods. The diagram labels correspond to the ones displayed in Figure 1. The column values correspond to the respective prefactor for each perturbation diagram.

Diagram	Exact	dRPA	SOSEX	NRPA1(rCCD)	NRPA2	NRPA3	NRPA4	AC-RPA
(1a)	1	1	1	1	1	1	1	1
(1b)	1	0	1	1	1	1	1	1
(2a)	1	1	1	$\frac{1}{2}$	1	1	1	1
(2b)	1	0	0	$\frac{1}{2}$	1	1	1	$\frac{2}{3}$
(2c)	1	0	0	$\frac{1}{2}$	1	0	1	$\frac{1}{3}$
(2d)	1	0	0	$\frac{1}{2}$	1	1	1	$\frac{1}{3}$
(2e)	1	0	1	$\frac{1}{2}$	1	1	1	$\frac{2}{3}$
(2f)	1	0	0	$\frac{1}{2}$	1	0	1	$\frac{2}{3}$
(2g)	1	0	0	$\frac{1}{2}$	1	0	0	$\frac{1}{3}$
(2h)	1	0	0	$\frac{1}{2}$	1	0	0	0
(2i)	1	0	0	0	0	0	0	0
(2j)	1	0	0	0	0	0	0	0
(2k)	1	0	0	0	0	0	0	0
(2l)	1	0	0	0	0	0	0	0

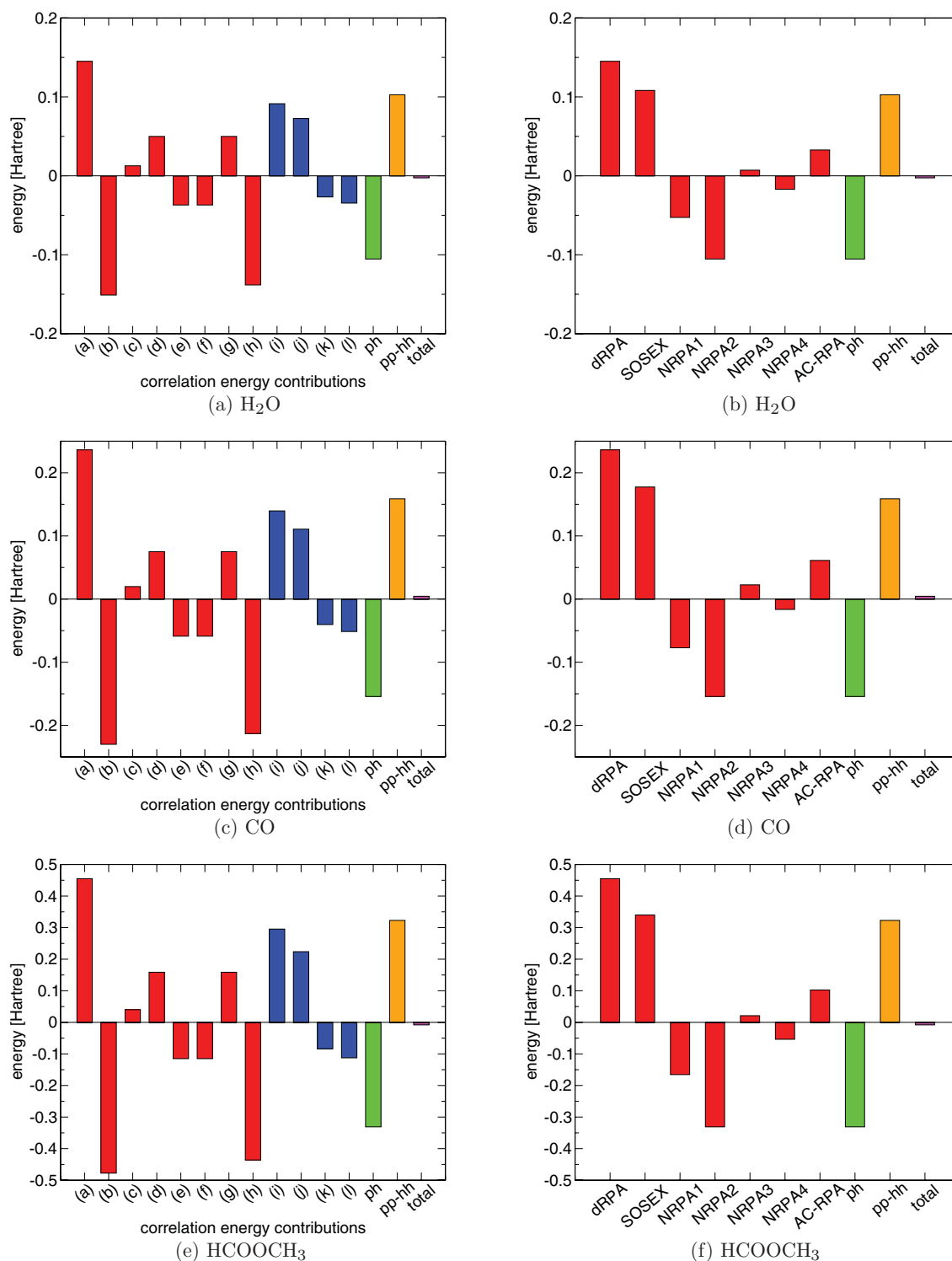


FIG. 2. Third-order correlation energy contributions for the molecules H₂O (subfigures (a) and (b)), CO (subfigures (c) and (d)), and HCOOCH₃ (subfigures (e) and (f)). Figures (a), (c), and (e) display the individual correlation contributions according to Figure 1 as well as the total third-order particle-hole (ph: sum of diagrams (2a)–(2h)), particle-particle–hole-hole (pp-hh: sum of diagrams (2i)–(2l)), and the total third-order correlation energy (sum of diagrams (2a)–(2l)). Figures (b), (d), and (f) show the third-order energies according to different RPA correlation methods, see Table I.

always very small, as shown in Figure 2. Because of this all RPA methods usually yield third order correlation energy contributions that largely deviate from the exact total third order energy, as can be seen in the Figures 2(b), 2(d), and 2(f). For example, the SOSEX method contains only the third order exchange diagram (2e) in addition to the direct ring diagram

(2a) and strongly overestimates the third order correlation energy on magnitude. The NRPA1 and NRPA2 methods give too strong negative third order contributions, because they contain all ph diagrams which sum up to a large negative value as discussed above. The best description of the correlation energy at the third order level is given by the NRPA3, NRPA4,

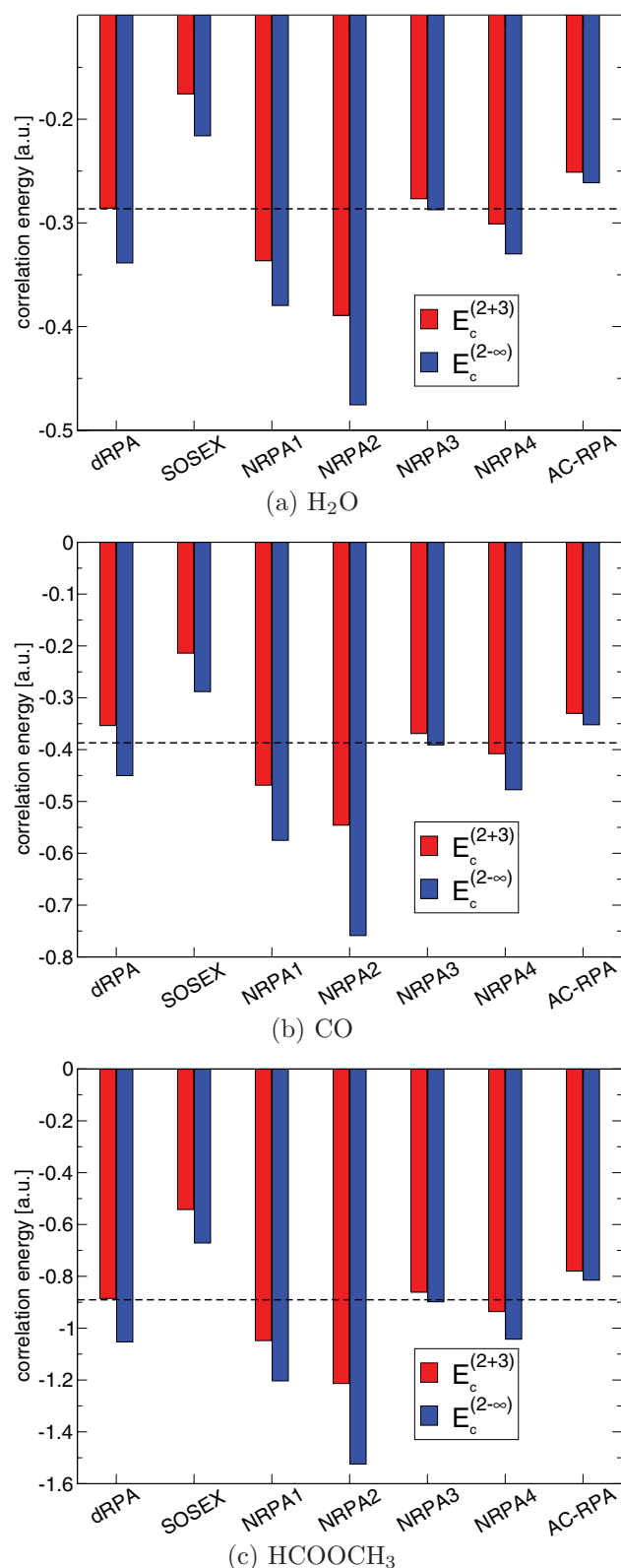


FIG. 3. Sum of second- and third-order (red bars) and total (blue bars) correlation energies of H₂O, CO, and HCOOCH₃ for the various RPA approaches. The dashed horizontal lines mark the MP3 correlation energy in each case.

and AC-RPA methods since in these methods at least partially the strong positive and negative ph contributions quench each other, as can be observed in Figures 2(b), 2(d), and 2(f). In this way one can argue that the NRPA3, NRPA4, and AC-RPA methods can mimic the missing pp-hh contributions.

Figure 3 shows the sum of the second- and third-order ($E_c^{(2+3)}$) correlation contributions as well as the total correlation energies ($E_c^{(2-\infty)}$) for the three molecules H₂O, CO, HCOOCH₃ for the different RPA methods. It can be seen that in all cases the higher order correlation contributions given by the difference $E_c^{(4-\infty)} = E_c^{(2-\infty)} - E_c^{(2+3)}$ have a negative value. With exception of NRPA3 and AC-RPA, this higher order contribution is relatively strong, especially for NRPA2 where $E_c^{(4-\infty)}$ amounts to 20% to 40% of the total correlation energy. The perturbation expansions underlying the methods dRPA, SOSEX, NRPA1, NRPA2, and NRPA4 are thus not well converged at the third-order level. In contrast to this the higher order correlation energies for NRPA3 and AC-RPA are very small on magnitude. In case of NRPA3 Figures 3(a)–3(c) show that the total correlation energies of this method are very close to the MP3 correlation energies marked by the horizontal dashed lines.

Because of the generally poor description of the correlation energy of the various RPA methods at third order of perturbation theory, here the following simple correction scheme is proposed:

$$E_c^{\text{total}}(\text{M}[3]) = E_c^{\text{total}}(\text{M}) - E_c^{(3)}(\text{M}) + E_c^{(3)}(\text{exact}), \quad (14)$$

where M stands for SOSEX, NRPA1–4, and AC-RPA (excluding dRPA which is not even exact in second order). The third order correlation contribution $E_c^{(3)}(\text{M})$ for each method is given by the respective sum of individual terms of Figure 1 with the corresponding prefactors from Table I. The exact third order contribution $E_c^{(3)}(\text{exact})$ corresponds to the sum of all diagrams (2a)–(2l) in Figure 1 and is, *de facto*, identical to the third-order Møller-Plesset correlation contribution since a Hartree-Fock orbital basis is used in this work. In Sec. IV the performance for total correlation energies, reaction energies, and intermolecular interaction energies of the standard RPA methods as well as the third-order corrected methods will be investigated.

IV. RESULTS

A. Total correlation energies

Total energies were calculated for a range of small organic molecules displayed in Figure 4 using the aug-cc-pVTZ basis set of Dunning.¹⁰⁶ The geometries for the molecules were optimised at the MP2 level using the aug-cc-pVTZ basis set and are taken from Ref. 107. In addition to the RPA calculations at the various levels described in Sec. II, correlation energies for the standard methods MP2 and MP3 (second- and third-order Møller-Plesset perturbation theory), CCSD, and CCSD(T) have been made. The latter method will serve as a reference in the following. Core electrons were correlated in the calculations. All calculations were done using the developers version of the Molpro quantum chemistry program.¹⁰⁸

Figure 4 shows the correlation energy differences of the different correlation methods to CCSD(T) correlation energies. In the upper panel in Figure 4 the energy differences are shown for the standard RPA methods described in Sec. II. For SOSEX, NRPA1, and NRPA2 one can observe relatively

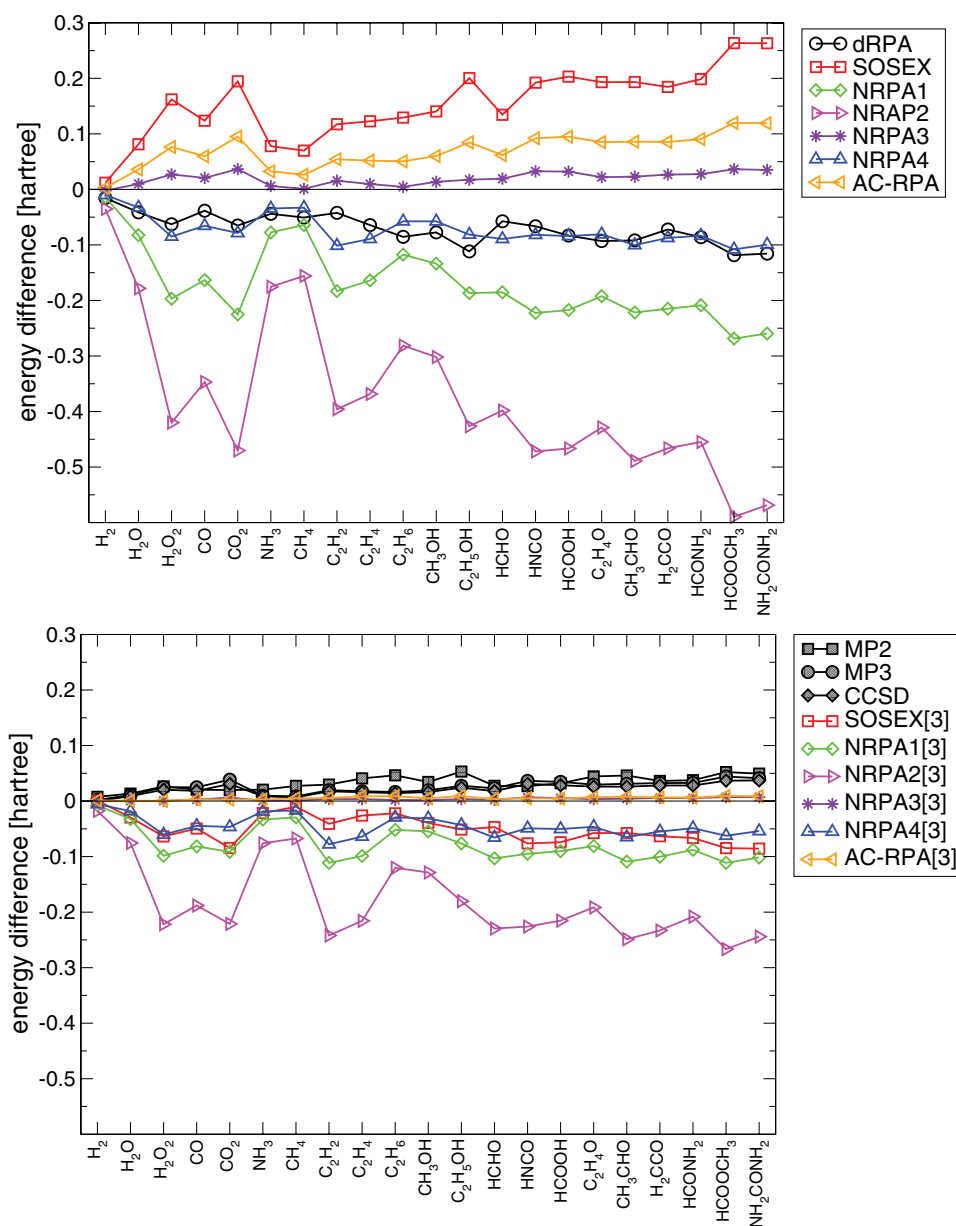


FIG. 4. Energy differences to CCSD(T) reference energies for standard RPA methods (upper panel) and third-order corrected RPA methods (lower panel). Also shown in the bottom diagram are the energy differences for MP2, MP3, and CCSD.

strong deviations to the CCSD(T) energies which can be explained with the findings from Sec. III and the analysis of Figure 3. In case of SOSEX the strong underestimation of the CCSD(T) correlation energies can be explained with the too small contribution of the exchange diagram (2e) from Figure 1 so that the sum of diagrams (2a)+(2e) (3rd order contribution in the SOSEX method) is always a quite large positive value, see Figure 2. Contrary to this, NRPA1 and NRPA2 strongly overestimate the CCSD(T) correlation energy because half the total (NRPA1) respectively the total sum (NRPA2) of the third-order ph diagrams always yield a large negative contribution, see Figure 4. The dRPA, NRPA4, and AC-RPA methods yield correlation energies much closer to the accurate CCSD(T) ones, but still there are significant differences if compared to the standard correlation methods

MP2/3 or CCSD shown in the bottom diagram in Figure 4. The best performance for the standard RPA methods regarding correlation energy differences is obtained with the NRPA3 method which shows similar deviations to the CCSD(T) values as CCSD, see upper diagram of Figure 4.

In the bottom diagram of Figure 4 the correlation energy differences for the third-order corrected RPA methods according to Eq. (14) are shown in addition to MP2, MP3, and CCSD differences. As the scale of the ordinate axis is the same for the top and bottom diagram in Figure 4, it can clearly be seen that the correction approach of Eq. (14) leads to strong improvements for all RPA methods (the dRPA method has been excluded here, see above). If compared to CCSD correlation energies, however, the methods SOSEX[3], NRPA1[3], NRPA4[3], and especially NRPA2[3] still

overestimate the correlation energies to a large extent. In contrast to this for NRPA3[3] and AC-RPA[3] the correlation energies are extremely close to the CCSD(T) reference values, see bottom panel in Figure 4. Indeed, both for NRPA3[3] and AC-RPA[3] the absolute correlation energy differences to CCSD(T) do not exceed 10 millihartree and in all cases, with exception of the H_2 molecule where NRPA3[3] overestimates the CCSD correlation energy by -0.6 millihartree, the total energies of NRPA3[3] and AC-RPA[3] lie slightly above the CCSD(T) energies. It can also be observed in Figure 4 that the NRPA3[3] and AC-RPA[3] energies are constantly closer to the CCSD(T) reference values than the corresponding MP2, MP3, and CCSD energies. It can therefore be argued that the higher than third order correlation energy contributions contained in the NRPA3[3] and AC-RPA[3] energies can effectively approximate the correlation energy differences between the CCSD(T) and MP3 method. In Subsections IV B and IV C it will be investigated whether the strong improvements of total energies using the correction approach of Eq. (14) also leads to improvements for energy differences, namely, reaction energies and intermolecular interaction energies that are usually two or more orders of magnitude smaller than total energies.

B. Reaction energies

The reaction energies of the 16 chemical reactions displayed in Table II were calculated using the various RPA methods with and without the third-order correction from Eq. (14), MP2, MP3, and CCSD without and with perturbative triples. The geometries and basis sets are the same as given in Sec. IV A. The total reaction energies for each chemical reaction can be found in the supporting information.¹⁰⁹

Figure 5 shows the root-mean squared errors (rms), the mean absolute errors (mae), and the relative percentual deviations ($|\Delta|$) from the CCSD(T) reference reaction energies for each method for the 16 chemical reactions of Table II. Note that the methods NRPA1, NRPA2, and NRPA4 are excluded

TABLE II. Chemical reactions.

Educts		Products
$C_2H_2 + H_2$	\rightarrow	C_2H_4
$C_2H_4 + H_2$	\rightarrow	C_2H_6
$C_2H_6 + H_2$	\rightarrow	$2CH_4$
$CO + H_2$	\rightarrow	H_2CO
$H_2CO + H_2$	\rightarrow	CH_3OH
$H_2O_2 + H_2$	\rightarrow	$2H_2O$
$C_2H_2 + H_2O$	\rightarrow	CH_3CHO
$C_2H_4 + H_2O$	\rightarrow	C_2H_5OH
$CH_3CHO + H_2$	\rightarrow	C_2H_5OH
$CO + NH_3$	\rightarrow	$HCONH_2$
$CO + H_2O$	\rightarrow	$CO_2 + H_2$
$HNCO + NH_3$	\rightarrow	NH_2CONH_2
$CH_3OH + CO$	\rightarrow	$HCOOCH_3$
$CO + H_2O_2$	\rightarrow	$CO_2 + H_2O$
$HCOOH + NH_3$	\rightarrow	$HCONH_2 + H_2O$
$H_2CCO + HCHO$	\rightarrow	$C_2H_4O + CO$

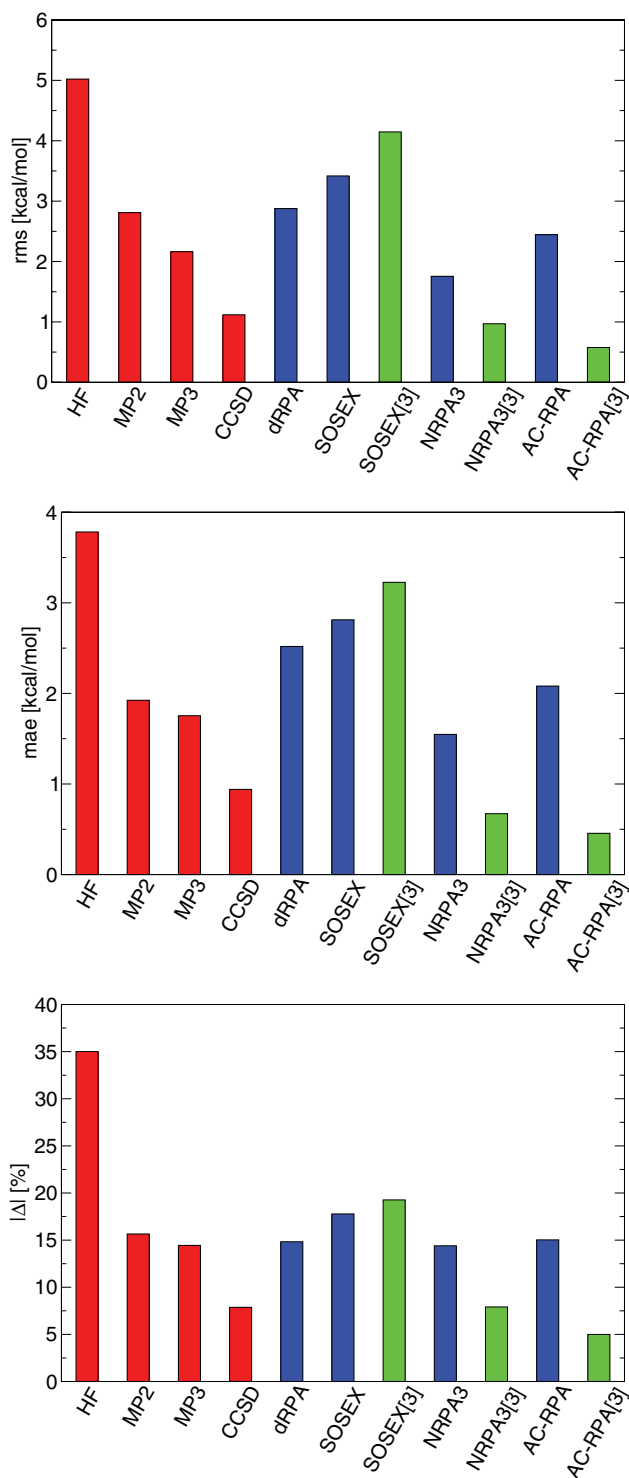


FIG. 5. Root-mean squared errors (rms), mean absolute errors (mae), and total relative deviations ($|\Delta|$) from CCSD(T) reference values for 16 chemical reactions shown in Table II.

due to their very poor performance for the chemical reactions, see Table II in the supporting information.¹⁰⁹ The red bars in Figure 5 display the respective errors of Hartree-Fock theory and the standard correlation methods MP2, MP3, and CCSD. It can be observed that MP2 and MP3 theory give strong corrections to Hartree-Fock, however there is little improvement from MP2 to MP3. A further clear improvement of MP3 is

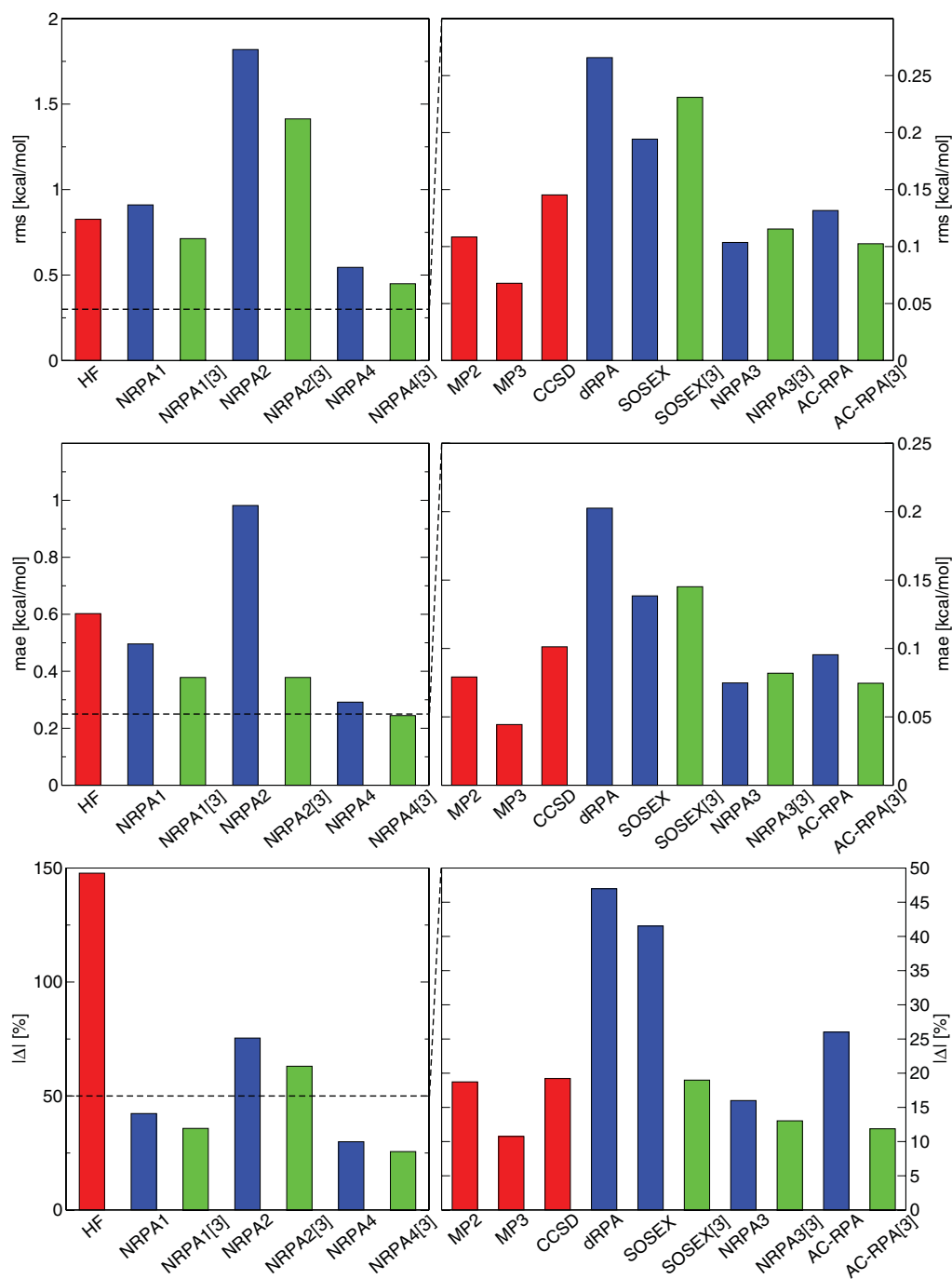


FIG. 6. Root-mean squared errors (rms), mean absolute errors (mae), and total relative deviations ($|\Delta|$) from CCSD(T) reference interaction energies for 8/23 different intermolecular complexes/structures, see text.

obtained with CCSD which reduces the rms error of MP3 from 2.2 kcal/mol to 1.1 kcal/mol on average.

The standard RPA methods shown in Figure 5 (blue bars) all to some extent improve Hartree-Fock theory, but with exception of NRPA3 their absolute or relative errors to the CCSD(T) reference values are not smaller than with MP2 or MP3. The NRPA3 approach gives a clearly smaller rms error for the chemical reactions than MP2 and MP3 theory, but its performance is worse than CCSD.

The errors for the third-order corrected RPA methods are displayed by the green bars in Figure 5. While one can

see that for the SOSEX method the third-order correction leads to even larger errors in comparison with CCSD(T), in case of NRPA3 and AC-RPA the corresponding corrected methods NRPA3[3] and AC-RPA[3] strongly improve the performance of the underlying uncorrected methods. With NRPA3[3] the rms error to the CCSD(T) reference values is only 1.0 kcal/mol and with AC-RPA[3] it is even only 0.6 kcal/mol for the chemical reactions considered. Thus one can observe not only a clear improvement of the original NRPA3 and AC-RPA methods, but the errors of NRPA3[3] and AC-RPA[3] are also significantly smaller than with CCSD.

Therefore the exceptionally good description of total correlation energies with NRPA3[3] and AC-RPA[3], see Figure 4, transfers also to the description of reaction energies.

C. Intermolecular interaction energies

Compared to chemical reaction energies intermolecular interaction energies present an even stronger challenge for correlation methods since the absolute energy differences are again one or two orders of magnitude smaller. In order to analyse the performance of electron correlation methods for the description of intermolecular interaction energies we have developed a small database of eight different dimers comprising the rare gas dimers He_2 , Ne_2 , Ar_2 , NeAr , the dimers NeHF , ArHF , $(\text{H}_2)_2$ and the hydrogen-bridged dimers $(\text{HF})_2$ and $(\text{H}_2\text{O})_2$ in 23 different orientations altogether. The geometries for the different intermolecular complexes can be found in Ref. 110. For the rare-gas dimers and the hydrogen molecule dimer the aug-cc-pVQZ basis set was used^{106,111,112} while in all other cases the aug-cc-pVTZ basis set was used.¹⁰⁶ The core electrons were correlated in all calculations. The individual values for the interaction energies can be found in the Tables IV-VI in the supporting information.¹⁰⁹

Here we again only consider the overall performance of the different correlation methods represented by the average statistical errors to CCSD(T) reference interaction energies for the 23 intermolecular complexes. These are shown in the diagrams in Figure 6. Note that due to strong differences in the performance of the respective methods the diagrams in Figure 6 are splitted into two parts: the left-hand side of the diagrams shows the methods with a larger deviation from the CCSD(T) values and the right-hand side comprises the methods that have a smaller deviation from the CCSD(T) interaction energies. The maximal scale of the ordinate axis of the diagrams on the right-hand side is marked by dashed horizontal lines in the respective diagrams on the left-hand side for comparison.

The left-hand parts of the diagrams in Figure 6 comprise the statistical errors for Hartree-Fock (red bar) and NRPA1, NRPA2, and NRPA4 (blue bars) together with their third-order corrected methods (green bars). It can be seen that the errors for the respective corrected approaches are smaller than with the standard RPA methods, however not significantly. The improvements over the Hartree-Fock interaction energies is limited, regarding the rms errors one can even see that the NRPA2 and NRPA2[3] methods yield errors that are about two times larger.

As expected, a clear improvement over the Hartree-Fock interaction energies is obtained by MP2, MP3, and CCSD, see right-hand side of Figure 6. It can be seen that among these standard correlation methods the MP3 method gives the smallest errors to the CCSD(T) reference values with an rms error of only 0.07 kcal/mol. The CCSD method is slightly worse than MP2 for the intermolecular complexes considered. This is partially because the CCSD interaction energies are less accurate for the ArHF complex than MP2, see Table IV in the supporting information.¹⁰⁹ The dRPA, SOSEX, and SOSEX[3] method yield interaction energies that are worse

than with the standard correlation methods, as can be seen in Figure 6. Similar to the findings for the reaction energies in Sec. IV B the SOSEX[3] approach does not improve the SOSEX interaction energies for the rms and mae errors, but it gives a smaller relative error which is due to the much smaller error for the T-shaped structure III of the hydrogen molecule dimer, see Tables V and VI in the supporting information.¹⁰⁹

The best performance among the RPA methods for the intermolecular interaction energies is obtained with the NRPA3, AC-RPA, and corresponding third-order corrected methods. In the top diagram in Figure 6 one can observe that the rms deviations for these methods are similar to those from MP2 theory and they are clearly better than CCSD, but the interaction energies are less accurate than the MP3 interaction energies on average. Contrary to the results for the reaction energies, here the third-order correlation energy correction does not lead to considerable improvements of the uncorrected approaches. Using the rms and mae errors as measure the NRPA3[3] values are even slightly worse than the NRPA3 interaction energies. For the relative errors, which more assess the weakly bound dimers of the intermolecular complexes considered, the third-order correlation energy corrected approaches NRPA3[3] and AC-RPA[3] are clearly better than the uncorrected counterparts and the relative average deviation for AC-RPA[3] is even almost as good as with MP3 (12% and 11%, respectively, see bottom diagram in Figure 6).

V. DISCUSSION AND CONCLUSION

Several random-phase approximation correlation methods were presented and tested for total energies, reaction energies, and intermolecular interactions. It has been shown that the earliest RPA methods, termed in this work NRPA1 (and which is identical to the ring coupled-cluster doubles method) from McLachlan and Ball^{43,88} and NRPA2 from Fukuda *et al.*⁸⁹, yield very poor total energies and energy differences, though, among the other “normal” RPA methods presented they are the most complete from the perturbation theory point of view since they contain half of (NRPA1) respectively all (NRPA2) particle-hole (ph) contributions in third order of perturbation theory. The numerical analysis from Sec. III shows, however, that the missing third-order particle-particle-hole-hole (pp-hh) contributions to the correlation energy are large and their sum has an opposite sign compared to the sum of all third-order ph terms. As a consequence the third-order correlation energies of the NRPA1 and NRPA2 methods are largely in error in comparison with the exact third-order correlation energy. This might explain why RPA methods have rarely been used to describe molecular ground-state correlation energies since their introduction in quantum chemistry in the mid sixties. The NRPA4 method from Szabo and Ostlund,^{46,99} which describes long-range electron correlation energies on the coupled Hartree-Fock level, indeed has been shown to yield intermolecular interactions that are better than with NRPA1 and NRPA2, but its accuracy is still much worse in comparison with standard correlation methods like MP2 or CCSD.

The best performance among the standard RPA approaches considered for reaction energies and intermolecular

interactions is found for the NRPA3 and AC-RPA methods. It has been shown in Sec. III that for these methods a partial cancellation of third-order correlation energy contributions occurs so that these methods contain a smaller error in third order than the corresponding NRPA1 and NRPA2 methods. One can also argue that in contrast to NRPA1,2 and 4 the NRPA3 and AC-RPA methods do not require triplet amplitudes. The triplet amplitudes are obtained from the solution of RPA equations for the triplet excited states and these can be very poorly described on the normal RPA or time-dependent Hartree-Fock level, see Sec. II. Indeed, the NRPA3 and AC-RPA methods yield similar statistical errors to CCSD(T) reference values for the set of chemical reactions and intermolecular interactions as the standard correlation methods MP2, MP3, or CCSD.

While all RPA methods (excluding direct RPA) considered in this work are exact to second order but not in third order of perturbation theory, a correction scheme is proposed (Eq. (14)) that enforces correctness also in third order for the several RPA methods. It has been shown that this almost always leads to improvements of the corresponding uncorrected RPA methods. For NRPA3 and AC-RPA the deduced NRPA[3] and AC-RPA[3] methods yield total correlation energies which are extremely close to accurate CCSD(T) values for a range of 21 small organic molecules. It has been shown that this high accuracy also transfers to a set of 16 chemical reactions built from this set of molecules. The statistical errors for NRPA3[3] and AC-RPA[3] are all smaller than with CCSD both for the set of chemical reactions and also for the intermolecular interaction energies of a set of 23 small dimer systems. Overall the third-order corrected AC-RPA[3] method yields the highest accuracy of the correlation methods considered in this work if compared with CCSD(T) reference values. This result is important from the point of view that formally all methods (excluding MP2, SOSEX and dRPA: \mathcal{N}^5) have a computational cost that grows as \mathcal{N}^6 with the molecular size measured by \mathcal{N} . In praxis the NRPA3[3] and AC-RPA[3] methods should be even more efficient than CCSD since the expensive integral transformations required for the four-external integrals occurring in the third-order pp-hh correlation energy contributions (diagrams (2i) and (2l) in Figure 1) can be done on the fly since these integrals are only required once for the third-order correction.

In summary this work presents a simple yet accurate scheme to improve common RPA methods that is based on perturbation theory. For some RPA methods, namely, NRPA3 and AC-RPA, the correction approach significantly improves the performance for the chemical reaction energies and intermolecular interactions that exceeds the accuracy of MP2 and CCSD. Therefore, while certainly the new methods should be further tested for other molecular properties, these RPA methods might become more attractive for describing electron ground-state correlation in chemical applications in the future.

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