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On the equivalence of ring-coupled cluster and adiabatic connection fluctuation-dissipation theorem random phase approximation correlation energy expressions

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The correlation energy in the direct random phase approximation (dRPA) can be written, among other possibilities, either in terms of the interaction strength averaged correlation density matrix, or in terms of the coupled cluster doubles amplitudes obtained in the direct ring approximation (drCCD). Although the corresponding dRPA correlation density matrix on the one hand, and the drCCD amplitude matrix on the other hand, differ significantly, they yield identical energies. Similarly, the analogous RPA and rCCD correlation energies calculated from antisymmetrized two-electron integrals are identical to each other despite very different underlying working equations. In the present communication, a direct correspondence between amplitudes and densities is established and investigated with perturbation theory arguments. Our analysis also sheds some light on the properties of recently proposed RPA/rCCD variants which use antisymmetrized integrals in part of the equations and nonantisymmetrized integrals in others. © 2010 American Institute of Physics. [doi:10.1063/1.3481575]

In the adiabatic-connection fluctuation-dissipation theorem (ACFDT) approach the correlation energy reads as^{1,2}

$$E_c^{\text{ACFDT}} = -\frac{1}{2} \int_0^1 d\alpha \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{tr}(\mathbb{V}\Pi_\alpha(i\omega) - \mathbb{V}\Pi_0(i\omega)), \quad (1)$$

where $\Pi_\alpha(z)$ is the polarization propagator (density matrix response function) at the interaction strength α , and $\Pi_0(z)$ is the polarization propagator of the noninteracting reference system

$$\Pi_0(z) = -(\Lambda_0 - z\Delta)^{-1} \quad (2)$$

with

$$\Lambda_0 = \begin{pmatrix} \Delta\epsilon & \mathbf{0} \\ \mathbf{0} & \Delta\epsilon \end{pmatrix} \quad \text{and} \quad \Delta = \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & -\mathbf{I} \end{pmatrix}. \quad (3)$$

In the random phase approximation (RPA), the elements of the Λ_0 matrix are the independent one-particle excitation energies, $(\Delta\epsilon)_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab}$, where ϵ_a is the energy of a virtual and ϵ_i is the energy of an occupied orbital. The polarization propagator at the interaction strength α , $\Pi_\alpha(z)$ is obtained from the following equation:

$$\Pi_\alpha^{-1}(z) = \Pi_0^{-1}(z) - \alpha\mathbb{F} \quad (4)$$

with \mathbb{F} interaction kernel matrix. In the direct RPA (dRPA) only the Coulomb kernel is retained and, in the case of real orbitals, the interaction part of the dRPA matrix $\mathbb{F}_{\text{dRPA}} = \mathbb{V}$ is constituted from four identical blocks

$$\mathbb{V} = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix}, \quad (5)$$

where $K_{ia,jb} = \langle ij|ab \rangle$ are nonantisymmetrized two-electron integrals. Alternatively, when both the Coulomb and the non-local Hartree-Fock exchange kernels are taken into account, the interaction matrix $\mathbb{F}_{\text{RPA}} = \mathbb{W}$ for real orbitals takes the form

$$\mathbb{W} = \begin{pmatrix} \mathbf{A}' & \mathbf{B} \\ \mathbf{B} & \mathbf{A}' \end{pmatrix} \quad (6)$$

with the antisymmetrized two-electron integrals $A'_{ia,jb} = \langle ib||aj \rangle$ and $B_{ia,jb} = \langle ij||ab \rangle$.

The dRPA equations are usually expressed in the form of an eigenvalue equation

$$\begin{pmatrix} (\Delta\epsilon + \alpha\mathbf{K}) & \alpha\mathbf{K} \\ -\alpha\mathbf{K} & -(\Delta\epsilon + \alpha\mathbf{K}) \end{pmatrix} \begin{pmatrix} \mathbf{X}_\alpha \\ \mathbf{Y}_\alpha \end{pmatrix} = \begin{pmatrix} \mathbf{X}_\alpha \\ \mathbf{Y}_\alpha \end{pmatrix} \boldsymbol{\omega}_\alpha, \quad (7)$$

where $\boldsymbol{\omega}_\alpha$ is a diagonal matrix collecting all the positive eigenvalues and the columns of \mathbf{X}_α and \mathbf{Y}_α are the corresponding eigenvectors.

In the density matrix approach the frequency integration of Eq. (1) is performed analytically,³ and the correlation energy is given by the correlation density matrix integrated along the adiabatic connection path as

$$E_c^{\text{AC-dRPA}} = \frac{1}{2} \int_0^1 d\alpha \text{tr}(\mathbf{K}\mathbf{P}_\alpha) \quad (8)$$

with

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$$\mathbf{P}_\alpha = (\mathbf{X}_\alpha + \mathbf{Y}_\alpha)(\mathbf{X}_\alpha + \mathbf{Y}_\alpha)^T - \mathbf{I}. \quad (9)$$

The density matrix formulation is strictly equivalent to the plasmon-pole formula, which can be derived from the ACFDT energy expression, as shown recently by Furche.⁴

Another possibility to evaluate the plasmon-pole formula for the dRPA case proceeds by the solution of the algebraic Riccati-equations associated to the fully interacting ($\alpha=1$) dRPA problem is

$$\mathbf{K} + \{(\Delta\epsilon + \mathbf{K}), \mathbf{T}\} + \mathbf{T}\mathbf{K}\mathbf{T} = \mathbf{0}. \quad (10)$$

As shown recently by Scuseria *et al.*,⁵ the resulting matrix $\mathbf{T} = \mathbf{Y}\mathbf{X}^{-1}$ is equivalent to the amplitudes arising in the direct ring approximation to the coupled-cluster doubles theory (drCCD), which in turn is obtained from the ring-approximation to CCD (rCCD) by neglecting antisymmetry in the two-electron integrals. In Eq. (10) the following $\{\cdot, \cdot\}$ denotes an anticommutator. The correlation energy in drCCD is given by the contraction of \mathbf{T} with the nonantisymmetrized two-electron integrals, \mathbf{K}

$$E_c^{\text{drCCD}} = \frac{1}{2} \sum_{ijab} \langle ij|ab \rangle T_{jb,ia} = \frac{1}{2} \text{tr}(\mathbf{K}\mathbf{T}). \quad (11)$$

An advantage of this method is that no numerical quadrature is needed to get the correlation energy: both frequency and interaction strength integrals have been done analytically.

Although the amplitude matrix \mathbf{T} and the interaction-strength averaged density matrix, $\bar{\mathbf{P}} = \int_0^1 d\alpha \mathbf{P}_\alpha$ play an analogous role in the correlation energy expression and lead exactly to the same result, these matrices themselves are *different*

$$\frac{1}{2} \text{tr}(\mathbf{K}\mathbf{T}) = \frac{1}{2} \text{tr}(\mathbf{K}\bar{\mathbf{P}}) \quad \text{but} \quad \mathbf{T} \neq \bar{\mathbf{P}}. \quad (12)$$

In the following we propose an explanation for this observation.

Similarly, the correlation energy⁶

$$\begin{aligned} E_c^{\text{AC-RPA}} &= \frac{1}{4} \int_0^1 d\alpha \text{tr}(\mathbf{A}'(\mathbf{X}_\alpha \mathbf{X}_\alpha^T + \mathbf{Y}_\alpha \mathbf{Y}_\alpha^T - \mathbf{I})) \\ &\quad + \text{tr}(\mathbf{B}(\mathbf{Y}_\alpha \mathbf{X}_\alpha^T + \mathbf{X}_\alpha \mathbf{Y}_\alpha^T)) \\ &= \frac{1}{4} \int_0^1 d\alpha \text{tr} \\ &\quad \times (\mathbf{B}\mathbf{P}_\alpha + (\mathbf{A}' - \mathbf{B})(\mathbf{X}_\alpha \mathbf{X}_\alpha^T + \mathbf{Y}_\alpha \mathbf{Y}_\alpha^T - \mathbf{I})) \end{aligned} \quad (13)$$

corresponding to the RPA equations with antisymmetrized integrals

$$\begin{pmatrix} (\Delta\epsilon + \alpha\mathbf{A}') & \alpha\mathbf{B} \\ -\alpha\mathbf{B} & -(\Delta\epsilon + \alpha\mathbf{A}') \end{pmatrix} \begin{pmatrix} \mathbf{X}_\alpha \\ \mathbf{Y}_\alpha \end{pmatrix} = \begin{pmatrix} \mathbf{X}_\alpha \\ \mathbf{Y}_\alpha \end{pmatrix} \boldsymbol{\omega}_\alpha \quad (14)$$

may be obtained⁵ from the solution of the Riccati-equations at coupling strength $\alpha=1$

$$\mathbf{B} + \{(\Delta\epsilon + \mathbf{A}'), \mathbf{T}\} + \mathbf{T}\mathbf{B}\mathbf{T} = \mathbf{0} \quad (15)$$

as

$$E_c^{\text{rCCD}} = \frac{1}{4} \sum_{ijab} \langle ij||ab \rangle T_{jb,ia} = \frac{1}{4} \text{tr}(\mathbf{B}\mathbf{T}). \quad (16)$$

Though E_c^{rCCD} and $E_c^{\text{AC-RPA}}$ yield identical correlation energies, the direct link between the two formulas seems to be even less clear than in the case of direct RPA. In the following such a link will be established and more closely investigated with a perturbational approach.

(a) *Relation between rCCD amplitudes and RPA density matrix.* Repeating all steps in the derivation of the rCCD equations⁵ the system of Eq. (14) may be converted into the nonlinear equation

$$\alpha\mathbf{B} + \{(\Delta\epsilon + \alpha\mathbf{A}'), \mathbf{T}_\alpha\} + \alpha\mathbf{T}_\alpha\mathbf{B}\mathbf{T}_\alpha = \mathbf{0}, \quad (17)$$

for the coupling-strength dependent amplitude matrix $\mathbf{T}_\alpha = \mathbf{Y}_\alpha \mathbf{X}_\alpha^{-1}$. Using the appropriate normalization condition for the RPA solution

$$\mathbf{X}_\alpha^T \mathbf{X}_\alpha - \mathbf{Y}_\alpha^T \mathbf{Y}_\alpha = \mathbf{I}, \quad (18)$$

and the equation $\mathbf{Y}_\alpha^T \mathbf{X}_\alpha = \mathbf{X}_\alpha^T \mathbf{Y}_\alpha$ (cf. Ref. 5) from

$$\begin{aligned} \mathbf{P}_\alpha(\mathbf{I} - \mathbf{T}_\alpha) &= (\mathbf{X}_\alpha + \mathbf{Y}_\alpha)(\mathbf{X}_\alpha + \mathbf{Y}_\alpha)^T(\mathbf{X}_\alpha - \mathbf{Y}_\alpha)\mathbf{X}_\alpha^{-1} \\ &\quad - (\mathbf{I} - \mathbf{Y}_\alpha \mathbf{X}_\alpha^{-1}) \\ &= 2\mathbf{Y}_\alpha \mathbf{X}_\alpha^{-1} \end{aligned}$$

a relation between the amplitude and density matrices is obtained

$$\mathbf{P}_\alpha = 2\mathbf{T}_\alpha(\mathbf{I} - \mathbf{T}_\alpha)^{-1} = 2(\mathbf{T}_\alpha + \mathbf{T}_\alpha^2 + \mathbf{T}_\alpha^3 + \mathbf{T}_\alpha^4 + \dots). \quad (19)$$

The second of these relations holds only if $\|\mathbf{T}\| < 1$, as it will be assumed in the following. Note that under this proviso Eq. (19) opens a way for an iterative determination of the density matrix from the amplitude matrix

$$\mathbf{P}_\alpha^{(n)} = \mathbf{T}_\alpha(2\mathbf{I} + \mathbf{P}_\alpha^{(n-1)}) = (2\mathbf{I} + \mathbf{P}_\alpha^{(n-1)})\mathbf{T}_\alpha. \quad (20)$$

Furthermore, from the normalization condition Eq. (18) and the definition of \mathbf{T}_α one gets $\mathbf{X}_\alpha^T \mathbf{X}_\alpha - \mathbf{X}_\alpha^T \mathbf{T}_\alpha^T \mathbf{T}_\alpha \mathbf{X}_\alpha = \mathbf{I}$ which, using $\mathbf{T}_\alpha^T = \mathbf{T}_\alpha$ (cf. Ref. 5), leads to

$$\mathbf{X}_\alpha^{-1} = \mathbf{X}_\alpha^T(\mathbf{I} - \mathbf{T}_\alpha^2). \quad (21)$$

Since $\mathbf{Y}_\alpha \mathbf{Y}_\alpha^T = \mathbf{T}_\alpha \mathbf{X}_\alpha \mathbf{X}_\alpha^T \mathbf{T}_\alpha^T$ we get

$$(\mathbf{X}_\alpha \mathbf{X}_\alpha^T + \mathbf{Y}_\alpha \mathbf{Y}_\alpha^T - \mathbf{I}) = 2\mathbf{T}_\alpha^2(\mathbf{I} - \mathbf{T}_\alpha^2)^{-1} = 2(\mathbf{T}_\alpha^2 + \mathbf{T}_\alpha^4 + \dots). \quad (22)$$

Using the above Eq. (13) may be written as

$$E_c^{\text{AC-RPA}} = \frac{1}{4} \int_0^1 d\alpha 2\text{tr}(\mathbf{B}\mathbf{T}_\alpha(\mathbf{I} - \mathbf{T}_\alpha^2)^{-1} + \mathbf{A}'\mathbf{T}_\alpha^2(\mathbf{I} - \mathbf{T}_\alpha^2)^{-1}) \quad (23)$$

showing that \mathbf{B} picks up the odd powers of \mathbf{T}_α while \mathbf{A}' picks up all even powers.

(b) *Coupling-strength integration.* Assuming that the amplitude matrix \mathbf{T}_α may be expanded as

$$\mathbf{T}_\alpha = \alpha\mathbf{T}^{(1)} + \alpha^2\mathbf{T}^{(2)} + \alpha^3\mathbf{T}^{(3)} + \dots \quad (24)$$

from Eq. (17) one gets the following equations for the different orders of α :

$$\alpha^1: \mathbf{B} + \{\Delta\epsilon, \mathbf{T}^{(1)}\} = \mathbf{0}, \quad (25)$$

$$\alpha^2: \{\Delta\epsilon, \mathbf{T}^{(2)}\} + \{\mathbf{A}', \mathbf{T}^{(1)}\} = \mathbf{0}, \quad (26)$$

$$\alpha^3: \{\Delta\epsilon, \mathbf{T}^{(3)}\} + \{\mathbf{A}', \mathbf{T}^{(2)}\} + \mathbf{T}^{(1)}\mathbf{B}\mathbf{T}^{(1)} = \mathbf{0}, \quad (27)$$

$$\alpha^4: \{\Delta\epsilon, \mathbf{T}^{(4)}\} + \{\mathbf{A}', \mathbf{T}^{(3)}\} + \mathbf{T}^{(1)}\mathbf{B}\mathbf{T}^{(2)} + \mathbf{T}^{(2)}\mathbf{B}\mathbf{T}^{(1)} = \mathbf{0}, \quad (28)$$

$$\alpha^n: \{\Delta\epsilon, \mathbf{T}^{(n)}\} + \{\mathbf{A}', \mathbf{T}^{(n-1)}\} + \sum_{i=1}^{n-2} \mathbf{T}^{(i)}\mathbf{B}\mathbf{T}^{(n-i-1)} = \mathbf{0}. \quad (29)$$

A completely analogous set of equations holds for the dRPA case, replacing both \mathbf{A}' and \mathbf{B} with \mathbf{K} . Note that there can be no constant contribution $\mathbf{T}^{(0)}$ to \mathbf{T}_α since from Eq. (17) for $\alpha=0$ one gets $\Delta\epsilon\mathbf{T}^{(0)} + \mathbf{T}^{(0)}\Delta\epsilon = \mathbf{0}$, meaning that $\mathbf{T}^{(0)} = \mathbf{0}$.

The series expansion of \mathbf{T}_α may now be inserted in the coupling-strength integral of the RPA density matrix

$$2 \int_0^1 d\alpha \mathbf{T}_\alpha (\mathbf{I} - \mathbf{T}_\alpha)^{-1} = \mathbf{T}^{(1)} + \frac{2}{3}(\mathbf{T}^{(2)} + (\mathbf{T}^{(1)})^2) + \frac{2}{4}(\mathbf{T}^{(3)} + \mathbf{T}^{(2)}\mathbf{T}^{(1)} + \mathbf{T}^{(1)}\mathbf{T}^{(2)} + (\mathbf{T}^{(1)})^3) + \dots \quad (30)$$

While the first-order term of this expansion coincides with that of Eq. (24) for $\alpha=1$, this is not the case for the higher-order terms.

(c) *Equivalence of rCCD and RPA energies.* Nevertheless, the equivalence of

$$E_c^{\text{rCCD}} = \frac{1}{4}(\text{tr}(\mathbf{B}\mathbf{T}^{(1)}) + \text{tr}(\mathbf{B}\mathbf{T}^{(2)}) + \text{tr}(\mathbf{B}\mathbf{T}^{(3)}) + \text{tr}(\mathbf{B}\mathbf{T}^{(4)}) + \dots) \quad (31)$$

and

$$E_c^{\text{AC-RPA}} = \frac{1}{4} \int_0^1 d\alpha 2\text{tr}(\mathbf{B}(\mathbf{T}_\alpha + \mathbf{T}_\alpha^3 + \dots) + \mathbf{A}'(\mathbf{T}_\alpha^2 + \mathbf{T}_\alpha^4 + \dots)) \\ = \frac{1}{4} \left(\text{tr}(\mathbf{B}\mathbf{T}^{(1)}) + \frac{2}{3}\text{tr}(\mathbf{B}\mathbf{T}^{(2)} + \mathbf{A}'(\mathbf{T}^{(1)})^2) + \frac{2}{4}\text{tr}(\mathbf{B}(\mathbf{T}^{(3)} + (\mathbf{T}^{(1)})^3) + \mathbf{A}'(\mathbf{T}^{(1)}\mathbf{T}^{(2)} + \mathbf{T}^{(2)}\mathbf{T}^{(1)})) + \frac{2}{5}\text{tr}(\mathbf{B}(\mathbf{T}^{(4)} + \mathbf{T}^{(1)}\mathbf{T}^{(2)}\mathbf{T}^{(1)} + (\mathbf{T}^{(1)})^2\mathbf{T}^{(2)} + \mathbf{T}^{(2)}(\mathbf{T}^{(1)})^2)) + \frac{2}{5}\text{tr}(\mathbf{A}'(\mathbf{T}^{(1)}\mathbf{T}^{(3)} + \mathbf{T}^{(3)}\mathbf{T}^{(1)} + (\mathbf{T}^{(2)})^2 + (\mathbf{T}^{(1)})^4)) + \dots \right) \quad (32)$$

and, in consequence, $E_c^{\text{drCCD}} = E_c^{\text{AC-dRPA}}$ may also be obtained from the above expansion, as shown in the following for terms up to and including fourth-order amplitudes. Note that the first term $\text{tr}\{\mathbf{B}\mathbf{T}^{(1)}\}$ in the sense of perturbation theory is actually a second-order energy contribution, and that this is

the term which trivially coincides between the expansions of E_c^{rCCD} and $E_c^{\text{AC-RPA}}$. In the above expansion all energy contributions up to and including fifth order are given explicitly.

The equivalence of the third-order energy contributions follows from the relation

$$\text{tr}(\mathbf{A}'(\mathbf{T}^{(1)})^2) = \frac{1}{2}\text{tr}(\mathbf{B}\mathbf{T}^{(2)}) \quad (33)$$

which may be derived from multiplying Eqs. (25) and (26) with $\mathbf{T}^{(2)}$ and $\mathbf{T}^{(1)}$, respectively, and employing the invariance of the trace under cyclic permutations of matrix products. This equation on the one hand verifies the identity of the third-order contributions to E_c^{rCCD} and $E_c^{\text{AC-RPA}}$, but on the other it also demonstrates that first-order amplitudes are sufficient to calculate energies up to third order. In a completely analogous way it is seen that

$$\text{tr}(\mathbf{A}'\{\mathbf{T}^{(1)}, \mathbf{T}^{(2)}\} + \mathbf{B}(\mathbf{T}^{(1)})^3) = \text{tr}(\mathbf{B}\mathbf{T}^{(3)}) \quad (34)$$

which proves the identity of the fourth-order contributions to E_c^{rCCD} and $E_c^{\text{AC-RPA}}$.

The demonstration of the equivalence of the fifth-order terms is more involved.⁷ The main result is

$$\frac{3}{2}\text{tr}(\mathbf{B}\mathbf{T}^{(4)}) = \text{tr}(\mathbf{B}(\mathbf{T}^{(1)}\mathbf{T}^{(2)}\mathbf{T}^{(1)} + \{\mathbf{T}^{(1)}\}^2, \mathbf{T}^{(2)})) + \text{tr}(\mathbf{A}'(\{\mathbf{T}^{(1)}, \mathbf{T}^{(3)}\} + (\mathbf{T}^{(2)})^2 + (\mathbf{T}^{(1)})^4)) \quad (35)$$

which allows to see the equivalence of the fifth-order contributions to E_c^{rCCD} and $E_c^{\text{AC-RPA}}$. Note that from the derivation of Eq. (35) it also follows that

$$\text{tr}(\mathbf{B}\mathbf{T}^{(4)}) = 2\text{tr}(\mathbf{B}\mathbf{T}^{(1)}\mathbf{T}^{(2)}\mathbf{T}^{(1)} + \mathbf{A}'((\mathbf{T}^{(2)})^2 + (\mathbf{T}^{(1)})^4)). \quad (36)$$

This, again, shows the validity of the usual $(2n+1)$ -rule of perturbation theory: fifth-order energy contributions may be calculated from first- and second-order amplitudes.

(d) *Second- and third-order contributions of rCCD and RPA variants.* Besides dRPA and drCCD on the one hand, and RPA and rCCD on the other also “mixed” approaches were proposed, where nonantisymmetrized integrals are used in part of the equations and antisymmetrized integrals in other parts. One of these approaches is RPax,^{8,9} in which the RPA density matrix is obtained with antisymmetrized two-electron integrals while its contraction to yield the correlation energy occurs with nonantisymmetrized integrals

$$E_c^{\text{AC-RPax}} = \frac{1}{2} \int_0^1 d\alpha \text{tr}(\mathbf{K}\mathbf{P}_\alpha^{\text{RPax}}). \quad (37)$$

For consistency RPax will be denoted as AC-RPax in the following. Another method augments drCCD with second-order screened exchange,^{10,11} an approach which for brevity is termed SOSEX. Here, the amplitudes obtained by drCCD are contracted with antisymmetrized two-electron integrals (equivalently one could contract the nonantisymmetrized integral matrix \mathbf{K} with *a posteriori* antisymmetrized drCCD amplitudes)

$$E_c^{\text{SOSEX}} = \frac{1}{2}\text{tr}(\mathbf{B}\mathbf{T}^{\text{drCCD}}). \quad (38)$$

This approach recently was named dRPA+SOSEX.¹² As will be shown below it is, however, not identical to augmenting

dRPA with SOSEX, which rather would correspond to

$$E_c^{\text{AC-SOSEX}} = \frac{1}{2} \int_0^1 d\alpha \text{tr}(\mathbf{B}\mathbf{P}_\alpha^{\text{dRPA}}). \quad (39)$$

Let us examine these approaches with the help of the perturbation theory arguments presented above. For the RPA/rCCD case solving Eqs. (25) and (26) yields

$$T_{ia,jb}^{(1)} = \frac{\langle ij||ab \rangle}{\omega_{ijab}}, \quad (40)$$

$$T_{ia,jb}^{(2)} = \sum_{kc} \left(\frac{\langle ic||ak \rangle \langle kj||cb \rangle}{\omega_{ijab}\omega_{kacb}} + \frac{\langle ik||ac \rangle \langle kb||cj \rangle}{\omega_{ijab}\omega_{ikac}} \right), \quad (41)$$

where $\omega_{ijab} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$ etc. Note that though the first-order amplitudes are antisymmetric, $T_{ib,ja}^{(1)} = -T_{ia,jb}^{(1)} = -T_{jb,ia}^{(1)}$, this is not true for $T_{ib,ja}^{(2)}$. While the resulting second-order energy formally becomes identical to that of Møller–Plesset perturbation theory (except for potential replacement of Hartree–Fock with Kohn–Sham orbitals)

$$E_c^{\text{AC-RPA,(2)}} = E_c^{\text{rCCD,(2)}} = \frac{1}{4} \sum_{ijab} \frac{\langle ij||ab \rangle^2}{\omega_{ijab}} \quad (42)$$

due to the restriction to ring diagrams this not the case for the third-order contribution which, employing integral symmetry, reads

$$E_c^{\text{AC-RPA,(3)}} = E_c^{\text{rCCD,(3)}} = \frac{1}{2} \sum_{ijkabc} \frac{\langle ij||ab \rangle \langle kb||cj \rangle \langle ac||ik \rangle}{\omega_{ijab}\omega_{ikac}}. \quad (43)$$

This expression is formally identical to half of the particle-hole part of the third-order Møller–Plesset energy, in agreement with an observation by Szabo and Ostlund (cf. the discussion of NRPA1 in Ref. 13, identical to what here is named RPA), while the prefactor is missing in the corresponding final expression of Oddershede.¹⁴

In AC-RPAx nonantisymmetrized integrals are used in the contraction with the coupling-strength integrated density matrix (30). Still, due to the antisymmetry of the first-order amplitudes and the prefactor of $\frac{1}{2}$ in Eq. (37) one finds $E_c^{\text{AC-RPAx,(2)}} = E_c^{\text{AC-RPA,(2)}}$. With Eq. (30) the third-order contribution becomes

$$E_c^{\text{AC-RPAx,(3)}} = \frac{1}{3} \sum_{ijkabc} \left(\frac{\langle ij||ab \rangle \langle jc||bk \rangle \langle ki||ca \rangle}{\omega_{ijab}\omega_{ikac}} + \frac{\langle ij||ab \rangle \langle jk||bc \rangle \langle ka||ci \rangle}{\omega_{ijab}\omega_{jkbc}} + \frac{\langle ij||ab \rangle \langle jk||bc \rangle \langle ki||ca \rangle}{\omega_{ikac}\omega_{jkbc}} \right). \quad (44)$$

In the dRPA/drCCD case the first- and second-order amplitudes are determined by Eqs. (25) and (26) with \mathbf{A}' and \mathbf{B} replaced with \mathbf{K} . One thus gets

$$T_{ia,jb}^{(1)} = \frac{\langle ij||ab \rangle}{\omega_{ijab}}, \quad (45)$$

$$T_{ia,jb}^{(2)} = \sum_{kc} \left(\frac{\langle ic||ak \rangle \langle kj||cb \rangle}{\omega_{ijab}\omega_{kacb}} + \frac{\langle ik||ac \rangle \langle kb||cj \rangle}{\omega_{ijab}\omega_{ikac}} \right). \quad (46)$$

The resulting energy contributions read

$$E_c^{\text{AC-dRPA,(2)}} = E_c^{\text{drCCD,(2)}} = \frac{1}{2} \sum_{ijab} \frac{\langle ij||ab \rangle^2}{\omega_{ijab}}, \quad (47)$$

$$E_c^{\text{AC-dRPA,(3)}} = E_c^{\text{drCCD,(3)}} = \sum_{ijkabc} \left(\frac{\langle ij||ab \rangle \langle kb||cj \rangle \langle ac||ik \rangle}{\omega_{ijab}\omega_{ikac}} \right). \quad (48)$$

Contracting the drCCD amplitudes with antisymmetrized integrals yields the second-order SOSEX contribution as $E_c^{\text{SOSEX,(2)}} = E_c^{\text{AC-RPA,(2)}}$, while the third-order contribution reads

$$E_c^{\text{SOSEX,(3)}} = \sum_{ijkabc} \left(\frac{\langle ij||ab \rangle \langle kb||cj \rangle \langle ac||ik \rangle}{\omega_{ijab}\omega_{ikac}} \right). \quad (49)$$

The SOSEX variant generated from dRPA through ACFDT clearly has the same second-order contribution, while the third-order energy differs

$$E_c^{\text{AC-SOSEX,(3)}} = \sum_{ijkabc} \left(\frac{2 \langle ij||ab \rangle \langle kb||cj \rangle \langle ac||ik \rangle}{3 \omega_{ijab}\omega_{ikac}} + \frac{1 \langle ij||ab \rangle \langle kj||cb \rangle \langle ac||ik \rangle}{3 \omega_{ijab}\omega_{ikac}} \right). \quad (50)$$

Numerical consequences of the differences between the various approaches for atomic and ionic electron correlation energies, for molecular properties, and for intermolecular interaction energies will be the topic of a forthcoming publication.

The label RPA is connected with a variety of promising approaches to include long-range dispersion effects into density functional theory on firm theoretical grounds. This actively developing field of research to some extent is plagued by the existence of a large variety of alternative methods with a lack of clear understanding of their relations. The situation is made even more complicated by the different conventions adopted by different communities working with RPA methods (e.g., in density functional theory one often neglects exchange, in quantum chemistry or nuclear physics, one retains it). The present study clarifies some of the fundamental relations between different RPA-based methods and the consequences of including or excluding antisymmetrization at various levels by perturbation theory arguments. It is hoped that this work contributes to establish a better understanding of the advantages of the different approximations and serves a basis for future development.

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