



## Spin flipping in ring-coupled-cluster-doubles theory

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### ABSTRACT

We report a critical analysis and comparison of a variety of random-phase-approximation (RPA) based approaches to determine the electronic ground-state energy. Interrelations between RPA variants are examined by numerical examples with particular attention paid to the role of spin-flipped excitations and the behaviour of the adiabatic-connection integrands where appropriate. In general, it is found that RPA variants that include Hartree–Fock exchange contributions are unsuitable as generally applicable methods for the determination of correlation energies. Of the remaining methods only the direct RPA and RPA with second-order screened exchange are recommended for general use.

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### 1. Introduction

Recently, there has been a revived interest in the problem of how to extract an accurate correlation energy from the random-phase approximation (RPA) [1–24]. In this Letter, we report a critical comparison and analysis of various variants of the RPA correlation energy. Within the purview of quantum chemistry, the number of RPA and beyond-RPA approaches to the calculation of the correlation energy has grown rapidly over recent years. The literature pertaining to these methodologies is not only vast, but also somewhat bewildering since different authors often use different (similar) acronyms for equivalent (different) methods, depending on the computational strategy used to calculate the correlation energy. Despite the increasingly large number of papers examining various aspects and equivalences between different RPA approaches, few straightforward correlation energies have been reported. Most applications to date report relative energies such as atomisation and binding energies. Jiang and Engel have reported some dRPA benchmark numerical results for atoms [25]. However, for finite basis-set implementations, these numbers are not easily reproduced as the RPA correlation energy suffers from the same slow basis-set convergence as do wave-function methodologies. In this Letter, we aim to provide a concise set of data for a range of simple systems using a standard Gaussian basis set and a Hartree–Fock reference determinant, thereby avoiding inaccuracies due to numerical integration.

We commence in Section 2 with a historical overview of the use of the RPA to obtain a ground-state correlation energy, setting the scene

for theoretical and numerical comparisons between the RPA variants in Sections 3 and 4. In Section 3, the key equations for the RPA variants studied in the present work are reviewed and, where appropriate, equivalences and similarities are highlighted. In Section 4, calculations are performed for a range of small atomic and molecular systems. Particular attention is paid to the role of spin-flipped excitations in the calculation of the correlation energy. The performance and stability of the various RPA based methods are then analysed in light of these results. Finally, we make some concluding remarks and recommendations for workers interested in implementing or utilising RPA based correlation energies in Section 5.

### 2. Overview of RPA variants

The roots of the RPA method as a means to calculate correlation energies may be traced back to the classical treatment of the plasma theory of the electron gas by Bohm and Pines in the early 1950s [26–29] and its later quantum–mechanical refinement by Nozières and Pines [30]. The name RPA was coined from approximations made in these early works, which provided the first quantitative estimates of the correlation energy in high-density free-electron gases, but which considered only the ‘direct’ (classical Coulomb) part of the two-electron interactions. In 1964, McLachlan and Ball reported a method for calculating RPA correlation energies (including exchange contributions) from time-dependent Hartree–Fock (TDHF) theory using the plasmon formula [31]. In quantum chemistry, the term RPA has later become synonymous with the successful TDHF method for the calculation of excitation energies [32,33], while the use of RPA theory for calculating correlation energies has been less successful due to afflictions arising from triplet instabilities—for a review of RPA correlation energy calculations, see Ref. [34]. In the present Letter, we will use RPA to refer generally to all RPA based methods, and denote the RPA method

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including only the direct part of the two-electron interaction as direct RPA (dRPA).

Present-day interest in RPA theory has been fuelled by the search for low-cost orbital-dependent functionals in Kohn–Sham (KS) density-functional theory (DFT). Previous work in this area has been dominated by perturbative approaches, but these are variationally unstable; therefore, various re-summations and denominator shifts have been explored, see for example Ref. [35]. In 2001, Furche demonstrated that, whilst poor for the description of atomisation energies, the dRPA method (unaffected by triplet instabilities) accounts well for both strong correlation and dispersion compared with standard correlation functionals [2]. This ‘atomisation-energy puzzle’ has been discussed further in terms of the associated correlation hole [21]. Since failures of the dRPA are associated with short-ranged interactions where local and semi-local correlation functionals are more accurate, attempts to form synergistic approaches have become widespread [1,13,15,21–23,25,36,37], driven by the observations that dRPA approaches include long-range dispersion, are parameter-free and stable to near degeneracies.

The dRPA correlation energy has a close connection to KS theory [2,5]. Langreth and Perdew used the fluctuation–dissipation theorem (FDT) to establish an adiabatic connection (AC) between the KS non-interacting system and the physical interacting system [38]. The exchange–correlation energy is expressed as a coupling-strength integral whose integrand is written in terms of the interacting and non-interacting density–response functions. Whilst the non-interacting response function may be expressed directly in terms of the KS orbitals, the interacting response function is available from a Dyson-like equation. Setting the exchange–correlation kernel to zero, we obtain the dRPA. The coupling-strength integrand may be constructed directly from the dRPA response matrices, as shown by Furche [2,5]. Several attempts to improve upon dRPA have been suggested, which typically attempt to introduce the exchange effects missing in dRPA without introducing the associated triplet instabilities. This can be achieved in a hybrid manner, such as in the RPA with second-order screened exchange (RPA + SOSEX) [11,39] approach, or by modification of the coupling-strength integrand as in the RPax (also known as RPA (HF), see Section 3) [15,17,22] and RPA (EXX) [7,17] approaches.

The applicability of dRPA methods has further been boosted by the implementation of algorithms for the evaluation of the correlation energy that scale as  $\mathcal{O}(N^4 \log N)$ , using a combination of imaginary-frequency integration and resolution-of-the-identity techniques by Eshuis et al. [16]. In addition, following the numerical equivalence between ring-coupled-cluster-doubles (rCCD) and RPA observed by Sanderson [40] (see also Freeman [39] and Paldus et al. [41]) and re-examined by Kresse and Grüneis [42] and by Scuseria et al. [9], the RPA correlation energy may be obtained from the algebraic Riccati equation. In this context it has been proposed to use Cholesky decomposition to obtain a scaling more favourable than that of second-order Görling–Levy theory [9]. It seems likely that RPA will become an increasingly common component of future orbital-dependent density functionals.

### 3. Theory

#### 3.1. Notation and definitions

Traditionally, the RPA correlation energy is obtained by explicit integration over the coupling-strength parameter  $\lambda$  from the non-interacting to the interacting system [31,43] within the framework of the adiabatic connection [38]. To define the quantities required for the evaluation of the RPA correlation energy in this manner,

consider the non-Hermitian eigenvalue problem at coupling strength  $\lambda$ :

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

where the eigenvalues are (approximate) excitation and de-excitation energies of the system. The matrices  $\mathbf{A}_\lambda$  and  $\mathbf{B}_\lambda$  are given by:

$$(\mathbf{A}_\lambda)_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \lambda(\mathbf{ia} | \mathbf{bj}); \quad (2)$$

$$(\mathbf{B}_\lambda)_{ia,jb} = \lambda(\mathbf{ia} | \mathbf{jb}), \quad (3)$$

where the  $\varepsilon_p$  are the energies of the canonical spin orbitals  $\varphi_p$  (calculated at  $\lambda = 1$ ) and the two-electron integrals are given by (in Mulliken notation):

$$(\mathbf{ia} | \mathbf{jb}) = \int \int \varphi_i(\mathbf{x}_1)\varphi_j(\mathbf{x}_2)r_{12}^{-1}\varphi_a(\mathbf{x}_1)\varphi_b(\mathbf{x}_2) \mathbf{d}\mathbf{x}_1 \mathbf{d}\mathbf{x}_2. \quad (4)$$

We assume real spin orbitals throughout, denoting occupied spin orbitals by  $i, j, k, \dots$  and virtual spin orbitals by  $a, b, c, \dots$ . From the eigenvectors of Eq. (1) normalized to  $\mathbf{X}_\lambda^\dagger \mathbf{X}_\lambda - \mathbf{Y}_\lambda^\dagger \mathbf{Y}_\lambda = \mathbf{I}$ , the *direct RPA (dRPA)* correlation energy is obtained by coupling-strength integration,

$$E_c^{\text{dRPA}} = \frac{1}{2} \int_0^1 \text{tr}(\mathbf{B}\mathbf{P}_\lambda) \mathbf{d}\lambda; \quad \mathbf{P}_\lambda = (\mathbf{X}_\lambda + \mathbf{Y}_\lambda)(\mathbf{X}_\lambda + \mathbf{Y}_\lambda)^\dagger - \mathbf{I}, \quad (5)$$

where the omission of the coupling-strength parameter as a subscript implies that  $\lambda = 1$ , that is,  $\mathbf{A} \equiv \mathbf{A}_1$  and  $\mathbf{B} \equiv \mathbf{B}_1$  [2,5].

We have above introduced the RPA without including exchange contributions in Eqs. (2) and (3). A similar theory may be set up with exchange included by defining the corresponding matrices in terms of ‘antisymmetrised’ two-electron integrals, which are indicated by an overbar,

$$(\overline{\mathbf{A}}_\lambda)_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \lambda(\mathbf{ia} | \mathbf{bj}) - \lambda(\mathbf{ij} | \mathbf{ab}); \quad (6)$$

$$(\overline{\mathbf{B}}_\lambda)_{ia,jb} = \lambda(\mathbf{ia} | \mathbf{jb}) - \lambda(\mathbf{ib} | \mathbf{ja}), \quad (7)$$

yielding the *RPA exchange (RPax)* correlation energy  $E_c^{\text{RPax}}$  of Toulouse et al. [22], which is precisely equivalent to the *RPA (HF)* method of Heßelmann and Görling [17],

$$E_c^{\text{RPax}} = \frac{1}{2} \int_0^1 \text{tr}(\mathbf{B}\overline{\mathbf{P}}_\lambda) \mathbf{d}\lambda. \quad (8)$$

This correlation energy differs from the direct RPA energy of Eq. (5) in that  $\overline{\mathbf{P}}_\lambda$  has been calculated from  $\overline{\mathbf{A}}_\lambda$  and  $\overline{\mathbf{B}}_\lambda$  rather than from  $\mathbf{A}_\lambda$  and  $\mathbf{B}_\lambda$ . We note that Toulouse et al. in their implementation make use of the fact that only the *singlet* spin-adapted component of  $\overline{\mathbf{P}}_\lambda$  contributes to the RPax correlation energy of closed-shell molecules, thereby avoiding difficulties with triplet instabilities. We furthermore note that the excitation energies calculated from Eq. (1) using  $\overline{\mathbf{A}}_\lambda$  and  $\overline{\mathbf{B}}_\lambda$  are the usual excitation energies of HF linear response theory, also known as time-dependent Hartree–Fock (TDHF) theory.

From the non-Hermitian dRPA eigenvalue problem, we obtain in the usual manner the following symmetric eigenvalue problem of reduced dimension for the squared excitation energies:

$$\mathbf{M}_\lambda \mathbf{Z}_\lambda = \mathbf{Z}_\lambda \omega_\lambda^2, \quad (9)$$

with

$$\mathbf{M}_\lambda = (\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{1/2} (\mathbf{A}_\lambda + \mathbf{B}_\lambda) (\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{1/2}; \quad (10)$$

$$\mathbf{Z}_\lambda = (\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{-1/2} (\mathbf{X}_\lambda + \mathbf{Y}_\lambda) \omega_\lambda^{1/2}, \quad (11)$$

where  $\mathbf{A}_\lambda - \mathbf{B}_\lambda$  is positive definite. Eliminating  $\mathbf{X}_\lambda + \mathbf{Y}_\lambda$  from  $\mathbf{P}_\lambda$  in Eq. (5) and using  $\mathbf{Z}_\lambda^\dagger \mathbf{Z}_\lambda = \mathbf{I}$ , we obtain

$$\mathbf{P}_\lambda = (\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{1/2} \mathbf{M}_\lambda^{-1/2} (\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{1/2} - \mathbf{I}. \quad (12)$$

Because of the special structure of  $\mathbf{A}_i$  and  $\mathbf{B}_i$ , the coupling-strength integration may be performed analytically, as observed by Furche [8],

$$E_c^{\text{drPA}} = \frac{1}{2} \text{tr}(\mathbf{M}^{1/2} - \mathbf{A}) = \frac{1}{2} \text{tr}(\boldsymbol{\omega} - \mathbf{A}), \quad (13)$$

where  $\mathbf{A} = \mathbf{M}_{i=0}^{1/2} = \boldsymbol{\omega}_{i=0}$ . By means of this *plasmon formula*, the main computational task is reduced to the calculation of the square root of  $\mathbf{M}$  for the fully interacting system. No such plasmon formula exists for the RPax energy.

As observed by Sanderson [40] and re-examined recently by Kresse and Grüneis [42] and by Scuseria et al. [9], the direct RPA correlation energy of Eq. (5) is equal to the *direct ring-coupled-cluster-doubles (drCCD)* energy defined by

$$E_c^{\text{drCCD}} = \frac{1}{2} \text{tr}(\mathbf{B}\mathbf{T}_{\text{dr}}) = E_c^{\text{drPA}}, \quad (14)$$

where  $\mathbf{T}_{\text{dr}}$  solves the *direct ring-coupled-cluster-doubles (drCCD)* equation

$$\mathbf{B} + \mathbf{A}\mathbf{T}_{\text{dr}} + \mathbf{T}_{\text{dr}}\mathbf{A} + \mathbf{T}_{\text{dr}}\mathbf{B}\mathbf{T}_{\text{dr}} = \mathbf{0}, \quad (15)$$

which is a special case of the algebraic Riccati equation obtained by removing all exchange integrals and retaining only the particle-hole ring contractions in the standard coupled-cluster doubles equations. As shown by Scuseria et al. [9], the drCCD equations are obtained from the dRPA equations in Eq. (5) by multiplying these equations on the right by  $\mathbf{X}^{-1}$  (which is always well-defined in dRPA) and introducing  $\mathbf{T}_{\text{dr}} = \mathbf{Y}\mathbf{X}^{-1}$ . In the drCCD method, only the Coulomb energy is correlated, neglecting all correlation contributions to the exchange energy. We also note that the algebraic Riccati equation associated with the RPA symplectic eigenvalue problem (including exchange) also appeared in Eq. (4.2) of Ref. [44], albeit with the implicit assumption of the existence of  $\mathbf{X}^{-1}$ , which is not guaranteed when exchange contributions are included.

In the RPA + SOSEX method, proposed by Freeman [39] and recently examined by Grüneis et al. [11], the correlation energy is obtained from the expression

$$E_c^{\text{RPA+SOSEX}} = \frac{1}{2} \text{tr}(\overline{\mathbf{B}}\mathbf{T}_{\text{dr}}), \quad (16)$$

using the matrix  $\mathbf{T}_{\text{dr}}$  that solves Eq. (15). Thus, the RPA + SOSEX energy differs from the drCCD (or dRPA) energy in the use of  $\overline{\mathbf{B}}$  rather than  $\mathbf{B}$  when the energy correction is calculated from the amplitudes. In the RPA + SOSEX method, therefore, the exchange energy is correlated using amplitudes determined for the Coulomb energy.

In contrast to the direct drCCD equation in Eq. (15), the *ring-coupled-cluster-doubles equation (rCCD)* itself is defined in terms of  $\overline{\mathbf{A}}$  and  $\overline{\mathbf{B}}$ ,

$$\overline{\mathbf{B}} + \overline{\mathbf{A}}\mathbf{T}_r + \mathbf{T}_r\overline{\mathbf{A}} + \mathbf{T}_r\overline{\mathbf{B}}\mathbf{T}_r = \mathbf{0}, \quad (17)$$

with the rCCD correlation energy

$$E_c^{\text{rCCD}} = \frac{1}{4} \text{tr}(\overline{\mathbf{B}}\mathbf{T}_r). \quad (18)$$

We note that the RPA + SOSEX correlation energy can be written in the form  $E_c^{\text{RPA+SOSEX}} = \frac{1}{2} \text{tr}(\overline{\mathbf{B}}\mathbf{T}_{\text{dr}})$  by introducing the antisymmetrised drCCD amplitudes

$$[\overline{\mathbf{T}}_{\text{dr}}]_{ia,jb} = [\mathbf{T}_{\text{dr}}]_{ia,jb} - [\mathbf{T}_{\text{dr}}]_{ib,ja}. \quad (19)$$

Finally, the second-order Møller–Plesset (MP2) energy is obtained by truncating the rCCD equation in Eq. (17) after the first order,

$$\overline{\mathbf{B}} + \overline{\mathbf{A}}_{i=0}\mathbf{T}_r^{(1)} + \mathbf{T}_r^{(1)}\overline{\mathbf{A}}_{i=0} = \mathbf{0}, \quad (20)$$

with the energy expression

$$E_c^{\text{MP2}} = \frac{1}{4} \text{tr}(\overline{\mathbf{B}}\mathbf{T}_r^{(1)}) = \frac{1}{2} \text{tr}(\overline{\mathbf{B}}\mathbf{T}_r^{(1)}). \quad (21)$$

Since  $\overline{\mathbf{A}}_{i=0}$  is diagonal, it follows that

$$T_{ia,jb}^{(1)} = \frac{(ia | jb) - (ib | ja)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}, \quad (22)$$

$$E_c^{\text{MP2}} = \frac{1}{4} \sum_{ia,jb} \frac{((ia | jb) - (ib | ja))^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}. \quad (23)$$

For comparison, we also indicate the *coupled-cluster-doubles (CCD)* energy and amplitude equation,

$$E_c^{\text{CCD}} = \frac{1}{4} \text{tr}(\overline{\mathbf{B}}\mathbf{T}_{\text{CCD}}) = \frac{1}{2} \text{tr}(\mathbf{B}\mathbf{T}_{\text{CCD}}), \quad (24)$$

$$- (\overline{\mathbf{A}}_{i=0}\mathbf{T}_{\text{CCD}} + \mathbf{T}_{\text{CCD}}\overline{\mathbf{A}}_{i=0}) = \overline{\mathbf{B}} + \text{linear and quadratic terms.} \quad (25)$$

**Table 1**  
Energies (in  $E_h$ ) from RHF based calculations (n.a., not available).

Species R/a <sub>0</sub>	He	Be	Ne	He <sub>2</sub> 5.6	HF 1.7329	N <sub>2</sub> 2.0749
SCF	-2.859895	-14.571874	-128.522553	-5.719782	-105.239955	-108.969375
MP2	-0.024682	-0.041555	-0.227939	-0.049383	-0.239703	-0.363627
CCD	-0.030589	-0.060775	-0.228820	-0.061197	-0.241662	-0.360461
CCSD	-0.030676	-0.061227	-0.229476	-0.061370	-0.242747	-0.364232
CCSDT	-0.030676	-0.061497	-0.231673	-0.061371	-0.246413	-0.378754
tr( $\mathbf{M}^{1/2}$ )	66.410779	456.244563	4827.763664	262.787645	4801.293630	7870.106350
tr( $\mathbf{A}$ )	66.497309	456.380970	4828.301923	262.960732	4801.850742	7870.907757
drCCD (dRPA)	-0.043265	-0.068204	-0.296130	-0.086544	-0.278556	-0.400704
RPA + SOSEX	-0.021633	-0.034446	-0.177576	-0.043279	-0.180970	-0.256036
RPax	-0.027492	-0.050733	-0.206715	-0.055001	-0.215420	-0.313973
<i>Spin-flipped (de) excitations excluded</i>						
$\Sigma\omega_{\text{TDHF}}$	25.459069	n.a.	2272.683931	112.329615	2250.188124	3698.461081
$\Sigma\omega_{\text{TDHF}}^0$	13.509638	101.525755	1142.739950	57.725154	1131.070292	1856.937202
$\Sigma\omega_{\text{TDHF}}^1$	11.949431	n.a.	1129.943981	54.604461	1119.117832	1841.523879
$\Sigma\omega_{\text{CIS}}$	25.527007	200.528419	2273.321161	112.465549	2250.881090	3699.685319
$\Sigma\omega_{\text{CIS}}^0$	13.540085	101.591310	1143.153920	57.786097	1131.503306	1857.609350
$\Sigma\omega_{\text{CIS}}^1$	11.986921	98.937109	1130.167241	54.679452	1119.377784	1842.075969
rCCD	-0.016984	n.a.	-0.159307	-0.033984	-0.173241	-0.306059
<i>Spin-flipped (de) excitations included</i>						
$\Sigma\omega_{\text{TDHF}}$	49.357931	n.a.	4532.571893	221.538537	4488.423789	7381.508840
$\Sigma\omega_{\text{CIS}}$	49.500849	398.402638	4533.655642	221.824453	4489.636659	7383.837258
rCCD	-0.035729	n.a.	-0.270937	-0.071479	-0.303218	-0.582105

For details on CCD theory, which is not the subject of this Letter, we refer the reader to the literature. The CCD results presented in this Letter were obtained by implementing Eqs. (1)–(13) of Ref. [45].

### 3.2. Spin-flipped (de) excitations

In Section 3.1, the sums over spin orbitals run over *all* spin orbitals, without restrictions. This is important to be aware of when comparing the computed correlation energy with sums of differences between excitation energies computed using TDHF theory and *configuration–interaction–singles* (CIS) theory (also known as the *Tamm–Dancoff approximation* (TDA)),

$$E_c^{\text{rCCD}} = \frac{1}{4} \sum_{ia} (\omega_{\text{TDHF}}^{ia} - \omega_{\text{CIS}}^{ia}), \quad (26)$$

where  $\omega_{\text{TDHF}}^{ia}$  is the excitation energy at the TDHF level, while  $\omega_{\text{CIS}}^{ia}$  is the excitation energy at the CIS level. In Eq. (26), the sum over the spin orbitals runs over all possible combinations—that is, both orbitals can have  $\alpha$ , both can have  $\beta$  spin, and the excitations can be spin-flipped in the sense of  $\varphi_i^\alpha \rightarrow \varphi_a^\beta$  and  $\varphi_i^\beta \rightarrow \varphi_a^\alpha$ .

Usually, codes meant to describe excited states in the framework of TDHF or time-dependent DFT (TDDFT) do not take into account these spin-flipped excitations. In such cases, Eq. (26) no longer holds, except when the spin-flipped excitations are also excluded from the rCCD equations. In this Letter, we have carried out rCCD calculations with and without spin-flipped excitations.

Let us consider a closed-shell system at the restricted Hartree–Fock (RHF) level of theory. With and without spin-flipped excitations, Eq. (26) becomes

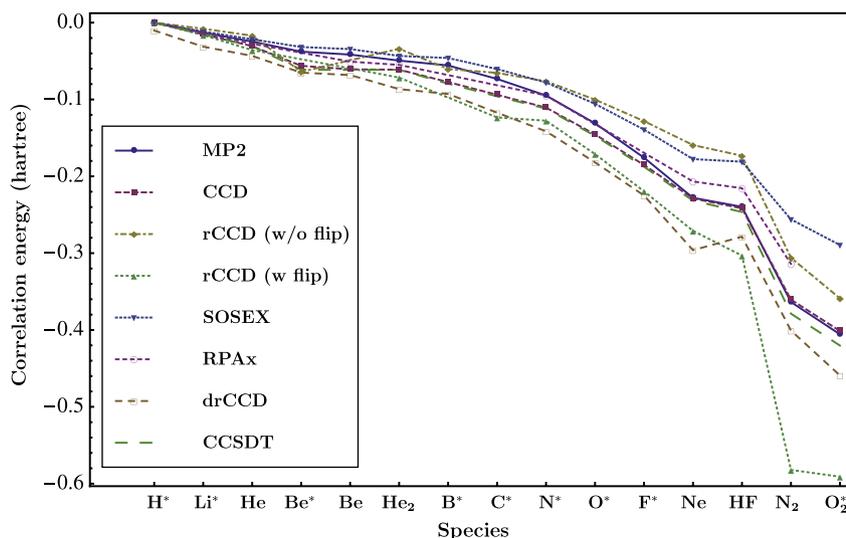
$$E_c^{\text{rCCD, w flip}} = \frac{1}{4} \{ (\Sigma\omega_{\text{TDHF}}^0 - \Sigma\omega_{\text{CIS}}^0) + 3(\Sigma\omega_{\text{TDHF}}^1 - \Sigma\omega_{\text{CIS}}^1) \}; \quad (27)$$

$$E_c^{\text{rCCD, w/o flip}} = \frac{1}{4} \{ (\Sigma\omega_{\text{TDHF}}^0 - \Sigma\omega_{\text{CIS}}^0) + (\Sigma\omega_{\text{TDHF}}^1 - \Sigma\omega_{\text{CIS}}^1) \}, \quad (28)$$

denoting the sums of all singlet excitation energies by  $\Sigma\omega_{\text{TDHF}}^0$  and  $\Sigma\omega_{\text{CIS}}^0$  and the corresponding triplet sums by  $\Sigma\omega_{\text{TDHF}}^1$  and  $\Sigma\omega_{\text{CIS}}^1$ . The spin-flipped excitations do not contribute to the dRPA correlation energy because the spin-flipped blocks of the matrices  $\mathbf{A}_i$  and  $\mathbf{B}_i$  in Eqs. (2) and (3) are diagonal and zero, respectively (see also Ref. [13]). Hence, with respect to the

**Table 2**  
Energies (in  $E_h$ ) from UHF based calculations (n.a., not available).

Species R/ $a_0$	H	Li	Be	B	C	N	O	F	O <sub>2</sub> 2.2828
SCF	−0.499810	−7.432026	−14.572204	−24.530103	−37.689049	−54.397980	−74.805211	−99.396874	−149.654946
MP2	0.000000	−0.012878	−0.037780	−0.055698	−0.073257	−0.094860	−0.131020	−0.175743	−0.405617
CCD	0.000000	−0.015196	−0.056177	−0.077310	−0.093875	−0.110590	−0.145472	−0.185216	−0.401271
CCSD	0.000000	−0.015205	−0.060887	−0.077927	−0.094353	−0.110812	−0.145869	−0.185732	−0.407219
CCSDT	0.000000	−0.015223	−0.061167	−0.079381	−0.095881	−0.111870	−0.147333	−0.187571	−0.420258
tr( $\mathbf{M}^{1/2}$ )	21.384454	226.412293	456.559651	799.697039	1278.095361	1906.948005	2692.080844	3667.429375	10931.490115
tr( $\mathbf{A}$ )	21.404937	226.474832	456.689769	799.882675	1278.329706	1907.230882	2692.444533	3667.879245	10932.408411
drCCD	−0.010241	−0.031270	−0.065059	−0.092818	−0.117172	−0.141438	−0.181845	−0.224935	−0.459148
RPA + SOSEX	0.000000	−0.011559	−0.031673	−0.046034	−0.060420	−0.077923	−0.105679	−0.139211	−0.289445
RPAx	0.000000	−0.013628	n.a.	n.a.	n.a.	−0.094741	n.a.	n.a.	n.a.
<i>Spin-flipped (de) excitations excluded</i>									
$\Sigma\omega_{\text{TDHF}}$	7.272541	96.475822	200.428038	357.221315	578.376413	871.268623	1246.264775	1714.324477	5179.699812
$\Sigma\omega_{\text{CIS}}$	7.272541	96.507559	200.684101	357.462538	578.637964	871.573908	1246.665616	1714.837069	5181.135202
rCCD	0.000000	−0.007934	−0.064016	−0.060306	−0.065388	−0.076321	−0.100210	−0.128148	−0.358848
<i>Spin-flipped (de) excitations included</i>									
$\Sigma\omega_{\text{TDHF}}$	14.545082	191.958686	n.a.	n.a.	1154.601039	1744.647184	2488.462287	3419.214273	10347.382340
$\Sigma\omega_{\text{CIS}}$	14.545082	192.023691	n.a.	n.a.	1155.094592	1745.157636	2489.146521	3420.092107	10349.746155
rCCD	0.000000	−0.016251	n.a.	n.a.	−0.123388	−0.127613	−0.171058	−0.219458	−0.590954



**Figure 1.** Correlation energies ( $E_h$ ) for the different electronic systems sorted in order of decreasing MP2 correlation energies; unrestricted calculations have been marked with an asterisk.

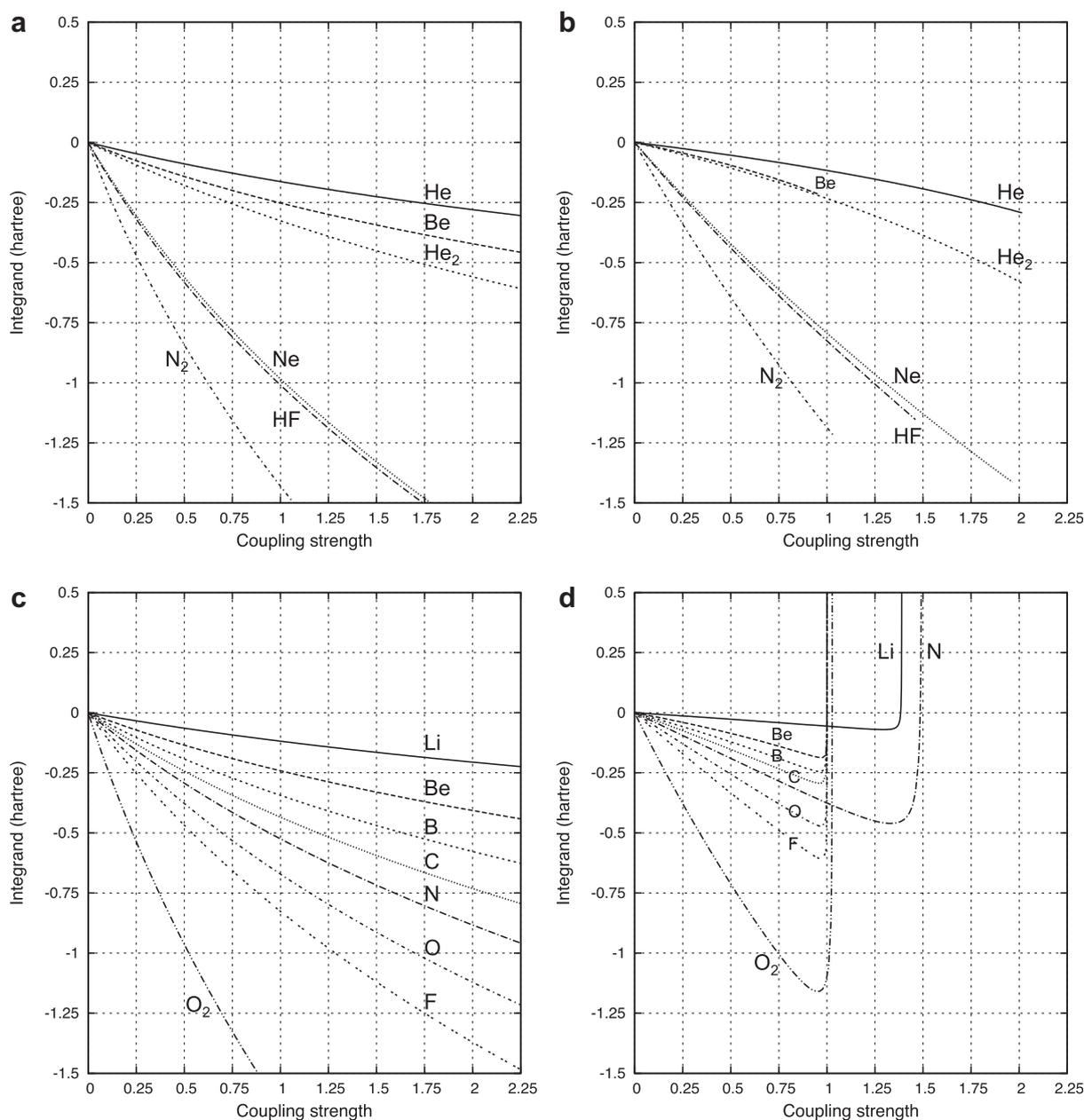
spin-flipped blocks,  $\mathbf{M}_\lambda = (\mathbf{A}_\lambda)^2$  and  $\mathbf{P}_\lambda = \mathbf{0}$  for all  $\lambda$ . Furthermore, Eq. (15) reduces to  $\mathbf{A}\mathbf{T}_{\text{dr}} + \mathbf{T}_{\text{dr}}\mathbf{A} = \mathbf{0}$  and hence  $\mathbf{T}_{\text{dr}} = \mathbf{0}$  for the spin-flipped block. Nor do the spin-flipped excitations contribute to the RPax energy, because the corresponding spin-flipped blocks of  $\mathbf{B}$  are zero in Eq. (8).

#### 4. Computational details and results

All calculations were performed using the 6-311G\*\* basis set [46] and all occupied orbitals were considered throughout (no frozen core). A computer program has been written specially for the calculations presented in this Letter, reading the one- and two-electron integrals over the atomic Gaussian basis functions from disk after they were computed by the DALTON program [47]. We here restrict ourselves to a Hartree–Fock reference determinant, thereby avoiding numerical uncertainties introduced by DFT

numerical quadrature. RPA energies from Hartree–Fock references may neither be theoretically rigorous nor relevant in practice, and furthermore, the 6-311G\*\* basis is not suited for correlating core orbitals. Our energies are given with the sole purpose of providing easily reproducible benchmark data. For this purpose, they are quoted to  $\mu E_h$  accuracy. For comparison, calculations at the coupled-cluster singles-and-doubles (CCSD) and coupled-cluster singles-doubles-triples (CCSDT) levels of theory were performed using the CFOUR program [48].

In Tables 1 and 2, we have listed the energies of all atoms from H to Ne, for the helium dimer, and for the three diatomic molecules HF, N<sub>2</sub> and O<sub>2</sub> using HF theory, MP2 theory, CCD theory, CCSD theory, CCSDT theory, rCCD theory [9] (with and without spin-flipped excitations included), drCCD (dRPA) theory [9,39], RPA + SOSEX theory [11,39] and RPax theory [15,22]. Unrestricted (UHF) and restricted (RHF) theories have been used for the open- and



**Figure 2.** Integrands  $\text{tr}(\mathbf{B}\mathbf{P}_\lambda)$  and  $\text{tr}(\mathbf{B}\bar{\mathbf{P}}_\lambda)$ , respectively, as a function of the coupling-strength parameter  $\lambda$ . (a)  $\text{tr}(\mathbf{B}\mathbf{P}_\lambda)$  for dRPA with RHF reference. (b)  $\text{tr}(\mathbf{B}\bar{\mathbf{P}}_\lambda)$  for RPax with RHF reference. (c)  $\text{tr}(\mathbf{B}\mathbf{P}_\lambda)$  for dRPA with UHF reference. (d)  $\text{tr}(\mathbf{B}\bar{\mathbf{P}}_\lambda)$  for RPax with UHF reference.

closed-shell systems, respectively; for the beryllium atom, calculations have been performed using both restricted and unrestricted theories. In addition, the rCCD and drCCD correlation energies have been decomposed into their TDHF and CIS (TDA) components, with a further decomposition of the rCCD energies into singlet and triplet components for the RHF case (no such decomposition is possible in the UHF case). For the decomposition of Eq. (26) into singlet and triplet components, see for example Refs. [44,49]. Some of the RPA-type calculations with exchange included in the optimisation step (RPax and rCCD calculations) could not be completed because of numerical instabilities; no such problems were encountered with RPA-type methods without exchange included in the optimisation step (drCCD and RPA + SOSEX) nor with the standard MP2 and CCD methods.

In Figure 1, we have plotted the correlation energies calculated using the different methods, with the electronic systems sorted in order of decreasing MP2 correlation energies. Comparing the MP2 and CCD correlation energies, we note that the CCD energy is lower than the MP2 energy except for N<sub>2</sub> and O<sub>2</sub>. Moreover, the CCD energy is close to the MP2 energy for the closed-shell systems, but differs significantly for the open-shell systems, the mean absolute relative deviation from the MP2 energy being 19%. Turning our attention to the rCCD approximation, we find that the rCCD correlation energy without spin-flipped contributions is typically much higher than the CCD energy (by about 30%), whereas the rCCD correlation energy with spin-flipped contributions is lower than the CCD energy (by about 40%). Typically, the two rCCD approximations differ by roughly a factor of two (as expected from a comparison of Eqs. (27) and (28)), mostly bracketing all other correlation energies considered here.

The drCCD model appears to be more stable and systematic than the rCCD model, from which it differs by the omission of a correlating exchange contribution. The drCCD correlation energy is lower than CCD energy in all cases, typically by 10% for the larger systems (and by more for the smaller ones). The RPA + SOSEX correlation energy is calculated from the same amplitudes as the drCCD model, but with the inclusion of exchange contributions—typically, the RPA + SOSEX correlation energy is about 50% of the drCCD energy and 80% of the MP2 correlation energy. Importantly, the RPA + SOSEX model is a stable model, deviating in a systematic manner from the MP2 model and converging in all cases. The RPax model, by contrast, is very close to the MP2 model but does not work for all systems because of difficulties with the numerical integration.

In the tables, we report only those RPax correlation energies where the integrand  $\text{tr}(\mathbf{B}\bar{\mathbf{P}}_\lambda)$  is a monotonically decreasing function of the coupling strength  $\lambda$  over the AC integration interval [0,1], see Figure 2. For the systems with RHF reference, this integrand is indeed monotonically decreasing in the interval [0,1] for all systems except Be (Figure 2b). The RHF determinant of Be exhibits a triplet instability that appears to make it impossible to compute  $\bar{\mathbf{P}}_\lambda$  for  $\lambda \geq 0.9764$ . We note, however, that this triplet-instability problem is an artefact of our spin-orbital-based implementation. When computing the RPax energy of a closed-shell system using a spin-adapted implementation [22], in which only the singlet spin-adapted component of  $\bar{\mathbf{P}}_\lambda$  contributes, then the integrand is monotonically decreasing in the interval [0,1] also for Be, and its correlation energy becomes  $E_c^{\text{RPax}} = -0.050733 E_h$ . In Figure 2, curves are shown for the interval [0,2.25]—that is, much beyond the range of AC integration, because we have for curiosity investigated the behaviour of the integrands for coupling strengths  $\lambda > 1$ . All RPax integrands based on a RHF reference exist up to a certain maximum value of the coupling strength (but note that the integrands may be computed beyond this maximum value using a spin-adapted algorithm). Moreover, the curves for He, Be and He<sub>2</sub> in Figure 2b are concave rather than convex functions.

By contrast, the curves of all of the dRPA integrands are convex (Figure 2a and c), consistent with the integrands calculated in Ref. [50].

All dRPA integrands are fully unproblematic. The absolute values of the integrands correlate nicely with the numbers of electrons in the system (cf. He and He<sub>2</sub>), and the integrands are all well-defined, monotonically decreasing convex functions everywhere. The situation is very different for the RPax integrands based on a UHF reference (Figure 2d). In particular, we observe that the atoms Be, B, C, O and F all exhibit a singularity at  $\lambda = 1$ . In all unrestricted TDHF calculations of these atoms, two degenerate excitation energies with a (near) zero real part are obtained. This degeneracy (note that these atoms have P-type ground states, including the UHF solution for Be) leads to the singularity at  $\lambda = 1$ . By contrast, Li and N have S-type ground states, making it possible to compute  $\bar{\mathbf{P}}_\lambda$  for values of  $\lambda$  greater than 1. Moreover, the Li and N curves are monotonically decreasing over the interval [0,1]; hence, the RPax correlation energy obtained by AC integration is reported for these atoms. Concerning the O<sub>2</sub> molecule ( $\Sigma$ -type ground state), AC integration over the interval [0,1] could in fact easily be carried out. However, since the integrand is not monotonically decreasing, we have refrained from reporting the result.

Finally, we note that the inclusion of spin-flipped excitations into the rCCD equations leads to instabilities in the UHF-based calculations on beryllium and boron.

## 5. Conclusions

The purpose of this Letter is twofold: first, to highlight the fact that ring-coupled-cluster calculations can be carried out either with or without spin-flipped excitations. Common coupled-cluster approaches such as the CCD and CCSD models include such excitations, but the use of spin-flipped excitations is usually not explicitly stated in the literature when it comes to the ring-coupled-cluster approach (see, e.g., Ref. [9]). Although the spin-flipped excitations contribute to the ring-coupled-cluster correlation energy, they neither contribute to the *direct* RPA correlation energy (dRPA, including the RPA + SOSEX energy) nor to the RPax correlation energy—sometimes referred to as RPA (HF) energy—of Toulouse et al. [15,22]. Second, the purpose of this Letter is to provide a benchmark set of correlation energies of small systems (atoms H–Ne and a few molecules) that can easily be reproduced up to the  $\mu E_h$  level. For this purpose, a commonly available basis set, well-defined molecular geometries and Hartree–Fock reference determinants were used (thereby avoiding inaccuracies due to numerical quadratures or pseudopotentials, for example).

From our initial experience with various RPA variants for the simple systems of the present study, we conclude that those RPA variants that include Hartree–Fock exchange seem less suitable as generally applicable methods for the determination of correlation energies of open- and closed-shell atoms and molecules. Only the direct RPA (dRPA) and direct RPA with second-order screened exchange (RPA + SOSEX) approaches seem promising methods for practical use.

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