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The ground state correlation energy of the random phase approximation from a ring coupled cluster doubles approach

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We present an analytic proof demonstrating the equivalence between the random phase approximation (RPA) to the ground state correlation energy and a ring-diagram simplification of the coupled cluster doubles (CCD) equations. In the CCD framework, the RPA equations can be solved in $\mathcal{O}(N^4)$ computational effort, where N is proportional to the number of basis functions. © 2008 American Institute of Physics. [DOI: 10.1063/1.3043729]

There has recently been a revival of interest in the random phase approximation (RPA) in the quantum chemistry community. The RPA is popular for calculations of excitation energies both in finite systems^{1,2} and in solids,^{3,4} and is related to time-dependent density functional theory (DFT).⁵⁻⁷ As a technique for describing electronic correlations, RPA has significant advantages, particularly for those interested in DFT. It describes dispersion and van der Waals interactions correctly,^{8,9} and is exact for long-range correlations.¹⁰ Left-right static correlations seem to be properly described by RPA,¹¹ and RPA fixes the pathologies of nonlocal Hartree-Fock-type exchange in metallic systems. Readers interested in details about RPA for ground state correlation can refer to the recent paper by Furche¹² where he discussed an interesting simplification to reduce the computational cost of RPA correlation and provided ample background information about RPA. Note that his work focuses on direct RPA, in which the exchange terms are neglected; as discussed later in this communication, this is the form of RPA most useful in the context of DFT.

In his 1977 coupled cluster (CC) paper on the correlation energy of the uniform electron gas, Freeman¹³ reported numerical results obtained by limiting coupled cluster doubles (CCD) to ring diagrams that agreed with RPA to the accuracy of the calculation. Very recently, Kresse and Grüneis¹⁴ reproduced this evidence and found numerical proof of the equivalence between these two approaches. Here, we offer an analytic proof that these two problems yield identical correlation energies. To the best of our knowledge, no such formal proof has been given before.

As a method for calculating electronic excitation spectra, RPA requires the solution of

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \boldsymbol{\omega}. \quad (1)$$

The matrices \mathbf{A} , \mathbf{B} , \mathbf{X} , and \mathbf{Y} are all $o\nu \times o\nu$, where o and ν are, respectively, the number of occupied and unoccupied spin-orbitals. The eigenvalue problem above can be com-

pleted by noting that if $\begin{pmatrix} \mathbf{X}_i \\ \mathbf{Y}_i \end{pmatrix}$ is an eigenvector with eigenvalue ω_i , then $\begin{pmatrix} \mathbf{Y}_i \\ \mathbf{X}_i \end{pmatrix}$ is also an eigenvector, with eigenvalue $-\omega_i$. In the (real) canonical spin-orbital basis we use throughout this letter, we have

$$A_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + \langle ib || aj \rangle, \quad (2a)$$

$$B_{ia,jb} = \langle ij || ab \rangle. \quad (2b)$$

Here, ϵ_p is a diagonal element of the Fock operator. Indices i , j , k , and l indicate occupied spin-orbitals, while a , b , c , and d indicate unoccupied spin-orbitals. For arbitrary spin-orbitals p , q , r , and s , the two-electron integral $\langle pq || rs \rangle$ is defined by

$$\langle pq || rs \rangle = \langle pq | rs \rangle - \langle pq | sr \rangle, \quad (3a)$$

$$\langle pq | rs \rangle = \iint d\mathbf{x}_1 d\mathbf{x}_2 \phi_p(\mathbf{x}_1) \phi_q(\mathbf{x}_2) \frac{1}{r_{12}} \phi_r(\mathbf{x}_1) \phi_s(\mathbf{x}_2), \quad (3b)$$

where \mathbf{x} is a combined space and spin electron coordinate.

The RPA correlation energy can be obtained by considering two harmonic excitation energy problems:^{12,15} RPA and the Tamm-Dancoff approximation (TDA) thereto, which sets $\mathbf{B} = \mathbf{0}$ and thus solves

$$\mathbf{AZ} = \mathbf{Z}\nu. \quad (4)$$

In the quantum chemistry community, TDA is also known as configuration interaction singles. While TDA includes only excitation operators, RPA also includes de-excitation operators, which can be thought of as correlating the ground state. The ground state correlation energy in RPA is given by the difference between the zero point energies of these two harmonic oscillator excitation problems with correlated (RPA) and uncorrelated (TDA) ground states. We thus have

$$E_c^{\text{RPA}} = \frac{1}{2} \sum_i' (\omega_i - \nu_i) = \frac{1}{2} \text{Tr}(\boldsymbol{\omega} - \mathbf{A}). \quad (5)$$

The prime on the summation means that we include only the positive excitation energies in defining $\boldsymbol{\omega}$.

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A different approach to calculating the correlation energy is CC theory. The simplest CC method includes only double excitations from the ground state, and is termed CCD. The CCD correlation energy is

$$E_c^{\text{CCD}} = \frac{1}{4} \sum \langle ij||ab \rangle t_{ij}^{ab} = \frac{1}{2} \sum \langle ij|ab \rangle t_{ij}^{ab}, \quad (6)$$

where in the last equation we have used antisymmetry of t_{ij}^{ab} under interchange of i with j or a with b . To determine the t_{ij}^{ab} , we solve the CCD equations in the spin-orbital basis (see, for example, Ref. 16),

$$\begin{aligned} 0 = & \langle ij||ab \rangle + (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) t_{ij}^{ab} + \frac{1}{2} t_{kl}^{ab} \langle ij||kl \rangle \\ & + \frac{1}{2} t_{ij}^{cd} \langle ab||cd \rangle + \frac{1}{4} t_{kl}^{ab} \langle kl||cd \rangle t_{ij}^{cd} - \frac{1}{2} P_{ab} t_{ij}^{cb} \langle kl||cd \rangle t_{kl}^{ad} \\ & - \frac{1}{2} P_{ij} t_{kj}^{ab} \langle kl||cd \rangle t_{il}^{cd} + P_{ij} P_{ab} t_{jk}^{bc} \langle ic||ak \rangle \\ & + \frac{1}{2} \langle kl||cd \rangle t_{il}^{ad}, \end{aligned} \quad (7)$$

where internal indices (k , l , c , and d) are to be summed, and P_{ij} and P_{ab} are permutation operators: ($P_{ab} g_{ac} = g_{ac} - g_{bc}$, etc.). Keeping only particle-hole ring contractions leads to what we shall here term “ring-CCD” (rCCD),

$$\begin{aligned} 0 = & \langle ij||ab \rangle + t_{ik}^{ac} (\epsilon_c - \epsilon_k) \delta_{bc} \delta_{jk} + (\epsilon_c - \epsilon_k) \delta_{ac} \delta_{ik} t_{kj}^{cb} \\ & + \langle ic||ak \rangle t_{kj}^{cb} + t_{ik}^{ac} \langle jc||bk \rangle + t_{ik}^{ac} \langle kl||cd \rangle t_{ij}^{db}. \end{aligned} \quad (8)$$

Defining $t_{ij}^{ab} = T_{ia,jb}$, and using Eq. (2), we obtain

$$\mathbf{B} + \mathbf{A}\mathbf{T} + \mathbf{T}\mathbf{A} + \mathbf{T}\mathbf{B}\mathbf{T} = \mathbf{0}. \quad (9)$$

Removing the exchange integrals (i.e., setting $\langle pq||rs \rangle \rightarrow \langle pq|rs \rangle$) in Eq. (8) gives us what we will call direct ring-CCD (drCCD), and in Eq. (2) gives us direct RPA. Thus, Eq. (9) holds both for rCCD and for drCCD with the \mathbf{A} and \mathbf{B} matrices defined as in RPA or direct RPA, respectively. In terms of \mathbf{B} and \mathbf{T} , the rCCD correlation energy is

$$E_c^{\text{rCCD}} = \frac{1}{4} \text{Tr}(\mathbf{B}\mathbf{T}), \quad (10)$$

while the drCCD correlation energy picks up an extra factor of 2 due to the different definition of \mathbf{B} , as follows:

$$E_c^{\text{drCCD}} = \frac{1}{2} \text{Tr}(\mathbf{B}\mathbf{T}). \quad (11)$$

We prove here that Eq. (9) can be obtained from the RPA equations, and that with \mathbf{T} thereby defined, the drCCD correlation energy of Eq. (11) is equal to the direct RPA correlation energy of Eq. (5).

We begin with the RPA equations, Eq. (1). Multiplying on the right by \mathbf{X}^{-1} , we have (for direct RPA, in which \mathbf{B} is positive definite, \mathbf{X}^{-1} exists, as proven in the Appendix; we must assume its existence for full RPA)

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{1} \\ \mathbf{T} \end{pmatrix} = \begin{pmatrix} \mathbf{1} \\ \mathbf{T} \end{pmatrix} \mathbf{R}, \quad (12)$$

where we have defined

$$\mathbf{T} = \mathbf{Y}\mathbf{X}^{-1}, \quad (13a)$$

$$\mathbf{R} = \mathbf{X}\boldsymbol{\omega}\mathbf{X}^{-1}. \quad (13b)$$

As seen below, $\mathbf{T} = \mathbf{Y}\mathbf{X}^{-1}$ corresponds to the solution of Eq. (9). Multiplying on the left by $(\mathbf{T} - \mathbf{1})$ yields

$$(\mathbf{T} - \mathbf{1}) \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{1} \\ \mathbf{T} \end{pmatrix} = (\mathbf{T} - \mathbf{1}) \begin{pmatrix} \mathbf{1} \\ \mathbf{T} \end{pmatrix} \mathbf{R}. \quad (14)$$

Carrying out the matrix multiplications, we see that this is just Eq. (9). From Eq. (12), we have

$$\mathbf{A} + \mathbf{B}\mathbf{T} = \mathbf{R}, \quad (15)$$

whence

$$\text{Tr}(\mathbf{B}\mathbf{T}) = \text{Tr}(\mathbf{R} - \mathbf{A}) = \text{Tr}(\boldsymbol{\omega} - \mathbf{A}). \quad (16)$$

The drCCD correlation energy is thus equal to the direct RPA correlation energy. The extra factor of 1/2 in the rCCD correlation energy on the right-hand side of Eq. (10) makes the correlation energy exact to lead order, and it has been argued that it should therefore be included in defining the full RPA correlation energy. See Ref. 1 and references therein for discussion of this point.

In the Appendix, we present a proof showing that rCCD (Eq. (9)) implies the eigenvalue problem of Eq. (1). The form of the rCCD wavefunction implied by our proof is a regular CCD expression but with the double excitation operator T limited to ring contractions and numerical coefficients given by Eq. (13a). Other mathematical details relevant to our results (existence of \mathbf{X}^{-1} , symmetry,¹⁷ and negative definiteness of \mathbf{T}) are also discussed in the Appendix.

Direct RPA is commonly used in condensed matter physics, where the exchange terms are usually removed from the two-particle Hamiltonian (and treated as vertex corrections), and where typically semilocal DFT orbitals and orbital energies (i.e., those coming from the local density approximation or a generalized gradient approximation) are used. The exchange-correlation energy in such a scheme is given by

$$E_{xc} = \tilde{E}_x^{\text{HF}} + E_c^{\text{dRPA}}, \quad (17)$$

where \tilde{E}_x^{HF} is the Hartree-Fock-type exchange energy with the semilocal orbitals and where “dRPA” indicates direct RPA. The pros and cons of keeping or neglecting vertex corrections in RPA correlation have been discussed in the literature.⁶

Given that both $\langle ib|aj \rangle$ and $-t_{ij}^{ab}$ are positive definite for dRPA (the latter is proven in the Appendix), we can use Cholesky decomposition to write

$$\langle ib|aj \rangle = \langle ij|ab \rangle = u_{ia}^A u_{jb}^A, \quad (18a)$$

$$-t_{ij}^{ab} = \theta_{ia}^A \theta_{jb}^A, \quad (18b)$$

where A is to be summed. This leads to the drCCD equation (Eq. (8) with no exchange integrals) becoming

$$\begin{aligned} t_{ij}^{ab} = & \frac{1}{\Delta \epsilon_{ij}^{ab}} (u_{ia}^A u_{jb}^A - u_{ia}^A u_{kc}^A \theta_{kc}^B \theta_{jb}^B - \theta_{ia}^A \theta_{kc}^A u_{kc}^B u_{jb}^B \\ & + \theta_{ia}^A \theta_{kc}^A u_{kc}^B u_{ld}^B \theta_{ld}^C \theta_{jb}^C) \end{aligned} \quad (19)$$

with

$$\Delta \epsilon_{ij}^{ab} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b. \quad (20)$$

Defining

$$M^{AB} = \theta_{kc}^A u_{kc}^B, \quad (21a)$$

$$N^{AB} = u_{kc}^A \theta_{kc}^B, \quad (21b)$$

the construction of which scale as $\mathcal{O}(ovc^2)$ where $c = \dim\{A\}$, leads to

$$t_{ij}^{ab} = \frac{1}{\Delta \epsilon_{ij}^{ab}} (u_{ia}^A u_{jb}^A - u_{ia}^A N^{AB} \theta_{jb}^B - \theta_{ia}^A M^{AB} \theta_{jb}^B + \theta_{ia}^A M^{AB} N^{BC} \theta_{jb}^C), \quad (22)$$

which can be solved by fixed point iteration with DIIS (Direct Inversion of Iterative Subspaces, Ref. 18) in $\mathcal{O}(ovc^2)$ operations. Analytic energy gradients can also be carried out using the standard CC approach.¹⁹

In the current framework, the cost of RPA is not much greater than that of MP2. The atomic orbital (AO) to molecular orbital integral transformation needed to build $\langle ib|aj \rangle$ scales as $\mathcal{O}(N^5)$ for N AOs, and the Cholesky decomposition for dense $\langle ib|aj \rangle$ and t_{ij}^{ab} will scale worse than $\mathcal{O}(N^4)$. However, transforming back into the AO basis (as in our AO-CC based formalism²⁰) will yield algorithms that scale near-linearly for sparse enough matrices.²¹

The connection between the symplectic eigenvalue problem (Eq. (1)) and its associated Riccati equation (Eq. (9)) is textbook material in optimal control theory (see, for example, Ref. 22). Sanderson²³ seems to have been the first to document this connection in the context of RPA; however, he neither mentioned CC theory nor the agreement of correlation energies between RPA and rCCD. His assumption about commuting boson excitation operators leads to a RPA ground state representation that is correct only for two-electron systems.²⁴ The size consistency of RPA was established on similar grounds.²⁵

In summary, we have offered an analytic proof that the excitation amplitudes of an approximate CCD model are related to the eigenvectors of the RPA model by $\mathbf{T} = \mathbf{Y}\mathbf{X}^{-1}$, and that the ground state correlation energies of these two models are identical. This connection also lets us establish an $\mathcal{O}(N^4)$ algorithm for the RPA correlation energy in a CC framework; thanks to the mathematical properties of the solution ($\mathbf{T} < \mathbf{0}$).

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APPENDIX A: MATHEMATICAL DETAILS

We here prove several statements about the solution of Eq. (9).

1. Symmetry of $\mathbf{Y}^T\mathbf{X}$

We begin by showing that $\mathbf{X}^T\mathbf{Y} = \mathbf{Y}^T\mathbf{X}$. Start with the RPA equation, Eq. (1), and multiply on the left by $(\mathbf{Y}^T - \mathbf{X}^T)$ to get

$$\mathbf{Y}^T\mathbf{A}\mathbf{X} + \mathbf{X}^T\mathbf{A}\mathbf{Y} + \mathbf{Y}^T\mathbf{B}\mathbf{Y} + \mathbf{X}^T\mathbf{B}\mathbf{X} = (\mathbf{Y}^T\mathbf{X} - \mathbf{X}^T\mathbf{Y})\boldsymbol{\omega}. \quad (A1)$$

Since the left-hand side is symmetric, we have

$$(\mathbf{Y}^T\mathbf{X} - \mathbf{X}^T\mathbf{Y})\boldsymbol{\omega} = \boldsymbol{\omega}(\mathbf{X}^T\mathbf{Y} - \mathbf{Y}^T\mathbf{X}). \quad (A2)$$

Defining $\mathbf{S} = \mathbf{Y}^T\mathbf{X} - \mathbf{X}^T\mathbf{Y}$, we thus have

$$\mathbf{S}\boldsymbol{\omega} + \boldsymbol{\omega}\mathbf{S} = 0. \quad (A3)$$

In indicial form, this is

$$S_{ij}(\omega_i + \omega_j) = 0. \quad (A4)$$

Since we have taken ω_i positive, we must have $\mathbf{S} = \mathbf{0}$, and hence $\mathbf{X}^T\mathbf{Y} = \mathbf{Y}^T\mathbf{X}$. Note that this result is given in Ref. 17.

2. Existence of \mathbf{X}^{-1}

For positive definite \mathbf{B} , the existence of \mathbf{X}^{-1} can be proven. In direct RPA, \mathbf{B} is always positive definite, but this is not necessarily true in full RPA.

Suppose that $\mathbf{X}\mathbf{z} = \mathbf{0}$ for some vector $\mathbf{z} \neq \mathbf{0}$. Multiplying both sides of the RPA equations by \mathbf{z} would then give us

$$\mathbf{B}\mathbf{Y}\mathbf{z} = \mathbf{X}\boldsymbol{\omega}\mathbf{z}, \quad (A5a)$$

$$-\mathbf{A}\mathbf{Y}\mathbf{z} = \mathbf{Y}\boldsymbol{\omega}\mathbf{z}. \quad (A5b)$$

Since $\mathbf{Y}^T\mathbf{X} = \mathbf{X}^T\mathbf{Y}$, we would have

$$\mathbf{z}^T\mathbf{Y}^T\mathbf{B}\mathbf{Y}\mathbf{z} = \mathbf{z}^T\mathbf{Y}^T\mathbf{X}\boldsymbol{\omega}\mathbf{z} = \mathbf{z}^T\mathbf{X}^T\mathbf{Y}\boldsymbol{\omega}\mathbf{z} = 0. \quad (A6)$$

Since \mathbf{B} is positive definite, this implies that $\mathbf{Y}\mathbf{z} = \mathbf{0}$. But this would mean that $(\frac{\mathbf{X}}{\mathbf{Y}})\mathbf{z} = \mathbf{0}$, contradicting the assumption that $(\frac{\mathbf{X}}{\mathbf{Y}})$ is of full rank made in writing the eigenvalue problem.

3. Symmetry of \mathbf{T}

Since \mathbf{X} is nonsingular, and $\mathbf{Y}^T\mathbf{X} = \mathbf{X}^T\mathbf{Y}$, we have

$$(\mathbf{X}^T)^{-1}(\mathbf{Y}^T\mathbf{X} - \mathbf{X}^T\mathbf{Y})\mathbf{X}^{-1} = \mathbf{0}. \quad (A7)$$

Expanding the foregoing shows that

$$\mathbf{T}^T - \mathbf{T} = \mathbf{0}, \quad (A8)$$

as also shown in Ref. 17.

4. Negative definiteness of \mathbf{T}

Since \mathbf{T} is real and symmetric, we can diagonalize it with a unitary transformation \mathbf{U} : $\mathbf{T}\mathbf{U} = \mathbf{U}\boldsymbol{\lambda}$. Multiplying the drCCD equation on the left by a particular eigenvector \mathbf{U}_k^\dagger and on the right by \mathbf{U}_k , we get

$$\mathbf{U}_k^\dagger\mathbf{B}\mathbf{U}_k(1 + \lambda_k^2) + 2\mathbf{U}_k^\dagger\mathbf{A}\mathbf{U}_k\lambda_k = 0. \quad (A9)$$

When \mathbf{B} and \mathbf{A} are positive definite, as they are for direct RPA, we see that we must have $\lambda_k < 0$ for all k , and \mathbf{T} is therefore negative definite.

5. An alternative proof

In Eqs. (12), (13a), (13b), and (14)–(16), we have shown the equivalence of the RPA eigenvalue problem (Eq. (1)) and

the rCCD equation (Eq. (9)) assuming the existence of \mathbf{X}^{-1} . Here, we give an alternative way of showing the equivalence.

Let us suppose we have solved the rCCD equation. We can use Schur decomposition to write

$$\mathbf{A} + \mathbf{B}\mathbf{T} = \mathbf{x}\mathbf{\Delta}\mathbf{x}^\dagger, \quad (\text{A10})$$

where $\mathbf{\Delta}$ is upper triangular and \mathbf{x} is unitary. Defining $\mathbf{y} = \mathbf{T}\mathbf{x}$, we thus have

$$\mathbf{A}\mathbf{x} + \mathbf{B}\mathbf{y} = \mathbf{x}\mathbf{\Delta}. \quad (\text{A11})$$

The rCCD equation implies that

$$\mathbf{B} + \mathbf{A}\mathbf{T} = -\mathbf{T}(\mathbf{A} + \mathbf{B}\mathbf{T}) = -\mathbf{T}\mathbf{x}\mathbf{\Delta}\mathbf{x}^\dagger = -\mathbf{y}\mathbf{\Delta}\mathbf{x}^\dagger, \quad (\text{A12})$$

whence

$$-\mathbf{B}\mathbf{x} - \mathbf{A}\mathbf{y} = \mathbf{y}\mathbf{\Delta}. \quad (\text{A13})$$

Combining Eqs. (A11) and (A13), we have

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{x} \\ \mathbf{y} \end{pmatrix} = \begin{pmatrix} \mathbf{x} \\ \mathbf{y} \end{pmatrix} \mathbf{\Delta}. \quad (\text{A14})$$

From the foregoing, we see that the diagonal elements of $\mathbf{\Delta}$ hold eigenvalues of the RPA matrix, and thus $\text{Tr}(\mathbf{B}\mathbf{T}) = \text{Tr}(\boldsymbol{\omega} - \mathbf{A})$, as desired.

Note that under the additional condition that $\mathbf{\Delta}$ is diagonalizable ($\mathbf{\Delta}\mathbf{P} = \mathbf{P}\boldsymbol{\omega}$), we have

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{x}\mathbf{P} \\ \mathbf{y}\mathbf{P} \end{pmatrix} = \begin{pmatrix} \mathbf{x}\mathbf{P} \\ \mathbf{y}\mathbf{P} \end{pmatrix} \boldsymbol{\omega}. \quad (\text{A15})$$

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