Random-phase approximation excitation energies from approximate equation-of-motion ring coupled-cluster doubles

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The ground-state correlation energy calculated in the random-phase approximation (RPA) is known to be identical to that calculated using a subset of terms appearing in coupled-cluster theory with double excitations. In particular, this equivalence requires keeping only those terms that generate time-independent ring diagrams, in the Goldstone sense. Here I show that this equivalence extends to neutral excitation energies, for which those calculated in the RPA are identical to those calculated using an approximation to equation-of-motion coupled-cluster theory with double excitations (EOM-CCD). The equivalence requires three approximations to EOM-CCD: first, the ground-state double-excitation amplitudes are obtained from the ring-CCD equations (the same as for the correlation energy); second, the EOM eigenvalue problem is truncated to the single-excitation (one particle + one hole) subspace; third, the similarity transformation of the Fock operator must be neglected, as it corresponds to a dressing of the single-particle propagator, which is not present in the conventional RPA.

I. INTRODUCTION

The random-phase approximation (RPA) plays a foundational role in quantum chemistry, condensed-matter physics, materials science, and nuclear physics.\textsuperscript{1–3} As a theory of the ground-state correlation energy, the RPA is an infinite-order resummation of all time-independent ring diagrams, which critically controls the leading-order divergence in the energy of metals at high density.\textsuperscript{2,4,5} Especially when combined with density functional theory via the adiabatic connection fluctuation-dissipation theorem,\textsuperscript{6,7} the RPA also provides a good description of long-range dispersion interactions.\textsuperscript{3,8–11}

The RPA correlation energy terms are a subset of those included in coupled-cluster theory with double excitations (CCD). Therefore, an approximate solution of the CCD equations, known as ring-CCD, can be used to calculate the RPA correlation energy, as shown by Freeman for the electron gas\textsuperscript{12} and proven analytically by Scuseria, Henderson, and Sorensen;\textsuperscript{13} see also Refs. 14 and 15 for subsequent studies and generalizations.

Alternatively, the RPA may be viewed as a theory of the dynamical polarizability, a context in which it is known to be identical to time-dependent Hartree or Hartree-Fock.\textsuperscript{16} For finite systems, such as molecules, the RPA leads to reasonably accurate electronic excitations\textsuperscript{17} and underlies the successful time-dependent density functional theory\textsuperscript{18–22} For solids, the RPA polarizability correctly predicts the properties of the collective plasmon excitation\textsuperscript{2} and forms the basis for screening the popular GW approximation.\textsuperscript{23} Analogous to the correlation energy, the RPA polarizability is a resummation of all time-dependent ring diagrams. This similarity suggests a relation between excitation energies calculated with the RPA and those calculated with an approximate version of coupled-cluster theory. In this manuscript, I provide the precise recipe for this analogy, showing that the RPA excitation energies (with or without exchange) can be obtained from an approximation to electronic-excitation equation-of-motion coupled-cluster theory with double excitations (EOM-CCD).

II. THEORY

The dynamical polarizability is the time-ordered density-density response function,\textsuperscript{2}

\[ \Pi(r_1, t_1; r_2, t_2) = -i\langle \Psi_0 | T [\delta n(r_1, t_1) \delta n(r_2, t_2)] | \Psi_0 \rangle \]  

(1)

where $| \Psi_0 \rangle$ is the ground-state wavefunction, $T$ is the time-ordering operator, and $\delta n(r, t) = n(r, t) - n_0(r)$ is the density fluctuation away from the ground-state density. In the frequency domain, the poles of the polarizability occur at all electronic excitation energies $\Omega_n$, with residues given by the square of the transition densities $|\langle \Psi_0 | n(r) | \Psi_0 \rangle|^2$.

In the usual diagrammatic route,\textsuperscript{24} the RPA polarizability is expressed in terms of the irreducible polarizability $\Pi_0$, via

\[ \Pi = \Pi_0 + \Pi_0 [\nu + K] \Pi_0 \]  

where $\nu$ is the direct Coulomb interaction and $K$ is its exchange counterpart. Taking the irreducible polarizability to be simply that of a noninteracting particle-hole pair, $\Pi_0 = -iG_0 G_0^\dagger$, generates the conventional RPA polarizability as a sum over all time-dependent ring diagrams. The location of the poles of the RPA polarizability, i.e. the excitation energies, are the eigenvalues of the well-known RPA matrix, given in the following subsection.

In order to precisely relate the RPA excitation energies to those of an approximate EOM-CCD calculation, in Sec. II A I perform a downfolding of the RPA matrix into the single particle-hole excitation subspace; in Sec. II B I show that this matrix is identical to the one obtained from EOM-CCD in the single particle-hole excitation subspace when the ground-state double excitation amplitudes satisfy the ring-CCD equations and the similarity transformation of the Fock operator is neglected. Having established the algebraic equivalence of the RPA excitation energies and those from approximate EOM-CCD, in Sec. II C I analyze the time-dependent Goldstone diagrams in the RPA polarizability and their construction in the coupled-cluster framework, with special attention paid to the

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non-Tamm-Dancoff diagrams; I also address the inclusion or neglect of exchange.

### A. RPA excitation energies

The RPA eigenvalue problem is given by the system of equations\(^1\)\(^1\)\(^3\) for simplicity, assuming real orbitals throughout

\[
\left( \begin{array}{cc} A & B \\ -B & -A \end{array} \right) \left( \begin{array}{c} X \\ Y \end{array} \right) = \left( \begin{array}{c} X \\ Y \end{array} \right) \Omega, \tag{2}
\]

where

\[
A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ab}\delta_{ij} + \langle ib|a j \rangle, \tag{3a}
\]

\[
B_{ia,jb} = \langle i j|ab \rangle \tag{3b}
\]

and \(\Omega\) is a diagonal matrix of RPA excitation energies, which come in positive and negative pairs. The antisymmetrized two-electron integrals are defined by \(\langle pq|rs \rangle = \langle pq|rs \rangle - \langle pq|sr \rangle\), with

\[
\langle pr|rs \rangle = \int dr_1 \int dr_2 \phi_p(r_1)\phi_q(r_1)\phi_r^{\dagger}(r_1)\phi_s(r_2), \tag{4}
\]

and the indices \(i, j, k, l\) are used to denote occupied orbitals and \(a, b, c, d\) to denote unoccupied orbitals. Formally solving the second equation, \(-BX + AY = \Omega X\), gives

\[
Y = -(A + Y\Omega^{-1})^{-1}BX. \tag{5}
\]

Using this expression to replace \(Y\) in the first of the RPA equations leads to an eigenvalue problem for \(X\) only,

\[
\left[ A - B(A + Y\Omega^{-1})^{-1}B \right] X = \Xi\Omega. \tag{6}
\]

Therefore, the matrix on the left-hand side, which only has support in a single particle-hole excitation subspace (and not the subspace twice as large), has all of the positive RPA excitation energies as its eigenvalues. As written, Eq. (6) is not practical because the construction of the downfolded matrix requires knowledge of all eigenvalues and the \(Y\) component of all eigenvectors; however, the matrix in Eq. (6) can be shown to be identical to an approximate matrix derived from EOM-CCD.

### B. Approximate EOM-CCD

In the typical EOM-CCD approach,\(^2\)\(^5\)\(^6\) the \(T_1\) and \(T_2\) amplitudes are obtained from the ground-state CCSD equations, and the EOM eigenvalue problem is obtained by projecting the similarity-transformed normal-ordered Hamiltonian, \(\tilde{H}_N \equiv e^{-T}He^{T} - \tilde{E}_{CC}\), into a basis of singly- and doubly-excited determinants. By contrast, to construct the relation with the RPA requires only the similarity transformation due to \(T_2\) (i.e. \(T_1 = 0\)) projected only in the space of singly-excited determinants, leading to

\[
\langle \Phi_{i}^{\dagger}|\tilde{H}_N|\Phi_{j}^{\dagger} \rangle = F_{ij}\delta_{ij} - F_{ij}\delta_{ab} + W_{ijab} \tag{7}
\]

where

\[
F_{ab} = \varepsilon_a\delta_{ab} - \frac{1}{2} \sum_{k\ell} \langle kl|bc\rangle\rho_{kl}^{\text{exc}}, \tag{8a}
\]

\[
F_{ij} = \varepsilon_i\delta_{ij} + \frac{1}{2} \sum_{k\ell} \langle ik|cd\rangle\rho_{k\ell}^{\text{exc}}, \tag{8b}
\]

\[
W_{abij} = \langle ib|a j \rangle + \sum_{kc} \langle ik|ac\rangle\rho_{kc}^{\text{exc}}, \tag{8c}
\]

However, the similarity-transformed Fock operators lead to a dressing of the single-particle propagators in the polarizability, in a manner which is absent in the RPA (see Sec. II C); neglecting this effect of \(T_2\) gives

\[
\langle \Phi_{i}^{\dagger}|\tilde{H}_N|\Phi_{j}^{\dagger} \rangle = \langle \Phi_{i}^{\dagger}|(f_1 + e^{-T_2}V_Ne^{T_2})|\Phi_{j}^{\dagger} \rangle = \varepsilon_i - \varepsilon_j\delta_{ab}\delta_{ij} + W_{ibaj} \tag{9}
\]

Using the definition of the \(A\) and \(B\) matrices leads to

\[
\langle \Phi_{i}^{\dagger}|\tilde{H}_N|\Phi_{j}^{\dagger} \rangle = A_{ia,jb} + \sum_{kc} B_{ia,kc}r_{kij}^{ab} = [A + BT_2]_{ia,jb}, \tag{10}
\]

where \([T_2]_{ia,jb} = r_{ij}^{ab}\). As shown in Refs. 1 and 13, the ring-CCD equations

\[
t_{ij}^{ab}(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b) = \langle ab|ij \rangle
\]

\[
+ \sum_{ck} t_{ik}^{ac}(kb|cj \rangle \sum_{ck} (ak|ic\rangle r_{kij}^{bc} + \sum_{cd\ell} r_{ik}^{ac}(kl|cd\rangle r_{kij}^{dh}) \tag{11}
\]

can be solved in closed form in terms of the eigenvectors of the RPA equations (2), \(T_2 = YY^{-1}\). Using this and Eq. (5) in Eq. (10) leads to the matrix

\[
\langle \Phi_{i}^{\dagger}|\tilde{H}_N|\Phi_{j}^{\dagger} \rangle = \left[ A - B(A + Y\Omega^{-1})^{-1}B \right]_{ia,jb} \tag{12}
\]

in exact agreement with Eq. (6). Therefore, the similarity-transformed Hamiltonian, using \(T_2\) amplitudes that satisfy the ring-CCD equations, has exactly the RPA eigenvalues when truncated to the single-excitation subspace and transformation of the Fock operator is neglected. Likewise, the EOM single-excitation operator \(R_1 = \sum_{ai} r_{ai}^{ii}a_i^\dagger a_i\), which gives the EOM-CC eigenstate, has amplitudes that are exactly equal to the columns of \(X\), i.e. \(r_{ai}^{ii} = X_{ia}\).

This proven equivalence can now be seen readily in the reverse direction. Equation (10) clearly implies the eigenvalue problem \(AX + BT_2X = \Xi\Omega\). Using the solution of the ring-CCD equations in terms of the RPA eigenvectors, \(T_2 = YY^{-1}\), leads to \(AX + BY = \Xi\Omega\), which is precisely the first of the RPA system of equations.

For the sake of discussion, I call the method described by Eqs. (7) and (8) EOM(S)-CCD, denoting a CCD ground state and single-excitation EOM treatment. When the CCD equations are approximated by the ring-CCD equations, I call the method EOM(S)-rCCD. Finally, when the transformation of the Fock operator is additionally neglected, I call the method EOM(Sf)-rCCD, which is identical to the conventional RPA.
C. Diagrammatic analysis and exchange

The time-dependent Goldstone diagrams of the RPA polarizability are straightforward to enumerate as all ring diagrams with all possible time-orderings. In order to compare with coupled-cluster theory, a diagrammatic analysis of the coupled-cluster polarization propagator is required along the lines of Refs. 29 and 30 for the one-particle Green’s function. While a forthcoming publication will present a more detailed analysis and numerical results, the diagrams of the coupled-cluster polarization propagator can be analyzed by cutting the diagram after each vertex; each connected diagram at previous time can be classified as generated by the ground-state cluster operators, the Λ operators, or the EOM excitation operators.

Figure 1 presents some example RPA ring diagrams included through third order in perturbation theory. Vertical cuts, indicated by dashed lines, indicate that the first three diagrams shown are described solely by the single-excitation EOM operator $R_1$. These are all examples of forward-time-ordered ring diagrams, i.e. those resulting from the Tamm-Dancoff approximation (TDA). When antisymmetrized vertices are assumed (exchange is included), then these TDA diagrams generate a polarizability whose poles are at the excitation energies produced by configuration interaction with single excitations.

The fourth diagram shown in Fig. 1 is an example of a non-TDA diagram, due to the permuted time ordering. Graphical analysis shows that this diagram is generated through a combination of the $T_2$ and $R_1$ operators. It is straightforward to show that all non-TDA ring diagrams included in the RPA can be deconstructed in the same manner, using disconnected products of $T_2$ and $R_1$, but never the EOM $R_2$ double excitation operator; this is why it was sufficient in Sec. II B to analyze the EOM eigenvalue equation in the single-excitation subspace only. Therefore, the RPA polarizability diagrams are exactly those produced by the EOM(Sf)-rCCD approach.

As explained in Sec. II B, this exact RPA equivalence requires the neglect of the transformed Fock operator. Figure 2 shows an example diagram generated by the EOM(S)-rCCD approximation, i.e. without neglect of this transformation. Clearly, including such terms leads to a dressing of the single-particle propagators used to construct the irreducible polarizability. In other words, this irreducible polarizability is of the RPA form $\Pi_0 = -iGG$, where $G$ is most similar to the self-consistent second-order Green’s function. More accurately, this $G$ is self-consistently determined by a second-order self-energy that only includes one out of two possible time orderings; to include the other time ordering requires the EOM $R_2$ excitation operator, and to include the other time ordering self-consistently requires EOM excitation operators to all orders.

All equations, as presented above, include exchange. Exchange can be trivially removed by neglecting the antisymmetrization of the two-electron integrals in the ring-CCD equations (leading to “direct” ring-CCD) and in the EOM eigenvalue problem (with a factor of 2 arising from the product of two antisymmetrized objects). This leads to a time-dependent Hartree theory of excitation energies, which is the more common variant of the RPA polarizability in the condensed-matter physics literature. Retaining exchange leads to particle-hole ladder diagrams in addition to the ring diagrams shown in Fig. 1. The particle-hole ladder diagrams are required for a description of excitonic effects in molecules or solids, and are responsible for a reduction in the excitation energies compared to the time-dependent Hartree theory that only includes direct ring diagrams.

III. CONCLUSIONS AND OUTLOOK

To summarize, I have shown that the relation between the RPA and CCSD ground states can be extended to all excited states, with a particular set of additional approximations in the EOM-CCSD equations, dubbed EOM(Sf)-rCCD. The exact equivalence presented here has been verified numerically, using modified implementations of the RPA and EOM-CCSD methodologies in the PySCF software package.

In the same way that previous work established ground-state CCD as the natural generalization of the RPA with correct fermionic behavior, the present work proposes EOM(S)-
CCD as the simplest fermionic theory of excited states that contains RPA physics. Naturally, this generalization comes with a cost: for a single low-lying excited state, an RPA calculation scales as $N^4$, whereas an EOM(S)-CCD calculation scales (canonically) as $N^6$. This latter scaling is no worse than that of EOM-CCSD, which is clearly preferred for a few low-lying excited states. However, the cost to obtain all excited states is $N^{15}$ for both RPA and EOM(S)-CCD, to be compared to $N^{18}$ for EOM-CCSD (for all excited states with dominant single-excitation character), which may be important for certain spectral quantities.

In addition to providing a properly fermionic theory, the present manuscript establishes the RPA polarizability diagrams as a strict subset of those from EOM-CCSD. In this sense, the CC hierarchy is a natural post-RPA route, distinct from time-dependent density functional theory and, importantly, systematically improvable. It is hoped that this connection will lead to fruitful developments in the simulation of excited states, especially in the condensed phase where RPA physics is essential. For example, various CC-derived polarizabilities can be used for a more accurate treatment of screening in the $GW$ approximation, leading to a well-defined class of vertex corrections. Similarly, a comparison of EOM-CCSD excited states to those predicted by the $GW$+Bethe-Salpeter equation approach will provide further insight and sow deeper connections between the condensed-matter and quantum chemistry communities. Work along both of these lines is currently in progress.

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