Equivalence of Particle-Particle Random Phase Approximation Correlation Energy and Ladder-Coupled-Cluster-Double

Degao Peng,1 Stephan N. Steinmann,1 Helen van Aggelen,1,2 and Weitao Yang1,3,a)

1) Department of Chemistry, Duke University, Durham, North Carolina, United States, 27708
2) Ghent University, Department of Inorganic and Physical Chemistry, 9000 Ghent, Belgium
3) Department of Physics, Duke University, Durham, North Carolina, United States, 27708

We present an analytical proof and numerical demonstrations of the equivalence of the correlation energy from particle-particle random phase approximation (pp-RPA) and ladder-couple-cluster-doubles (ladder-CCD). These two theories reduce to the identical algebraic matrix equation and correlation energy expressions, under the assumption that the pp-RPA equation is stable. The numerical examples illustrate that the correlation energy missed by pp-RPA in comparison with couple-cluster single and double is largely canceled out when considering reaction energies. This theoretical connection will be beneficial to future pp-RPA studies based on the well established couple cluster theory.

Keywords: Particle-particle random phase approximation, ladder-couple-cluster-double, ladder diagrams, correlation energy

a) Electronic mail: weitao.yang@duke.edu
I. INTRODUCTION

The random-phase approximation (RPA) was originally proposed back in the 1950s by Pine and Bohm\(^1\) to treat the homogeneous electron gas. Since then, the idea of RPA has spawned the studies of excitation energies, linear-response functions and correlation energies in solid state physics\(^3\)-\(^6\), nuclear physics\(^7\)-\(^12\), and quantum chemistry\(^13\)-\(^16\). In the recent decade, there is a renaissance of interest in the RPA correlation energy in molecular science because of its correct description of van der Waals interaction\(^16\), the correct dissociation limit of H\(_2\)\(^17\) and its perspective of the adiabatic connection in density-functional theory (DFT)\(^16\), with relatively low scaling (\(O(N^4 \log N)\) by Eshuis \textit{et al.}\(^18\) and \(O(N^4)\) by Ren \textit{et al.}\(^19\) with \(N\) the number of basis functions). Correlation energy studies beyond RPA is an active field of research that achieves exciting results\(^20\)-\(^26\).

Usually, RPA describes exclusively the particle-hole channel of correlations in molecular science. In nuclear physics, however, the particle-particle channel of RPA (pp-RPA) is also widely discussed\(^7\)-\(^8\),\(^27\)-\(^35\). In chemistry, the pp-RPA has only been used in computational study of Auger spectroscopy which involves double ionization of molecules\(^36\),\(^37\). The application of pp-RPA to calculate the correlation energy for molecular systems is absent until the recent work of van Aggelen \textit{et al.} on pp-RPA\(^38\), which shows promising results in describing systems with both fractional charge and fractional spin. Furthermore, Ref\(^38\) establishes an adiabatic connection for the exchange-correlation energy in terms of the dynamic paring matrix fluctuation, parallel to the adiabatic connection fluctuation dissipation (ACFD) theorem in terms of the density fluctuation\(^5\),\(^39\). Like the ACFD theorem, this new adiabatic connection is in principle exact, but requires the particle-particle propagator as a function of the interaction strength. The pp-RPA has been shown to be the first-order approximation to the paring matrix fluctuation. To distinguish the two RPAs of different channels, we will, hereafter, refer to the conventional particle-hole RPA as ph-RPA.

According to Scuseria \textit{et al.}\(^40\), the ph-RPA correlation energy is equivalent to a direct ring coupled cluster double (direct-ring-CCD). We now prove that pp-RPA is equivalent to ladder-CCD, assuming that the pp-RPA equation of the system is stable. The pp-RPA correlation energy can be interpreted as the sum of all ladder diagrams\(^7\) or zero-point pairing vibrational energy beyond the mean-field approximation\(^8\). The pp-RPA wavefunction of an exponential form has been proposed\(^8\) with the argument of Thouless theorem\(^9\) under the
quasi-boson approximation. However, its ladder-CCD nature has never been explicitly stated in the literature. The establishment of the equivalence of pp-RPA and ladder-CCD will be beneficial to study pp-RPA properties. Furthermore, in the coupled cluster framework, the excited states based on the pp-RPA wavefunction can be strategically obtained via equation-of-motion coupled-cluster or, equivalently, linear-response coupled-cluster theory.

II. THE PP-RPA EQUATION AND ITS STABILITY

The pp-RPA equation can be derived from the two-particle Green’s function, the equation-of-motion ansatz, or the linear-response time-dependent Hartree-Fock-Bogoliubov approximation (TDHFB). The resulting generalized eigenvalue equation is very similar to the ph-RPA equation (see, for example, Refs. for the ph-RPA equation),

\[
\begin{bmatrix}
A & B \\
B^\dagger & C
\end{bmatrix}
\begin{bmatrix}
x_n \\
y_n
\end{bmatrix}
= \begin{bmatrix}
I & 0 \\
0 & -I
\end{bmatrix}
\begin{bmatrix}
x_n \\
y_n
\end{bmatrix},
\]

(1)

where

\[
A_{ab,cd} = (\epsilon_c + \epsilon_d - 2\nu)\delta_{ac}\delta_{bd} + \langle ab||cd\rangle,
\]

(2)

\[
C_{ij,kl} = -(\epsilon_k + \epsilon_l - 2\nu)\delta_{ki}\delta_{jl} + \langle ij||kl\rangle,
\]

(3)

and

\[
B_{ab,ij} = \langle ab||ij\rangle.
\]

(4)

We use indexes \(i, j, k, l\ldots\) for occupied spin orbitals (holes), \(a, b, c, d\ldots\) for unoccupied spin orbitals (particles), and \(u, v, s, t\ldots\) for general spin orbitals. Furthermore, \(m, n\) are used to denote eigenvector and eigenvalue indexes. Additionally, \(\epsilon_u\) is the molecular orbital eigenvalue, and \(\langle uv||st\rangle\) is the antisymmetrized two-electron integral

\[
\langle uv||st\rangle = \langle uv|st\rangle - \langle uv|ts\rangle,
\]

(5)

where

\[
\langle uv|st\rangle = \sum_{\sigma_1\sigma_2} \int dr_1 dr_2 \frac{\phi_u^*(r_1\sigma_1)\phi_v^*(r_2\sigma_2)\phi_s(r_1\sigma_1)\phi_t(r_2\sigma_2)}{|r_1 - r_2|}.
\]

(6)

The chemical potential \(\nu\) is not a necessity in the equation-of-motion derivation, while during the derivation from the two-particle Green’s function and the TDHFB, \(\nu\) is used to ensure that the ground state has the desired number of electrons \(N\). In practice, it is usually
approximated to be half of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) eigenvalues. We will later show that the exact choice of the chemical potential is unimportant within a certain range as long as the pp-RPA equation is stable.

The indexes of the matrix are either hole pairs or particle pairs, but no particle-hole pairs. These indexes have only \( i > j \) for hole pairs and \( a > b \) for particle pairs to eliminate the redundancy. The number of particle (hole) pairs is

\[
N_{pp(hh)} = \frac{1}{2} N_{\text{vir(occ)}}(N_{\text{vir(occ)}} - 1),
\]

where \( N_{\text{vir(occ)}} \) is the number of virtual (occupied) orbitals. In general, \( N_{pp} \) is much larger than \( N_{hh} \). The dimension of the upper left (lower right) identity matrix in Eq. (1) is \( N_{pp} \times N_{pp} \) \((N_{hh} \times N_{hh})\), the same dimension of \( A \) (\( C \)). For the rest of the paper, the dimensions of identity matrices will be omitted as they are clear from the context. The difference of the dimensions of \( A \) and \( C \) makes the pp-RPA equation quite different from the usual ph-RPA equation or the linear-response time-dependent density-functional theory equation.

For simplicity, we use a compact matrix notation

\[
M z_n = \omega_n W z_n,
\]

to denote Eq. (1), where \( M \) is the Hermitian matrix on the left hand side

\[
M = \begin{bmatrix} A & B \\ B^\dagger & C \end{bmatrix},
\]

\( W \) is the non-positive definite metric

\[
W = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix},
\]

and \( z_n \) is the full eigenvector

\[
z_n = \begin{bmatrix} x_n \\ y_n \end{bmatrix},
\]

with its eigenvalue \( \omega_n \). Due to the non-positive definite metric \( W \), Eq. (1) is not guaranteed to have all real eigenvalues. We call \( z_n^\dagger W z_n \) the signature of an eigenvector \( z_n \). The signature can be positive, zero, or negative. The zero signature coincides with an imaginary eigenvalue.
(see Subsection A1 in Appendix), while positive and negative signatures are associated with real eigenvalues. We categorize the eigenvectors according to their signature, where eigenvectors with positive signatures are called $N+2$ excitations and eigenvectors with negative signatures are called $N-2$ excitations. For a diagonalizable pp-RPA equation with all real eigenvalues, according to Subsection A2 in Appendix, the orthonormalization of the eigenvectors can be written as,

$$Z^\dagger WZ = W,$$  \hspace{1cm} (12)

with all $N+2$ eigenvectors to the left of all $N-2$ eigenvectors in $Z$. This special arrangement will be kept all through the paper.

When all the eigenvalues of a diagonalizable pp-RPA equation are real, the pp-RPA equation is defined to be stable if all the $N+2$ excitation eigenvalues are positive and $N-2$ excitation eigenvalues are negative, i.e. $\min_n \omega_n^{N+2} > 0 > \max_m \omega_m^{N-2}$. With the eigenvector arrangement according to signatures, the stability condition can be expressed in a concise equation,

$$\text{sign}(\omega) = W,$$ \hspace{1cm} (13)

where $\text{sign}(\omega)$ is the sign function\cite{48} of the eigenvalue matrix $\omega$, which gives $[\text{sign}(\omega)]_{nm} = \delta_{nm}\text{sign}(\omega_n)$ since $\omega$ is diagonal. Note that Eq. (12) is a necessary but not sufficient condition for the stability of Eq. (13).

These eigenvalues are interpreted as the double ionization and double electron attachment energies in a molecular system, i.e.

$$\omega_n^{N+2} = E_n^{N+2} - E_0^N - 2\nu,$$ \hspace{1cm} (14)

for $N+2$ excitation energies, and

$$\omega_n^{N-2} = E_0^N - E_n^{N-2} - 2\nu,$$ \hspace{1cm} (15)

or the $N-2$ excitation energies. With the eigenvalue interpretation of Eqs. (14)-(15), an unstable pp-RPA equation violates the energetic convexity condition\cite{49}. It has not been proved that such stability is intrinsic for a self-consistent solution of a Hartree-Fock or Kohn-Sham/generalized Kohn-Sham molecular system, but in practice unstable solutions have never been encountered for molecular systems so far in Ref.\cite{38} and in present work.
The stability condition of the pp-RPA equation is equivalent to the positive definiteness of the matrix $M$. See Subsection A3 in Appendix for further details. The positive definiteness as the stability criterion has been used in Ref. [7].

With the whole spectrum of a stable pp-RPA equation, the pp-RPA correlation energy can be expressed in several equivalent ways:

$$
E_{\text{pp-RPA}} = \sum_m \omega_m^{N+2} - \text{Tr} A = - \sum_n \omega_n^{N-2} - \text{Tr} C = \frac{1}{2} \sum_n |\omega_n| - \frac{1}{2} \text{Tr} M. \tag{16}
$$

The precise value of $\nu$ is irrelevant for a stable pp-RPA equation as long as

$$
\min_m (E_m^{N+2} - E_m^N) > 2\nu > \max_n (E_0^N - E_n^{N-2}),
$$

as they cancel out in the correlation energy expression. Yet a proper chemical potential can categorize $M$ to be positive definite, an equivalent condition of the stability.

III. PROOF OF THE EQUIVALENCE OF PP-RPA AND LADDER-CCD

The CCD ansatz, the simplest method in the coupled cluster family, expresses the wavefunction as

$$
|\text{CCD}\rangle = e^{\hat{T}_2} |\Phi_0\rangle, \tag{17}
$$

where $|\Phi_0\rangle$ is a single Slater determinant, and $\hat{T}_2$ is the two-body cluster operator

$$
\hat{T}_2 = \frac{1}{2!} \sum_{ijab} t_{ij}^{ab} \hat{a}_i^{\dagger} \hat{b}_j^{\dagger} = \sum_{ijab} t_{ij}^{ab} \hat{a}_i^{\dagger} \hat{b}_j^{\dagger}, \tag{18}
$$

where $\hat{a}_i^{\dagger}$, $\hat{b}_j$ are the creation and annihilation operators for spin orbital $a$ and $i$, respectively and $t_{ij}^{ab}$ the double excitation amplitudes, having the symmetry

$$
t_{ij}^{ab} = -t_{ji}^{ab} = -t_{ij}^{ba} = t_{ij}^{ba}. \tag{19}
$$

The correlation energy is expressed in terms of the amplitudes through the energy equation

$$
E_{\text{ccd}} = \sum_{ijab} \langle ij||ab|t_{ij}^{ab}, \tag{20}
$$
while the amplitudes $t^a_{ij}$ are solved for by the CCD amplitude equation,

\[
(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) t^a_{ij} = \langle ab||ij \rangle + \frac{1}{2} \sum_{cd} \langle ab||cd \rangle t^c_{ij} \frac{1}{2} \sum_{kl} \langle ij||kl \rangle t^b_{kl} - \sum_{kc} \langle bk||cj \rangle t^a_{ik} - \langle bk||ci \rangle t^b_{ij} + \langle ak||cj \rangle t^b_{jk} + \langle ak||ci \rangle t^b_{ij} = \langle ab||ij \rangle + \frac{1}{2} \sum_{cd} \langle ab||cd \rangle t^c_{ij} + \frac{1}{2} \sum_{kl} \langle ij||kl \rangle t^b_{ij} + \frac{1}{4} \sum_{kl,cd} t^b_{kl} \langle kl||cd \rangle t^c_{ij}.
\]

Refer to Ref. 44 for details of the CCD equations.

By allowing only particle-hole summations in Eq. (21), Scuseria et al. 40 have shown that the amplitude equation reduces to the ph-RPA equation with exchange, i.e., the time-dependent Hartree-Fock (TDHF) equation. Further eliminating the exchange term in the two-electron integral yields the conventional direct ph-RPA. Similarly, if we allow only summations of particle pairs and hole pairs, Eq. (21) becomes

\[
\sum_{kl} \langle kl||cd \rangle \frac{1}{4} t^c_{ij} t^d_{kl} = \langle ab||ij \rangle + \frac{1}{2} \sum_{cd} \langle ab||cd \rangle t^c_{ij} + \frac{1}{2} \sum_{kl} \langle ij||kl \rangle t^b_{ij} + \frac{1}{4} \sum_{kl,cd} t^b_{kl} \langle kl||cd \rangle t^c_{ij}.
\]

We refer to this restricted CCD as ladder-CCD, due to their inclusion of only ladder diagrams in the correlation energy. By utilizing the antisymmetry of the two-electron integrals $\langle uv||st \rangle = -\langle uv||ts \rangle$, Eq. (22) can be rearranged as

\[
\sum_{cd}^{c>d} A_{ab,cd} t^c_{ij} + \sum_{kl}^{k>l} C_{ij,kl} t^b_{kl} + B_{ab,ij} + \sum_{kl,cd}^{k>l,c>d} t^b_{kl} B_{cd,kl}^* t^c_{ij} = 0,
\]

with $A$, $B$, and $C$ defined in Eqs. (2)-(4). Denoting the amplitude as a matrix $T_{ab,ij} = t^a_{ij}$, Eq. (23) results in an algebraic matrix equation

\[
AT + TC + B + TB^\dagger T = 0.
\]

Now, we will show that the pp-RPA equation of Eq. (1) is equivalent to the ladder-CCD amplitude equation under the assumption that the pp-RPA equation is stable.

The pp-RPA equation for only the $N+2$ excitations reads,

\[
\begin{bmatrix} A & B \\ B^\dagger & C \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} \omega^{N+2},
\]

(25)
where $\dim X = N_p \times N_p$, $\dim Y = N_h \times N_p$, and $\dim \omega^{N+2} = N_p \times N_p$. Multiplying $X^{-1}$ from the right on Eq. (25) gives

$$
\begin{bmatrix}
A & B \\
B^{\dagger} & C
\end{bmatrix}
\begin{bmatrix}
I \\
\tilde{T}^{\dagger}
\end{bmatrix}
= 
\begin{bmatrix}
I & 0 \\
0 & -I
\end{bmatrix}
\begin{bmatrix}
I \\
\tilde{T}^{\dagger}
\end{bmatrix}
R,
$$

(26)

where

$$
\tilde{T} = (YX^{-1})^{\dagger},
$$

(27)

and

$$
R = X\omega^{N+2}X^{-1}.
$$

(28)

The invertibility of $X$ is guaranteed by a stable pp-RPA equation. See Subsection A.4 in Appendix for the detailed proof. Multiplying $[\tilde{T}^{\dagger} 1]$ from the left to Eq. (26) results in

$$
\tilde{T}^{\dagger}A + \tilde{T}^{\dagger}B\tilde{T}^{\dagger} + B^{\dagger} + C\tilde{T}^{\dagger} = 0.
$$

(29)

Comparing Eq. (24) and Eq. (29), we infer that $T = \tilde{T}$.

The particle-particle block of Eq. (26) gives

$$
A + BT^{\dagger} = R.
$$

(30)

Then, the ladder-CCD correlation energy of Eq. (20) can be expressed as

$$
E_{c}^{\text{ladder-CCD}} = \text{Tr}(B^{\dagger}T) = [\text{Tr}(R - A)]^* = \sum_{m} \omega_{m}^{N+2} - \text{Tr}A,
$$

(31)

which is identical to the pp-RPA correlation energy in Eq. (16). From Eqs. (22)-(24), it is also clear that the chemical potential has no contribution because they cancel each other in the CCD equations through $AT + TC$.

Alternatively, one can also derive the equivalence using the $N - 2$ excitation eigenvectors with similar techniques. The resulting amplitude will be the same, while the correlation energy expression will be the second equation in Eq. (16).

In conclusion, the correlation energy from pp-RPA is equivalent to that of ladder-CCD, assuming that the pp-RPA equation is stable. The exponential wavefunction of Eq. (17) with exponent of Eq. (27) has been proposed in Ref[8], together with a similar form for ph-RPA, however without exploring their connection to the form of truncated CCD.
IV. NUMERICAL DEMONSTRATIONS

All coupled cluster and Møller-Plesset perturbation theory (MP2) computations reported herein are performed in a locally modified version of CFOUR\textsuperscript{51}, while pp-RPA is performed with QM4D\textsuperscript{52}.

Truncating the CCD equations to include only the ladder diagrams (Eq. (22)) can be seen as a small modification of the CCD equations or a small extension of the linearized CCD, also known as CEPA(0) or D-MBPT(\(\infty\))\textsuperscript{44}, amplitude equations. Note that the computationally most expensive term of coupled-cluster single and double (CCSD), scaling as \(N_{\text{occ}}^2N_{\text{vir}}^4\), is the major part of the term quadratic in the amplitudes of Eq. (22). In terms of efficiency, the matrix multiplications necessary for solving the non-linear system of equations in standard coupled cluster algorithms are traded against the diagonalization in the pp-RPA algorithm, which, at the non-optimized stage of the code\textsuperscript{52} is significantly slower than solving the non-linear equations. However, the diagonalization has the indisputable advantage that the solution is unique, whereas the non-linear coupled cluster equations have multiple minima (most of them lacking any physical meaning), without an \textit{a priori} guarantee or check that the “correct” solution is found\textsuperscript{44}.

All computations are carried out in the unrestricted Hartree-Fock (UHF) framework, but without breaking space symmetry. The correlation consistent basis sets of Dunning and coworkers\textsuperscript{53,54} have been applied with cartesian d- and f- atomic-orbitals. The ladder-CCD amplitudes are found to converge essentially as fast (or with a couple of iterations less) than the corresponding CCSD equations.

All total energies of ladder-CCD and pp-RPA (see Table I) agree exceedingly well, the largest difference being \(10^{-5}\) Hartree, which is on the same order of magnitude as the difference in nuclear repulsion energy between the two programs and can have its origin in, e.g., integral screening (SCF and CC iteration convergence has been checked carefully). In terms of correlation energy, ladder-CCD captures between 43\% (Be) to 80\% (Ne) of CCSD, while the full CCD energy recovers about 99\%. Note that MP2 has min and max values of 70\% and 99\% for the same systems. Furthermore, changing to a DFT reference\textsuperscript{55} leads to an increased (in absolute terms) correlation energy, with min/max values reaching 51(54)\% and 92 (95)\% for B3LYP\textsuperscript{56,57} (PBE\textsuperscript{58}) orbitals.
Table I: Total energies of various methods. Geometries are taken from the G3 set\textsuperscript{59,60}. The basis set is cc-pVTZ, except for benzene where cc-pVDZ is applied. All energies are in Hartree.

|     | HF    | pp-RPA@HF | ladder-CCD | pp-RPA@PBE | pp-RPA@B3LYP | MP2    | CCD     | CCSD    |
|-----|-------|-----------|------------|------------|--------------|--------|---------|---------|
| He  | 2.861154 | -2.885608 | -2.885608  | -2.889343  | -2.888504    | -2.894441 | -2.900328 | -2.900351 |
| Li  | -7.432706 | -7.443903 | -7.443903  | -7.444664  | -7.444540    | -7.446781 | -7.449184 | -7.449243 |
| Be  | -14.572875 | -14.598923 | -14.598923 | -14.605231 | -14.603533   | -14.614751 | -14.632242 | -14.632817 |
| B   | -24.532104 | -24.566435 | -24.566436 | -24.575674 | -24.573063   | -24.584950 | -24.604746 | -24.605490 |
| C   | -37.691663 | -37.746778 | -37.760145 | -37.756583 | -37.769564   | -37.789208 | -37.789809 |         |
| N   | -54.400883 | -54.482916 | -54.482916 | -54.508083 | -54.496235   | -54.509992 | -54.525553 | -54.525893 |
| O   | -74.811910 | -74.933839 | -74.933839 | -74.959853 | -74.953384   | -74.969918 | -74.985506 | -74.986128 |
| F   | -99.405657 | -99.576884 | -99.611587 | -99.603292 | -99.622736   | -99.663484 | -99.634177 |         |
| Ne  | -128.532010 | -128.760771 | -128.760771 | -128.804849 | -128.794546 | -128.816523 | -128.817814 | -128.818536 |
| CH₄ | -40.213408 | -40.372051 | -40.372054 | -40.411910 | -40.402169   | -40.432266 | -40.452031 | -40.452991 |
| H₂O | -76.056687 | -76.266046 | -76.266049 | -76.318304 | -76.305731   | -76.336459 | -76.340863 | -76.342084 |
| NH₃ | -56.217964 | -56.404439 | -56.404440 | -56.452289 | -56.440556   | -56.471921 | -56.483441 | -56.484474 |
| CH₂O | -113.910280 | -114.227562 | -114.227552 | -114.313824 | -114.293495 | -114.341669 | -114.347547 | -114.351726 |
| C₆H₆ | -230.722701 | -231.315273 | -231.315273 | -231.508132 | -231.460711 | -231.540504 | -231.571751 | -231.577366 |

As a graphical illustration, Figure 1a shows the case of a dissociating cationic dimer \((\text{Ne}^+)\), a typical probe for (de)localization error. Again, the total energies of ladder-CCD and pp-RPA are identical to numerical precision (considering the two very different algorithms and programs), but not in very good agreement with CCSD. To further investigate the (de)localization error\textsuperscript{61}, Figure 1b shows the binding energy with respect to the separated fragments. The binding energy of ladder-CCD is in fairly good agreement with CCSD and only a small “bump” is observed somewhere between 3 and 4 Å, revealing that the missing absolute correlation energies in ladder-CCD compared to CCSD are almost irrelevant for the binding energy. The localization error of HF is over-corrected by MP2, but increasing the correlation treatment to the coupled cluster level improves the dissociation limit further, leading to the previously reported\textsuperscript{38} negligible fractional charge error.
Figure 1: The potential energy surface (a) and the binding curve (b) of Ne$_2^+$ of various methods with basis set aug-cc-pVTZ. The total energies of pp-RPA are substantially overestimated (a), since the correlation energy of the ladder diagrams is not very well balanced (MP2 total energies are, on the scale of the figure, indistinguishable from CCD, and pp-RPA is correct through second order [38]). However, the binding energy (b) reveals that the missing correlation energy cancels almost perfectly out, yielding a pp-RPA binding energy curve very close to CCD, while MP2 deviates from CCSD in the other direction (overbinding).
Table II: Atomization energies (in kcal mol\(^{-1}\)) of various methods. Geometries are taken from the G3 set\(^{59,60}\). The basis set is cc-pVTZ, except for benzene where cc-pVDZ is applied. The mean absolute deviation (MAD) is with respect to CCSD.

|       | HF    | pp-RPA@HF | ladder-CCD | pp-RPA@PBE | pp-RPA@B3LYP | MP2   | CCD   | CCSD |
|-------|-------|-----------|------------|------------|--------------|-------|-------|-------|
| CH\(_4\) | 327.88 | 392.84    | 392.84     | 410.65     | 406.40       | 416.33| 416.40| 416.63|
| H\(_2\)O | 153.84 | 208.70    | 208.70     | 225.76     | 221.74       | 230.25| 223.23| 223.60|
| NH\(_3\) | 199.33 | 264.87    | 264.87     | 284.51     | 279.78       | 290.22| 287.69| 288.12|
| CH\(_2\)O | 255.45 | 343.45    | 343.45     | 373.46     | 366.81       | 378.12| 359.70| 361.55|
| C\(_6\)H\(_6\) | 1008.42| 1237.59   | 1237.59    | 1315.30    | 1296.70      | 1315.24| 1258.08| 1259.81|
| MAD   | 120.96 | 20.45     | 20.45      | 15.83      | 12.52        | 16.21 | 0.92  | --    |

Similarly to the binding energy of Ne\(_2^+\), the atomization energies (Table II) illustrate that the correlation energy missing in ladder-CCD largely cancels out when computing reaction energies. For the five molecules considered, ladder-CCD provides 73% (CH\(_4\)) to 91% (C\(_6\)H\(_6\)) of the correction between the HF and CCSD atomization energy. This is to be compared with MP2 which recovers between 100% and 122%. The range for pp-RPA@B3LYP (pp-RPA@PBE) is, with 88 (93)% for methane to 115 (122)% for benzene somewhat larger. In summary, the numerical analysis shows that ladder-CCD and pp-RPA are equivalent and that the chemically relevant correlation contributions missing in ladder-CCD compared to CCSD are relatively small. An efficient pp-RPA implementation has, therefore, the potential to become a valuable electronic structure theory.

V. CONCLUSIONS

The equivalence of the pp-RPA correlation energy and the ladder-CCD approach has been analytically proved, with the assumption that the pp-RPA equation is stable, and numerically demonstrated. The numerical assessment suggests that the missing correlation in pp-RPA is favorably canceled out in reaction energies. The ladder-CCD perspective of
the pp-RPA correlation energy purveys a concrete wavefunction of the ground state, which makes the study of its ground and excited state properties straight forward.

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REFERENCES

1D. Bohm and D. Pines, Phys. Rev. 82, 625 (1951).
2D. Pines and D. Bohm, Phys. Rev. 85, 338 (1952).
3J. Lindhard, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. 28, 8 (1954).
4A. G. Eguiluz, Phys. Rev. Lett. 51, 1907 (1983).
5D. C. Langreth and J. P. Perdew, Solid State Commun. 17, 1425 (1975).
6G. Giuliani and G. Vignale, Quantum Theory Of The Electron Liquid (Cambridge University Press, 2005).
7J. Blaizot and G. Ripka, Quantum Theory of Finite Systems (Cambridge, MA, 1986).
8P. Ring and P. Schuck, The Nuclear Many-Body Problem (Springer, 2004).
9D. J. Thouless, Nucl. Phys. 21, 225 (1960).
10D. J. Thouless, Nucl. Phys. 22, 78 (1961).
11D. J. Thouless and J. G. Valatin, Nucl. Phys. 31, 211 (1962).
12E. R. Marshalek and J. Weneser, Ann. Phys. 53, 569 (1969).
13H. Eshuis, J. Yarkony, and F. Furche, J. Chem. Phys. 132, 234114 (2010).
14F. Furche, J. Chem. Phys. 129, 114105 (2008).
15S. Kurth and J. P. Perdew, Phys. Rev. B 59, 10461 (1999).
16F. Furche, Phys. Rev. B 64, 195120 (2001).
17M. Fuchs, Y.-M. Niquet, X. Gonze, and K. Burke, J. Chem. Phys. 122, 094116 (2005).
18H. Eshuis and F. Furche, J. Chem. Phys. 136, 084105 (2012).
19X. Ren, P. Rinke, C. Joas, and M. Scheffler, J. Mater. Sci. 47, 7447 (2012).
20W. Zhu, J. Toulouse, A. Savin, and J. G. Angyan, J. Chem. Phys. 132, 244108 (2010).
21J. Toulouse, W. Zhu, J. G. Ángyán, and A. Savin, Phys. Rev. A 82, 032502 (2010).
22A. Hesselmann and A. Görling, Mol. Phys. 109, 2473 (2011).
23P. Mori-Sánchez, A. J. Cohen, and W. Yang, Phys. Rev. A 85, 042507 (2012).
24M. Hellgren, D. R. Rohr, and E. K. U. Gross, J. Chem. Phys. 136, 034106 (2012).
25F. Furche and T. Van Voorhis, J. Chem. Phys. 122, 164106 (2005).
26T. Gould and J. F. Dobson, J. Chem. Phys. 138, 014109 (2013).
27J. Toivanen and J. Suhonen, Phys. Rev. Lett. 75, 410 (1995).
28N. Fukuda, F. Iwamoto, and K. Sawada, Phys. Rev. 135, A932 (1964).
29W. J. Mulhall, R. J. Liotta, J. A. Evans, and R. P. Perazzo, Nucl. Phys. A 93, 261 (1967).
30D. J. Rowe, Phys. Rev. 175, 1283 (1968).
31D. J. Rowe, Rev. Mod. Phys. 40, 153 (1968).
32G. Ripka and R. Padjen, Nucl. Phys. A 132, 489 (1969).
33J. Vary and J. N. Ginocchio, Nucl. Phys. A 166, 479 (1971).
34G. Blanchon, N. V. Mau, A. Bonaccorso, M. Dupuis, and N. Pillet, Phys. Rev. C 82, 034313 (2010).
35J. C. Pacheco and N. Vinh Mau, Phys. Rev. C 65, 044004 (2002).
36C.-M. Liegener, J. Chem. Phys. 104, 2940 (1996).
37C.-M. Liegener, Chem. Phys. Lett. 90, 188 (1982).
38H. van Aggelen, Y. Yang, and W. Yang, (2013), arXiv:1306.4957.
39O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).
40G. E. Scuseria, T. M. Henderson, and D. C. Sorensen, J. Chem. Phys. 129, 231101 (2008).
41M. Nooijen and R. J. Bartlett, J. Chem. Phys. 102, 3629 (1995).
42M. Nooijen and R. J. Bartlett, J. Chem. Phys. 106, 6441 (1997).
43S. R. Gwaltney, R. J. Bartlett, and M. Nooijen, J. Chem. Phys. 111, 58 (1999).
44I. Shavitt and R. Bartlett, Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory (Cambridge University Press, 2009).
45H. Sekino and R. J. Bartlett, Int. J. Quantum Chem 26, 255 (1984).
46K. Kowalski, J. R. Hammond, and W. A. d. Jong, J. Chem. Phys. 127, 164105 (2007).
47M. E. Casida, “Time-dependent density functional response theory for molecules,” in Recent Advances in Density Functional Methods, Part I, edited by D. P. Chong
Scientific, Singapore, 1995) p. 155.

48 N. Higham, Functions of Matrices: Theory and Computation, SIAM e-books (Society for Industrial and Applied Mathematics (SIAM, 3600 Market Street, Floor 6, Philadelphia, PA 19104), 2008).

49 R. G. Parr and W. Yang, Density-Functional Theory of Atoms And Molecules (Oxford University Press, New York, 1989).

50 Note that the expression in Ref. 7 corresponding to the second equation in Eq. (16) is wrong. The correct expression is present in Ref. 38.

51 CFOUR, Coupled-Cluster techniques for Computational Chemistry, a quantum-chemical program package by
J.F. Stanton, J. Gauss, M.E. Harding, P.G. Szalay
with contributions from A.A. Auer, R.J. Bartlett, U. Benedikt, C. Berger, D.E. Bernholdt, Y.J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Juselius, K. Klein, W.J. Lauderdale, D.A. Matthews, T. Metzroth, L.A. Muck, D.P. O’Neill, D.R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, S. Stopkowicz, A. Tajti, J. Vazquez, F. Wang, J.D. Watts and the integral packages MOLECULE (J. Almlof and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jorgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wullen. For the current version, see http://www.cfour.de.

52 An in-house program for QM/MM simulations (http://www.qm4d.info).

53 J. Dunning, Thom H., J. Chem. Phys. 90, 1007 (1989).

54 D. E. Woon and J. Dunning, Thom H., J. Chem. Phys. 98, 1358 (1993).

55 Pp-RPA@DFT is not equivalent to ladder-CCD with a DFT reference when following the usual practice in the coupled cluster community: in pp-RPA@DFT, the molecular orbital energies are the eigenvalues of the Kohn-Sham Hamiltonian. However, the use of DFT orbitals in coupled cluster computations is considered as a “non-HF” reference wave function, for which the one-particle Hamiltonian is not diagonal and the corresponding terms are accounted for, yielding results that are much closer to HF based computations.

56 A. D. Becke, J. Chem. Phys. 98, 5648 (1993).

57 C. T. Lee, W. T. Yang, and R. G. Parr, Phys. Rev. B 37, 785 (1988).

58 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
Appendix A: Mathematical analysis of the pp-RPA equation

1. The zero signature of an eigenvector with an imaginary eigenvalue

For an eigenvalue $\omega_n$ and eigenvector $z_n$, we have

$$ Mz_n = \omega_n Wz_n. \quad (A1) $$

The Hermitian conjugate of Eq. (A1) becomes

$$ z_n^\dagger M = \omega_n^* z_n^\dagger W. \quad (A2) $$

Multiplying $z_n^\dagger$ to the left of Eq. (A1) and $z_n$ to the right of Eq. (A2), we have

$$ z_n^\dagger Mz_n = \omega_n z_n^\dagger Wz_n = \omega_n^* z_n^\dagger Wz_n. $$

Therefore

$$ (\omega_n - \omega_n^*) (z_n^\dagger Wz_n) = 0. \quad (A3) $$

For an imaginary eigenvalue $\omega_n \neq \omega_n^*$, the signature $z_n^\dagger Wz_n = 0$.

2. The orthonormalization of eigenvectors with all real eigenvalues

Using the same approach in Subsection [A1] in Appendix but with two different eigenvalues and eigenvectors, we have

$$ z_n^\dagger Mz_m = \omega_m z_n^\dagger Wz_m = \omega_m^* z_n^\dagger Wz_m, $$
and

\[(\omega_m - \omega_n^*)(z_n^\dagger Wz_m) = 0. \tag{A4}\]

Therefore, when two real eigenvalues are different \((\omega_m \neq \omega_n^*)\), the two eigenvectors are orthogonal under the metric \(W\) \((z_n^\dagger Wz_m = 0)\). Since linear combination of eigenvectors of a degenerate eigenvalue stays in the same eigenspace, we can choose the eigenvectors of a degenerate eigenvalue to orthogonal to each other within the eigenspace. When all eigenvalues are real, eigenvectors can, therefore, be chosen to be orthogonalized under the metric \(W\). For a diagonalizable pp-RPA equation with all real eigenvalues, \(z_n^\dagger Wz_n\) should not be zero, otherwise we have \(z_n^\dagger WZ = 0\), which indicates the eigenvector matrix is rank-deficit, which contradicts with the diagonalizability assumption. Therefore, the signatures of eigenvectors are all nonzero for a diagonalizable pp-RPA equation with all real eigenvalues. The resulting orthonormalization can be written as

\[Z^\dagger WZ = \Lambda, \tag{A5}\]

where \(\Lambda\) is a diagonal matrix with only \(\pm 1\) diagonal elements. According to Sylvester’s law of inertia, \(W\) and \(\Lambda\) share the same number of \(+1\)’s and \(-1\)’s. In another word, there are \(N_{pp} N + 2\) excitations and \(N_{hh} N - 2\) excitations, according to the definition of \(N \pm 2\) excitations in Sec. II. We can further arrange the eigenvectors such that eigenvectors with positive signatures stay in the left of \(Z\), then finally we reach the normalization condition

\[Z^\dagger WZ = W. \tag{A6}\]

3. The equivalence between stability and positive definiteness of \(M\)

First we show that the stability condition of Eq. (13) leads to the positive definiteness of \(M\).

From the stability of the pp-RPA equation (Eq. (13)) and the normalization (Eq. (12)),
we have
\[
\mathbf{c}^\dagger \mathbf{M} \mathbf{c} = \sum_{mn} (\mathbf{z}_m^\dagger \mathbf{c}_m^\dagger) \mathbf{M} (\mathbf{z}_n \mathbf{c}_n)
\]
\[
= \sum_{mn} c_m^* z_m^\dagger \omega_n \mathbf{W} z_n \mathbf{c}_n
\]
\[
= \sum_{n} c_m^* \delta_{mn} W_{mn} \omega_n \mathbf{c}_n
\]
\[
= \sum_{mn} c_m^* |\omega_m| \delta_{mn} \mathbf{c}_n
\]
\[
= \sum_{m} |c_m|^2 |\omega_m| > 0,
\]
with an arbitrary nonzero column vector \( \mathbf{c} \). Thus, \( \mathbf{M} \) is positive definite for a pp-RPA equation.

Next, we show that the reverse is also true.

Given that \( \mathbf{M} \) is positive definite, the pp-RPA equation in the compact form reads

\[
\mathbf{M} \mathbf{z}_n = \omega_n \mathbf{W} \mathbf{z}_n. \tag{A7}
\]
Since \( \mathbf{M} \) is positive definite, Eq. (8) could be rewritten as

\[
\mathbf{L}^\dagger \mathbf{z}_n = \omega_n \mathbf{L}^{-1} \mathbf{W} (\mathbf{L}^{-1})^\dagger \mathbf{L}^\dagger \mathbf{z}_n,
\]
where \( \mathbf{M} = \mathbf{L} \mathbf{L}^\dagger \) is the Cholesky decomposition. With \( \tilde{\mathbf{z}}_n = \mathbf{L}^\dagger \mathbf{z}_n \) and \( \tilde{\mathbf{W}} = \mathbf{L}^{-1} \mathbf{W} (\mathbf{L}^{-1})^\dagger \), then the eigenvalue problem

\[
\tilde{\mathbf{W}} \tilde{\mathbf{z}}_n = \tilde{\omega}_n \tilde{\mathbf{z}}_n \tag{A8}
\]
is diagonalizable with all real eigenvalues, since \( \tilde{\mathbf{W}}^\dagger = \tilde{\mathbf{W}} \) by definition. Additionally, all eigenvalues of \( \tilde{\mathbf{W}} \), \( \tilde{\omega}_n \)'s, will be nonzero, since zero eigenvalue indicates \( \det(\tilde{\mathbf{W}}) = 0 \) which contradicts the definition of \( \tilde{\mathbf{W}} \). With orthonormalization of the eigenvectors \( \tilde{\mathbf{z}}_n^\dagger \tilde{\mathbf{z}}_m = \delta_{nm} |\tilde{\omega}_n|^{-1} \), Eq. (8) can be diagonalized with real eigenvalues

\[
\omega_n = \tilde{\omega}_n^{-1}, \tag{A9}
\]
and eigenvector orthonormalization with the eigenvalue sign constraints (the eigenvectors are arranged in the same way as in Subsection A2 in Appendix),

\[
\mathbf{z}_n^\dagger \mathbf{W} \mathbf{z}_m = \delta_{mn} \text{sign}(\omega_m) = W_{nm}. \tag{A10}
\]
Eq. (A10) guarantees that the $\min_n \omega_n^{N+2} > 0 > \max_m \omega_m^{N-2}$. Therefore, by definition, this pp-RPA equation is stable since all the eigenvalues are real and the $N + 2$ and $N - 2$ excitation spectra are nicely separated.

In summary, the stability condition of an pp-RPA equation is equivalent to the positive definiteness of $M$.

4. The invertibility of $X$ for a stable pp-RPA equation

We now prove the invertibility of $X$ in Sec. III. According to Subsection A2 in Appendix, the eigenvalues of a stable pp-RPA equation are orthonormalized according to

$$Z^\dagger WZ = W. \quad (A11)$$

For only $N + 2$ excitation vectors,

$$Z_{N+2}^\dagger WZ_{N+2} = I, \quad (A12)$$

where

$$Z_{N+2} = \begin{bmatrix} X \\ Y \end{bmatrix},$$

with $X$ and $Y$ the particle-particle and hole-hole block of the $N + 2$ excitation eigenvector matrices. Expanding Eq. (A12), we have

$$X^\dagger X - Y^\dagger Y = I. \quad (A13)$$

Therefore, $X^\dagger X = I + Y^\dagger Y$ is positive definite, and $X$ is invertible, otherwise $X^\dagger X$ will not be positive definite.