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ABSTRACT

We extend the random-phase approximation (RPA) to the non-Hermitian transcorrelated (TC) Hamiltonian, which explicitly includes three-body interactions generated by a Jastrow correlation factor. We consider both the direct RPA (dRPA) and RPA with exchange (RPAx). We apply the resulting TC-dRPA and TC-RPAx methods to calculate ground-state correlation energies and vertical excitation energies for atoms (He and Ne) and small molecules (H_2O, NH_3, CH_4, and H_2CO). For ground-state correlation energies, the TC treatment substantially improves accuracy and accelerates basis set convergence, reducing errors by nearly an order of magnitude relative to conventional RPA calculations. By contrast, it yields only marginal improvements in vertical excitation energies. We attribute this limited effect to the ground-state optimization of the Jastrow factor, which does not adequately capture the distinct electronic character of excited states. These results establish TC-RPA as an accurate and computationally efficient approach to ground-state energetics, while highlighting the need for state-specific Jastrow optimization to achieve reliable descriptions of excited states.

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I. INTRODUCTION

The difficulty of electronic structure calculations is not only that the many-electron Schrödinger equation is hard to solve, but also that its exact solution has features that are poorly matched to standard orbital expansions. In particular, the electronic wavefunction has a cusp at the electron–electron coalescence points,[1–4] a short-range nonanalyticity that finite Gaussian basis sets recover only slowly.[5–9] Even a formally exact treatment of correlation within a given orbital space can, therefore, retain sizable basis set incompleteness errors, motivating approaches that build short-range correlation directly into the theory.

This issue is especially relevant for the random-phase approximation (RPA),[10–12] which provides a compact description of long-range correlation and collective electronic fluctuations, but converges slowly with respect to the one-electron basis set.[13–16] At the same time, RPA occupies a distinctive position in quantum chemistry because of its close formal connections to coupled-cluster theory,[17–26] density-functional theory (DFT),[27–32] and one-body Green's function methods.[33–38] This combination of theoretical appeal and practical basis set sensitivity makes RPA an attractive target for explicitly correlated or Hamiltonian-transformed approaches.

The RPA was originally developed in plasma, condensed-matter, and nuclear physics,[10–12,39–47] where it became a foundational many-body technique. In quantum chemistry, it has been used both for atomic and molecular excited-state calculations.[48–61] In its conventional equation-of-motion (EOM) formulation, RPA restricts the excitation operator to the one-hole–one-particle manifold and invokes the quasiboson approximation. The latter replaces the exact commutators of fermionic particle–hole operators by their expectation values over an uncorrelated Hartree–Fock (HF)

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reference. Particle–hole pairs are, therefore, treated as approximately bosonic collective modes, yielding a simple linear eigenvalue problem. This simplification does not exactly preserve the Pauli constraints associated with the underlying fermionic operators and can lead to an overestimation of ground-state correlation effects.[62–64]

Many extensions of RPA have been proposed to improve its formal structure, including perturbative corrections,[65–71] density-matrix formulations,[72–78] self-consistent RPA variants,[61,79–84] boson-mapping approaches,[85–92] and second-RPA schemes including two-hole–two-particle excitations.[93–102] Particle–particle and quasiparticle formulations have also provided useful alternatives, especially for strongly correlated systems and pairing correlations.[19,20,22,103–108] These developments address important limitations of the standard approximation, but they do not directly target the short-range correlation responsible for slow basis set convergence in RPA calculations.

Several strategies have been designed to alleviate this short-range deficiency. Range-separated RPA partitions the electron–electron interaction into a short-range DFT component and a long-range RPA component.[109,110] Explicitly correlated F12 methods instead accelerate basis set convergence by introducing geminal functions that depend explicitly on the interelectronic distance.[8,9,15,111–114] A related density-functional route, developed by Toulouse, Giner, and co-workers, corrects finite-basis wave-function calculations using short-range correlation functionals designed to recover the correlation missing from an incomplete orbital space.[16,115–119] These approaches all point to the same physical requirement: an efficient RPA scheme should incorporate the electron–electron cusp, or at least its dominant short-range consequences, more directly than is possible with a finite orbital expansion alone.

In this work, we pursue this goal through transcorrelated (TC) theory. In the transcorrelated approach, dynamical correlation is incorporated into the Hamiltonian by a similarity transformation generated by a Jastrow correlation factor.[120–122] The transformed Hamiltonian is non-Hermitian and contains effective two- and three-body interaction terms. This Hamiltonian-level treatment of short-range correlation has been successfully combined with several post-HF methods, including second-order many-body perturbation theory,[123,124] (selected) configuration interaction,[125–131] full configuration interaction quantum Monte Carlo (FCIQMC),[132–138] coupled-cluster theory,[139–142] density matrix renormalization group (DMRG),[143,144] and DFT.[145,146] In addition to these developments, transcorrelated methods have been explored in several other directions. These include perturbative treatments based on transcorrelated Hamiltonians,[147] extensions to the thermodynamic limit,[148] and Jastrow-factor optimization for multireference systems and excited states.[149] More recently, transcorrelated approaches have also been investigated in the context of quantum computing, including applications on quantum computing hardware.[150–153]

Here, we derive the RPA equations for the non-Hermitian TC Hamiltonian, including the contributions induced by the explicit three-body interaction. This defines a TC-RPA framework in which short-range correlation is incorporated at the Hamiltonian level before the linear-response problem is constructed. We consider two variants: direct random-phase approximation (DRPA), in which only the direct Coulomb contribution to the particle–hole interaction kernel is retained, and random-phase approximation with exchange (RPAX), in which exchange is included through the corresponding antisymmetrized interaction kernel. The resulting TC-DRPA and TC-RPAX methods are assessed for both ground-state correlation energies and vertical excitation energies. This dual benchmark is important because the Jastrow factor used in the TC Hamiltonian is optimized for the ground state: one may, therefore, expect the largest benefits for ground-state energetics, while excited-state properties provide a more stringent test of transferability.

The remainder of this article is organized as follows: In Sec. II, we derive the TC-RPA equations using the EOM formalism, analyze the structure of the resulting non-Hermitian response problem, and present spin-adapted working equations for both variants. In Sec. III, we benchmark these methods against their conventional RPA counterparts. We draw our conclusions in Sec. IV.

II. RANDOM-PHASE APPROXIMATION FOR A NON-HERMITIAN HAMILTONIAN

A. Transcorrelated Hamiltonian

The RPA can be derived from several theoretical frameworks, including the adiabatic-connection fluctuation–dissipation theorem,[30,109,110,154–159] coupled-cluster theory,[17–20,22,23,28,160–164] many-body perturbation theory,[58,165,166] and time-dependent Hartree–Fock (TDHF) or time-dependent density-functional theory (TDDFT).[30,48,167–174] Here, we adopt the EOM approach.[175,176] A detailed derivation is provided in the supplementary material. Throughout this work, we restrict our attention to closed-shell systems. Occupied, virtual, and general spin-orbitals are denoted by $i,j,\ldots$, $a,b,\ldots$, and $p,q,\ldots$, respectively, while the corresponding spatial orbitals are denoted by $I,J,\ldots$, $A,B,\ldots$, and $P,Q,\ldots$.

We outline below the key steps leading to the RPA equations for a three-body non-Hermitian Hamiltonian of the following form:

$$\hat{H} = \hat{h} + \frac{1}{2!}\sum_{i}^{N}\sum_{j\neq i}^{N}\hat{V}(\boldsymbol{r}_i,\boldsymbol{r}_j) + \frac{1}{3!}\sum_{i}^{N}\sum_{j\neq i}^{N}\sum_{k\notin\{i,j\}}^{N}\hat{L}(\boldsymbol{r}_i,\boldsymbol{r}_j,\boldsymbol{r}_k). \quad (1)$$

This is the standard structure of the TC Hamiltonian, where $\hat{h}$, $\hat{V}$, and $\hat{L}$ denote the one-, two-, and three-body contributions, respectively. The non-Hermitian character of $\hat{V}$, and therefore of $\hat{H}$, originates from the gradient terms generated by the similarity transformation. Explicit definitions and detailed expressions for these operators are given in Sec. II A of Ref. 177.

B. Biorthogonal formalism

Because $\hat{H}$ is non-Hermitian, we formulate the theory in a biorthogonal one-particle basis.[178,179] Let $\{\phi_p\}$ denote a set of right spin-orbitals that is complete but not necessarily orthonormal. The associated creation and annihilation operators then satisfy

$$\left\{\hat{a}_p^\dagger, \hat{a}_q\right\} = \langle\phi_p|\phi_q\rangle = S_{pq} \neq \delta_{pq}, \quad (2)$$

where $\{\cdot,\cdot\}$ denotes the anticommutator. To recover canonical anticommutation relations, we introduce the dual basis $\{\tilde{\phi}_p\}$,

$$\tilde{\phi}_p = \sum_q \left(\boldsymbol{S}^{-1}\right)_{pq}\phi_q, \quad (3)$$

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such that $\langle\tilde{\phi}_p|\phi_q\rangle = \delta_{pq}$. Using the corresponding dual annihilation operators, one obtains

$$\left\{\tilde{a}_p, \hat{a}_q^\dagger\right\} = \delta_{pq}, \qquad \left\{\hat{a}_p^\dagger, \hat{a}_q^\dagger\right\} = 0, \qquad \{\tilde{a}_p, \tilde{a}_q\} = 0. \tag{4}$$

In this biorthogonal representation, the second-quantized Hamiltonian reads

$$\begin{aligned}\hat{H} &= \sum_{p,q} h_q^p\, \hat{a}_p^\dagger \tilde{a}_q + \frac{1}{2!}\sum_{p_1,p_2}\sum_{q_1,q_2} V_{q_1q_2}^{p_1p_2}\, \hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \tilde{a}_{q_2}\tilde{a}_{q_1} \\ &\quad + \frac{1}{3!}\sum_{p_1,p_2,p_3}\sum_{q_1,q_2,q_3} L_{q_1q_2q_3}^{p_1p_2p_3}\hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \hat{a}_{p_3}^\dagger \tilde{a}_{q_3}\tilde{a}_{q_2}\tilde{a}_{q_1} \\ &= \sum_{p,q} h_q^p\, \hat{a}_p^\dagger \tilde{a}_q + \frac{1}{4}\sum_{p_1,p_2}\sum_{q_1,q_2} \bar{V}_{q_1q_2}^{p_1p_2}\, \hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \tilde{a}_{q_2}\tilde{a}_{q_1} \\ &\quad + \frac{1}{36}\sum_{p_1,p_2,p_3}\sum_{q_1,q_2,q_3} \bar{L}_{q_1q_2q_3}^{p_1p_2p_3}\hat{a}_{p_1}^\dagger \hat{a}_{p_2}^\dagger \hat{a}_{p_3}^\dagger \tilde{a}_{q_3}\tilde{a}_{q_2}\tilde{a}_{q_1}. \end{aligned} \tag{5}$$

The one-, two-, and three-body integrals are defined as

$$h_q^p = \left\langle \tilde{\phi}_p \middle| \hat{h} \middle| \phi_q \right\rangle, \tag{6a}$$

$$V_{q_1q_2}^{p_1p_2} = \left\langle \tilde{\phi}_{p_1}\tilde{\phi}_{p_2} \middle| \hat{V} \middle| \phi_{q_1}\phi_{q_2} \right\rangle, \tag{6b}$$

$$L_{q_1q_2q_3}^{p_1p_2p_3} = \left\langle \tilde{\phi}_{p_1}\tilde{\phi}_{p_2}\tilde{\phi}_{p_3} \middle| \hat{L} \middle| \phi_{q_1}\phi_{q_2}\phi_{q_3} \right\rangle. \tag{6c}$$

We also introduce the antisymmetrized matrix elements,

$$\bar{V}_{q_1q_2}^{p_1p_2} = V_{q_1q_2}^{p_1p_2} - V_{q_2q_1}^{p_1p_2}, \tag{7a}$$

$$\begin{aligned}\bar{L}_{q_1q_2q_3}^{p_1p_2p_3} &= L_{q_1q_2q_3}^{p_1p_2p_3} - L_{q_1q_3q_2}^{p_1p_2p_3} + L_{q_2q_3q_1}^{p_1p_2p_3} \\ &\quad - L_{q_2q_1q_3}^{p_1p_2p_3} + L_{q_3q_1q_2}^{p_1p_2p_3} - L_{q_3q_2q_1}^{p_1p_2p_3}. \end{aligned} \tag{7b}$$

Finally, we assume that the left and right spin-orbitals diagonalize the non-symmetric Fock operator,[130,131,177,180,181]

$$F_q^p = h_q^p + \sum_i \bar{V}_{iq}^{ip} + \frac{1}{2}\sum_{i,j} \bar{L}_{ijq}^{ijp} = \varepsilon_p\, \delta_{pq}. \tag{8}$$

C. Equation-of-motion formalism

Let $\hat{Q}_\nu^\dagger$ and $\tilde{Q}_\nu^\dagger$ be the excitation operators that generate the right and left excited states from the corresponding RPA ground states,[182]

$$\hat{Q}_\nu^\dagger|\Psi_0\rangle = |\Psi_\nu\rangle, \qquad \tilde{Q}_\nu^\dagger|\tilde{\Psi}_0\rangle = |\tilde{\Psi}_\nu\rangle, \tag{9}$$

with $\langle\tilde{\Psi}_\mu|\Psi_\nu\rangle = \delta_{\mu\nu}$. The right and left eigenstates satisfy

$$\hat{H}|\Psi_\mu\rangle = E_\mu|\Psi_\mu\rangle, \qquad \hat{H}^\dagger|\tilde{\Psi}_\mu\rangle = E_\mu|\tilde{\Psi}_\mu\rangle, \tag{10}$$

where the energies are assumed to be real, i.e., $E_\mu = E_\mu^*$. The direct and dual RPA ground states are assumed to exist and to satisfy the killing conditions $\hat{Q}_\nu|\Psi_0\rangle = \tilde{Q}_\nu|\tilde{\Psi}_0\rangle = 0$.

As shown in the supplementary material, for an arbitrary operator $\hat{O}$, the following two EOM identities hold:

$$\left\langle\tilde{\Psi}_0\middle|\left[\hat{O},\left[\hat{H},\hat{Q}_\nu^\dagger\right]\right]\middle|\Psi_0\right\rangle = \Omega_\nu\left\langle\tilde{\Psi}_0\middle|\left[\hat{O},\hat{Q}_\nu^\dagger\right]\middle|\Psi_0\right\rangle, \tag{11a}$$

$$\langle\tilde{\Psi}_0|\left[\left[\tilde{Q}_\nu,\hat{H}\right],\hat{O}\right]|\Psi_0\rangle = \Omega_\nu\langle\tilde{\Psi}_0|\left[\tilde{Q}_\nu,\hat{O}\right]|\Psi_0\rangle. \tag{11b}$$

Here, $[\cdot,\cdot]$ denotes the commutator and $\Omega_\nu = E_\nu - E_0$ is the excitation energy associated with the νth excited state. The two EOM expressions become identical only in the Hermitian limit.

The RPA equations are obtained by using the excitation operators,

$$\hat{Q}_\nu^\dagger = \sum_{ia} X_{ia}^\nu \hat{a}_a^\dagger \tilde{a}_i - \sum_{ia} Y_{ia}^\nu \hat{a}_i^\dagger \tilde{a}_a, \tag{12a}$$

$$\tilde{Q}_\nu^\dagger = \sum_{ia} \tilde{X}_{ia}^\nu \tilde{a}_a^\dagger \hat{a}_i + \sum_{ia} \tilde{Y}_{ia}^\nu \tilde{a}_i^\dagger \hat{a}_a, \tag{12b}$$

and by choosing the first-order variations $\hat{O} = \delta\tilde{Q}_\nu$ and $\hat{O} = \delta\hat{Q}_\nu^\dagger$ in the first and second EOM, respectively. This yields the two sets of equations,

$$\sum_{jb}\left[+A_{ia,jb}X_{jb}^\nu + B_{ia,jb}Y_{jb}^\nu\right] = \Omega_\nu\left\langle\tilde{\Psi}_0\middle|\left[\hat{a}_i^\dagger\tilde{a}_a,\hat{Q}_\nu^\dagger\right]\middle|\Psi_0\right\rangle, \tag{13a}$$

$$\sum_{jb}\left[-C_{ia,jb}X_{jb}^\nu - D_{ia,jb}Y_{jb}^\nu\right] = \Omega_\nu\left\langle\tilde{\Psi}_0\middle|\left[\hat{a}_a^\dagger\tilde{a}_i,\hat{Q}_\nu^\dagger\right]\middle|\Psi_0\right\rangle, \tag{13b}$$

and

$$\sum_{jb}\left[+\tilde{A}_{ia,jb}\tilde{X}_{jb}^\nu - \tilde{C}_{ia,jb}\ \tilde{Y}_{jb}^\nu\right] = \Omega_\nu\left\langle\tilde{\Psi}_0\middle|\left[\tilde{Q}_\nu,\hat{a}_a^\dagger\tilde{a}_i\right]\middle|\Psi_0\right\rangle, \tag{14a}$$

$$\sum_{jb}\left[-\tilde{B}_{ia,jb}\tilde{X}_{jb}^\nu + \tilde{D}_{ia,jb}\ \tilde{Y}_{jb}^\nu\right] = \Omega_\nu\left\langle\tilde{\Psi}_0\middle|\left[\tilde{Q}_\nu,\hat{a}_i^\dagger\tilde{a}_a\right]\middle|\Psi_0\right\rangle. \tag{14b}$$

The matrices appearing in these equations are

$$A_{ia,jb} = +\left\langle\tilde{\Psi}_0\middle|\left[\hat{a}_i^\dagger\tilde{a}_a,\left[\hat{H},\hat{a}_b^\dagger\tilde{a}_j\right]\right]\middle|\Psi_0\right\rangle, \tag{15a}$$

$$B_{ia,jb} = -\left\langle\tilde{\Psi}_0\middle|\left[\hat{a}_i^\dagger\tilde{a}_a,\left[\hat{H},\hat{a}_j^\dagger\tilde{a}_b\right]\right]\middle|\Psi_0\right\rangle, \tag{15b}$$

$$C_{ia,jb} = -\left\langle\tilde{\Psi}_0\middle|\left[\hat{a}_a^\dagger\tilde{a}_i,\left[\hat{H},\hat{a}_b^\dagger\tilde{a}_j\right]\right]\middle|\Psi_0\right\rangle, \tag{15c}$$

$$D_{ia,jb} = +\left\langle\tilde{\Psi}_0\middle|\left[\hat{a}_a^\dagger\tilde{a}_i,\left[\hat{H},\hat{a}_j^\dagger\tilde{a}_b\right]\right]\middle|\Psi_0\right\rangle, \tag{15d}$$

and

$$\tilde{A}_{ia,jb} = +\left\langle\tilde{\Psi}_0\middle|\left[\left[\hat{a}_j^\dagger\tilde{a}_b,\hat{H}\right],\hat{a}_a^\dagger\tilde{a}_i\right]\middle|\Psi_0\right\rangle, \tag{16a}$$

$$\tilde{B}_{ia,jb} = -\left\langle\tilde{\Psi}_0\middle|\left[\left[\hat{a}_j^\dagger\tilde{a}_b,\hat{H}\right],\hat{a}_i^\dagger\tilde{a}_a\right]\middle|\Psi_0\right\rangle, \tag{16b}$$

$$\tilde{C}_{ia,jb} = -\left\langle\tilde{\Psi}_0\middle|\left[\left[\hat{a}_b^\dagger\tilde{a}_j,\hat{H}\right],\hat{a}_a^\dagger\tilde{a}_i\right]\middle|\Psi_0\right\rangle, \tag{16c}$$

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$$\tilde{D}_{ia,jb} = +\left\langle \tilde{\Psi}_0 \middle| \left[\left[\hat{a}_b^\dagger \tilde{a}_j, \hat{H} \right], \hat{a}_i^\dagger \tilde{a}_a \right] \middle| \Psi_0 \right\rangle. \tag{16d}$$

At this stage, we introduce the quasiboson approximation.[183] The commutator between the direct particle–hole annihilation operator $\tilde{b}_\mu \equiv \hat{a}_i^\dagger \tilde{a}_a$ and the dual particle–hole creation operator $\hat{b}_\nu^\dagger \equiv \hat{a}_b^\dagger \tilde{a}_j$ is approximated as

$$\left[\tilde{b}_\mu, \hat{b}_\nu^\dagger \right] = \delta_{ab} \hat{a}_i^\dagger \tilde{a}_j - \delta_{ij} \hat{a}_b^\dagger \tilde{a}_a \approx \delta_{ij} \delta_{ab} = \delta_{\mu\nu}. \tag{17}$$

Equivalently, the quasiboson operators are assumed to satisfy

$$\left[\tilde{b}_\mu, \hat{b}_\nu^\dagger \right] = \delta_{\mu\nu}, \qquad \left[\hat{b}_\mu^\dagger, \hat{b}_\nu^\dagger \right] = 0, \qquad \left[\tilde{b}_\mu, \tilde{b}_\nu \right] = 0. \tag{18}$$

In addition, expectation values over the correlated RPA ground states are replaced by expectation values over the HF Slater determinant and its dual, $\langle \tilde{\Psi}_0 | \cdots | \Psi_0 \rangle \to \langle \tilde{\Phi}_0 | \cdots | \Phi_0 \rangle$. The quasiboson approximation, therefore, treats fermionic particle–hole excitations as effective bosonic modes. This approximation considerably simplifies the many-body problem, but it relaxes the Pauli constraints imposed by the underlying fermionic algebra and can lead to an artificial lowering of the ground-state energy.

After applying the quasiboson approximation (see the supplementary material for details), the amplitudes $\boldsymbol{X}, \boldsymbol{Y}$ and $\tilde{\boldsymbol{X}}, \tilde{\boldsymbol{Y}}$ are obtained as the right and left eigenvectors of the RPA matrix,

$$\boldsymbol{M} = \begin{pmatrix} +\boldsymbol{A} & +\boldsymbol{B} \\ -\boldsymbol{C} & -\boldsymbol{A}^\top \end{pmatrix}. \tag{19}$$

The matrix blocks are

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ab}\delta_{ij} + \tilde{U}_{ib}^{aj}, \tag{20a}$$

$$B_{ia,jb} = \tilde{U}_{ij}^{ab}, \tag{20b}$$

$$C_{ia,jb} = \tilde{U}_{ab}^{ij}, \tag{20c}$$

where

$$\tilde{U}_{q_1q_2}^{p_1p_2} = \tilde{V}_{q_1q_2}^{p_1p_2} + \sum_k \tilde{L}_{kq_1q_2}^{kp_1p_2}. \tag{21}$$

The blocks $\boldsymbol{B}$ and $\boldsymbol{C}$ are symmetric, whereas $\boldsymbol{A}$ is not. Indeed, the non-Hermiticity of $\hat{V}$ implies $\tilde{V}_{q_1q_2}^{p_1p_2} \neq \tilde{V}_{p_1p_2}^{q_1q_2} \neq \tilde{V}_{p_2p_1}^{q_2q_1}$, and analogous relations hold for $\tilde{U}$. Consequently, the RPA matrix in Eq. (19) contains four distinct blocks, instead of the two independent blocks that appear in conventional Hermitian RPA.

Although the TC-RPA eigenvalue problem retains a structure similar to that of conventional RPA, its individual components have a markedly different physical content. First, the orbital-energy differences entering the diagonal part of $\boldsymbol{A}$ are constructed from TC-HF orbital energies rather than conventional HF ones. Indeed, the TC Fock operator defined in Eq. (8) contains contractions of both the Jastrow-transformed two-electron interaction and the explicit three-electron operator. The resulting orbital energies can, therefore, be regarded as effective quantities that are already dressed by the short-range correlation encoded in the Jastrow factor. Second, the effective particle–hole interaction $\tilde{U}$ is no longer constructed from the bare Coulomb interaction. Its two-electron component generates Jastrow-dressed direct and exchange-like contributions, while the contraction $\sum_k \tilde{L}_{kq_1q_2}^{kp_1p_2}$ introduces an additional effective two-electron contribution of three-body origin. The transcorrelated treatment, therefore, modifies both the underlying particle–hole spectrum and the interaction kernel that couples these excitations. Consequently, the difference between conventional RPA and TC-RPA cannot be interpreted as a simple additive correction to the conventional RPA kernel.

In this respect, TC-RPA shares a common conceptual structure with the Bethe–Salpeter equation formalism[24,184] and similarity-transformed EOM coupled-cluster methods:[185–187] in all three cases, excitation energies are obtained from an effective eigenvalue problem in which both the underlying one-particle spectrum and the interaction between particle–hole excitations are dressed by electronic correlation.

D. Properties of TC-RPA

Unlike conventional RPA, the present formalism is characterized by a non-symmetric $\boldsymbol{A}$ block and by $\boldsymbol{B} \neq \boldsymbol{C}$. The right and left eigenvectors, therefore, no longer have the standard Hermitian-RPA structure, i.e.,

$$\boldsymbol{R} = \begin{pmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{X} \end{pmatrix}, \qquad \boldsymbol{L} = \begin{pmatrix} \boldsymbol{X} & -\boldsymbol{Y} \\ -\boldsymbol{Y} & \boldsymbol{X} \end{pmatrix}. \tag{22}$$

Instead, the right eigenvectors contain four distinct blocks,

$$\boldsymbol{R} = \begin{pmatrix} \boldsymbol{X}_1 & \boldsymbol{Y}_2 \\ \boldsymbol{Y}_1 & \boldsymbol{X}_2 \end{pmatrix}, \tag{23}$$

while the corresponding left eigenvectors can be written as

$$\boldsymbol{L} = \begin{pmatrix} \boldsymbol{X}_2 & -\boldsymbol{Y}_1 \\ -\boldsymbol{Y}_2 & \boldsymbol{X}_1 \end{pmatrix}, \tag{24}$$

as shown in the supplementary material. These blocks satisfy

$$\boldsymbol{M} \cdot \boldsymbol{R} = \boldsymbol{R} \cdot \begin{pmatrix} \boldsymbol{\Omega} & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{\Omega} \end{pmatrix}, \tag{25a}$$

$$\boldsymbol{M}^\top \cdot \boldsymbol{L} = \boldsymbol{L} \cdot \begin{pmatrix} \boldsymbol{\Omega} & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{\Omega} \end{pmatrix}. \tag{25b}$$

As in conventional RPA, the eigenvalues of the TC-RPA matrix occur in opposite-sign pairs $(\boldsymbol{\Omega}, -\boldsymbol{\Omega})$ as a consequence of the symplectic structure of Eq. (19).

The biorthogonality condition $\boldsymbol{L}^\top \cdot \boldsymbol{R} = \boldsymbol{1}$ gives

$$\boldsymbol{X}_2^\top \cdot \boldsymbol{X}_1 - \boldsymbol{Y}_2^\top \cdot \boldsymbol{Y}_1 = \boldsymbol{1} = \boldsymbol{X}_1^\top \cdot \boldsymbol{X}_2 - \boldsymbol{Y}_1^\top \cdot \boldsymbol{Y}_2, \tag{26a}$$

$$\boldsymbol{X}_2^\top \cdot \boldsymbol{Y}_2 - \boldsymbol{Y}_2^\top \cdot \boldsymbol{X}_2 = \boldsymbol{0} = \boldsymbol{Y}_2^\top \cdot \boldsymbol{X}_2 - \boldsymbol{X}_2^\top \cdot \boldsymbol{Y}_2, \tag{26b}$$

$$-\boldsymbol{Y}_1^\top \cdot \boldsymbol{X}_1 + \boldsymbol{X}_1^\top \cdot \boldsymbol{Y}_1 = \boldsymbol{0} = -\boldsymbol{X}_1^\top \cdot \boldsymbol{Y}_1 + \boldsymbol{Y}_1^\top \cdot \boldsymbol{X}_1. \tag{26c}$$

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These relations ensure the quasiboson commutation rules,

$$\left[\tilde{Q}_\mu, \hat{Q}_\nu^\dagger\right] = \delta_{\mu\nu}, \qquad \left[\hat{Q}_\mu^\dagger, \hat{Q}_\nu^\dagger\right] = 0, \qquad \left[\tilde{Q}_\mu, \tilde{Q}_\nu\right] = 0. \tag{27}$$

As in conventional RPA, a Tamm–Dancoff approximation can be obtained by setting the off-diagonal blocks to zero, i.e., $\boldsymbol{B} = \boldsymbol{C} = \boldsymbol{0}$.

E. RPA correlation energy

To derive the RPA correlation energy, we introduce a quadratic bosonic Hamiltonian $\hat{H}_\mathrm{B}$ associated with the RPA eigenproblem.[183,188–190] As shown in the supplementary material, this Hamiltonian is non-Hermitian and reads

$$\hat{H}_\mathrm{B} = E_\mathrm{TC-HF} - \frac{1}{2}\,\mathrm{Tr}\,(\boldsymbol{A}) + \frac{1}{2}\begin{pmatrix}\boldsymbol{b}^\dagger & \tilde{\boldsymbol{b}}\end{pmatrix}\cdot\begin{pmatrix}\boldsymbol{A} & \boldsymbol{B}\\ \boldsymbol{C} & \boldsymbol{A}^\top\end{pmatrix}\cdot\begin{pmatrix}\tilde{\boldsymbol{b}}\\ \boldsymbol{b}^\dagger\end{pmatrix}. \tag{28}$$

Here, $\boldsymbol{b}^\dagger$ and $\tilde{\boldsymbol{b}}$ collect the quasiboson creation and annihilation operators, which are assumed to obey the bosonic commutation relations of Eq. (18).

The Hamiltonian is diagonalized through a Bogoliubov-like transformation of the bosonic operators. In the present non-Hermitian setting, this transformation involves two matrices, $\boldsymbol{T}_1$ and $\boldsymbol{T}_2$, satisfying

$$\boldsymbol{T}_1 = \boldsymbol{\Delta}\cdot\boldsymbol{R}^\top\cdot\boldsymbol{\Delta}, \qquad \boldsymbol{T}_2 = \boldsymbol{L}^\top, \tag{29}$$

where

$$\boldsymbol{\Delta} = \begin{pmatrix}\boldsymbol{1} & \boldsymbol{0}\\ \boldsymbol{0} & -\boldsymbol{1}\end{pmatrix}. \tag{30}$$

After this transformation, the quadratic Hamiltonian becomes

$$\hat{H}_\mathrm{B} = E_\mathrm{TC-HF} + E_\mathrm{TC-RPA} + \sum_\mu \Omega_\mu \hat{Q}_\mu^\dagger \tilde{Q}_\mu, \tag{31}$$

with the TC-RPA correlation energy,

$$E_\mathrm{TC-RPA} = \frac{1}{2}\,\mathrm{Tr}\,(\boldsymbol{\Omega} - \boldsymbol{A}). \tag{32}$$

F. Direct random-phase approximation

The RPA formulation derived above [see Eqs. (31) and (32)] corresponds to TC-RPAX, because the effective interaction entering the $\boldsymbol{A}$, $\boldsymbol{B}$, and $\boldsymbol{C}$ blocks contains both direct and exchange contributions from the two- and three-body terms. In the presence of explicit three-body interactions, however, the definition of a direct approximation is not unique. Here, we define TC-DRPA by discarding exchange contributions directly in the effective interaction entering the particle–hole kernel, which gives

$$U^{p_1p_2}_{q_1q_2} = V^{p_1p_2}_{q_1q_2} + \sum_k L^{kp_1p_2}_{kq_1q_2}. \tag{33}$$

Another possible definition is obtained by interpreting only the three terms with a negative sign in Eq. (7) as exchange terms. In this case, one obtains

$$U^{p_1p_2}_{q_1q_2} = V^{p_1p_2}_{q_1q_2} + \sum_k \left(L^{kp_1p_2}_{kq_1q_2} + L^{kp_1p_2}_{q_1q_2k} + L^{kp_1p_2}_{q_2kq_1}\right). \tag{34}$$

The corresponding RPA matrix is

$$\boldsymbol{\mathcal{M}} = \begin{pmatrix}+\boldsymbol{\mathcal{A}} & +\boldsymbol{\mathcal{B}}\\ -\boldsymbol{\mathcal{C}} & -\boldsymbol{\mathcal{A}}^\top\end{pmatrix}, \tag{35}$$

with

$$\mathcal{A}_{ia,jb} = (\varepsilon_a - \varepsilon_i)\,\delta_{ab}\,\delta_{ij} + U^{aj}_{ib}, \tag{36a}$$

$$\mathcal{B}_{ia,jb} = U^{ab}_{ij}, \tag{36b}$$

$$\mathcal{C}_{ia,jb} = U^{ij}_{ab}. \tag{36c}$$

G. Spin adaptation

For restricted Hartree–Fock (RHF) orbitals, the spin-orbital RPA problem can be decomposed into singlet and triplet sectors. This avoids the diagonalization of the full spin-orbital matrix and instead requires the diagonalization of two smaller spatial-orbital matrices, ${}^1\boldsymbol{M}$ and ${}^3\boldsymbol{M}$,

$${}^1\boldsymbol{M} = \begin{pmatrix}+{}^1\boldsymbol{A} & +{}^1\boldsymbol{B}\\ -{}^1\boldsymbol{C} & -{}^1\boldsymbol{A}^\top\end{pmatrix}, \qquad {}^3\boldsymbol{M} = \begin{pmatrix}+{}^3\boldsymbol{A} & +{}^3\boldsymbol{B}\\ -{}^3\boldsymbol{C} & -{}^3\boldsymbol{A}^\top\end{pmatrix}. \tag{37}$$

For RPAX, the singlet blocks are

$${}^1A_{IA,JB} = (\varepsilon_A - \varepsilon_I)\,\delta_{IJ}\,\delta_{AB} + 2\left\langle\!\left\langle \tilde{\phi}_A\,\tilde{\phi}_J | \phi_I\,\phi_B\right\rangle\!\right\rangle - \left\langle\!\left\langle \tilde{\phi}_A\,\tilde{\phi}_J | \phi_B\,\phi_I\right\rangle\!\right\rangle, \tag{38a}$$

$${}^1B_{IA,JB} = 2\left\langle\!\left\langle \tilde{\phi}_A\,\tilde{\phi}_B | \phi_I\,\phi_J\right\rangle\!\right\rangle - \left\langle\!\left\langle \tilde{\phi}_A\,\tilde{\phi}_B | \phi_J\,\phi_I\right\rangle\!\right\rangle, \tag{38b}$$

$${}^1C_{IA,JB} = 2\left\langle\!\left\langle \tilde{\phi}_I\,\tilde{\phi}_J | \phi_A\,\phi_B\right\rangle\!\right\rangle - \left\langle\!\left\langle \tilde{\phi}_I\,\tilde{\phi}_J | \phi_B\,\phi_A\right\rangle\!\right\rangle, \tag{38c}$$

and the triplet blocks are

$${}^3A_{IA,JB} = (\varepsilon_A - \varepsilon_I)\,\delta_{IJ}\,\delta_{AB} - \left\langle\!\left\langle \tilde{\phi}_A\,\tilde{\phi}_J | \phi_B\,\phi_I\right\rangle\!\right\rangle, \tag{39a}$$

$${}^3B_{IA,JB} = -\left\langle\!\left\langle \tilde{\phi}_A\,\tilde{\phi}_B | \phi_J\,\phi_I\right\rangle\!\right\rangle, \tag{39b}$$

$${}^3C_{IA,JB} = -\left\langle\!\left\langle \tilde{\phi}_I\,\tilde{\phi}_J | \phi_B\,\phi_A\right\rangle\!\right\rangle. \tag{39c}$$

The effective spatial-orbital matrix elements are defined as

$$\left\langle\!\left\langle \tilde{\phi}_P\,\tilde{\phi}_Q | \phi_R\,\phi_S\right\rangle\!\right\rangle = V^{PQ}_{RS} + \sum_{k=1}^{N}\left[L^{PQk}_{RSk} - L^{PQk}_{RkS} - L^{PQk}_{kSR}\right]. \tag{40}$$

The RPAX correlation energy is then obtained as[29,30]

$$E_\mathrm{TC-RPAx} = \frac{1}{4}\,\mathrm{Tr}\left({}^1\boldsymbol{\Omega} - {}^1\boldsymbol{A}\right) + \frac{3}{4}\,\mathrm{Tr}\left({}^3\boldsymbol{\Omega} - {}^3\boldsymbol{A}\right). \tag{41}$$

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For DRPA, the singlet blocks are

$$ {}^{1}\mathcal{A}_{IA,JB} = (\varepsilon_A - \varepsilon_I)\delta_{IJ}\delta_{AB} + U^{AJ}_{IB}, \tag{42a} $$

$$ {}^{1}\mathcal{B}_{IA,JB} = 2U^{AB}_{IJ}, \tag{42b} $$

$$ {}^{1}\mathcal{C}_{IA,JB} = 2U^{IJ}_{AB}, \tag{42c} $$

while the triplet blocks reduce to

$$ {}^{3}\mathcal{A}_{IA,JB} = (\varepsilon_A - \varepsilon_I)\delta_{IJ}\delta_{AB}, \tag{43a} $$

$$ {}^{3}\mathcal{B}_{IA,JB} = 0, \tag{43b} $$

$$ {}^{3}\mathcal{C}_{IA,JB} = 0. \tag{43c} $$

The triplet eigenproblem is, therefore, diagonal and does not contribute to the DRPA correlation energy. Accordingly,

$$ E_{\text{TC-dRPA}} = \frac{1}{2}\,\text{Tr}\left({}^{1}\boldsymbol{\Omega} - {}^{1}\boldsymbol{\mathcal{A}}\right). \tag{44} $$

III. RESULTS

A. Computational details

In this work, we adopt the Jastrow factor proposed by Boys and Handy,[121] whose functional form and parameters are detailed in Sec. II F of Ref. 177. These parameters, optimized at the single-determinant level within a variational Monte Carlo framework, were taken from the literature. In particular, the atomic parameters were extracted from Table V of Ref. 191 and the molecular parameters from Table 2 of Ref. 192.

The approach to evaluating the TC integrals is outlined in Sec. II G of Ref. 177. We should mention here that the three-electron contribution to the TC-DRPA and TC-RPAX calculations is computed on the fly using a quadrature grid,[177,193,194] without the need to store a 6-index tensor (see the supplementary material and Sec. III H of Ref. 177 for more details).

All calculations were carried out with Quantum Package.[195] We employed Dunning's augmented correlation-consistent basis sets, aug-cc-pVXZ (abbreviated as aXZ), with cardinal numbers X = D, T, Q, 5, and 6.[196–198] Equilibrium molecular geometries and theoretical best estimates (TBEs) for the vertical excitation energies were retrieved from the QUEST database,[199–202] available at https://github.com/pfloos/QUESTDB.

B. Ground-state energies

We begin by assessing the accuracy and basis set convergence of RPA and TC-RPA ground-state energies for the helium and neon atoms. Figure 1 compares DRPA and RPAX with their transcorrelated counterparts, TC-DRPA and TC-RPAX, as a function of the basis set cardinal number. Exact non-relativistic energies are also shown for Ref. 203.

Two distinct effects of the transcorrelated treatment are apparent: it substantially accelerates basis set convergence and modifies the limiting energy toward which the RPA approximation converges. These effects should be distinguished from the behavior of conventional explicitly correlated F12 methods. By incorporating the short-range electron–electron cusp explicitly, F12 methods accelerate basis set convergence while formally preserving the complete basis set (CBS) limit of the underlying electronic structure method.[8,9] The TC transformation is also isospectral when treated exactly and, therefore, leaves the exact energy spectrum unchanged. In the present context, however, the RPA approximation is applied to the transformed, non-Hermitian Hamiltonian and is not invariant under this similarity transformation. Consequently, conventional RPA and TC-RPA need not share the same approximate CBS limit. The displacement of the limiting energy observed here should, therefore, be attributed to the interplay between the TC transformation and the RPA approximation, rather than to a modification of the exact spectrum.

These two effects are particularly striking for helium. At the DRPA level, the error on the total energy evolves from +0.8 mH with aVDZ to −23.4 mH with aV5Z, with the energy continuing to decrease appreciably as the basis set is enlarged. This behavior does not signal a failure of basis set convergence itself; rather,

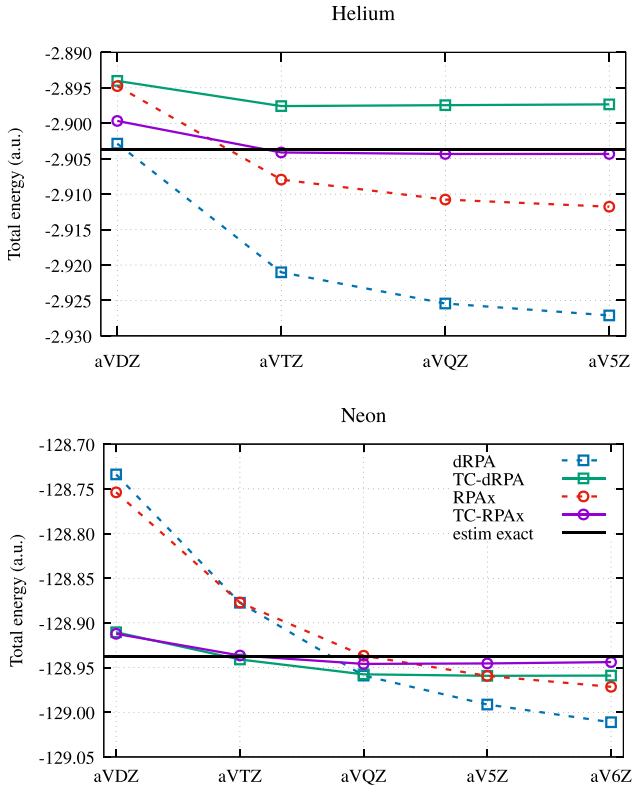


FIG. 1. Basis set convergence of the total ground-state energies (in a.u.) of the He and Ne atoms. The energies are plotted as a function of the basis set cardinal number X (aug-cc-pVXZ) for dRPA (blue dashed), TC-dRPA (green solid), RPAx (red dashed), and TC-RPAx (purple solid). The horizontal black line denotes the estimated exact non-relativistic ground-state energy, which serves as the CBS Ref. 203. Raw data can be found in the supplementary material.

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DRPA progressively approaches its own CBS limit, which lies substantially below the exact fermionic energy. In contrast, TC-DRPA exhibits a much weaker basis set dependence, with errors ranging from +9.7 mH at aVDZ to 6.4 mH at aV5Z and the energy already nearly converged at the aVTZ level. The TC treatment, therefore, both accelerates convergence and profoundly alters the limiting energy.

A similar behavior is observed for RPAX. The conventional RPAX energy continues to evolve significantly with increasing basis set size, with its error changing from +8.9 mH at aVDZ to −8.1 mH at aV5Z as it approaches its own CBS limit. By contrast, TC-RPAX converges much more rapidly: its energy is essentially stabilized from aVTZ onward and remains remarkably close to the exact non-relativistic value of −2.9037 hartree. The corresponding error decreases from +4.0 mH at aVDZ to only −0.6 mH at aV5Z.

The same qualitative picture emerges for neon. The conventional DRPA energy retains a pronounced basis set dependence throughout the sequence, with the error evolving from +203.7 mH at aVDZ to −73.6 mH at aV6Z. TC-DRPA converges considerably faster, becoming nearly stationary at the largest basis sets and remaining close to the exact energy, with errors ranging from +27.2 to −21.4 mH. Similarly, the RPAX error evolves from +183.7 mH at aVDZ to −33.9 mH at aV6Z, whereas TC-RPAX displays a much weaker basis set dependence and rapidly approaches a limiting energy very close to the exact reference, with errors decreasing from +25.3 mH to only −6.3 mH.

Overall, Fig. 1 highlights two complementary benefits of the transcorrelated treatment. First, both TC-DRPA and TC-RPAX exhibit substantially faster convergence with respect to the one-electron basis, reaching near-asymptotic energies with considerably smaller basis sets than their conventional counterparts. Second, the TC transformation modifies the effective many-body space explored by the RPA approximation, leading to CBS limits that lie much closer to the exact fermionic ground-state energies. These results suggest that the transcorrelated formulation simultaneously alleviates the slow basis set convergence of conventional RPA and reduces the energetic consequences of the unphysical bosonic components introduced by the quasiboson approximation.

Importantly, the TC transformation does not restore the fermionic commutation relations lost in the quasiboson approximation. Rather, by incorporating a substantial part of the short-range dynamical correlation directly into the Hamiltonian through the Jastrow factor, it reduces the amount of residual correlation that must be generated through repeated quasibosonic particle–hole excitations. The remaining correlation is consequently more dominated by longer-range collective fluctuations, for which the

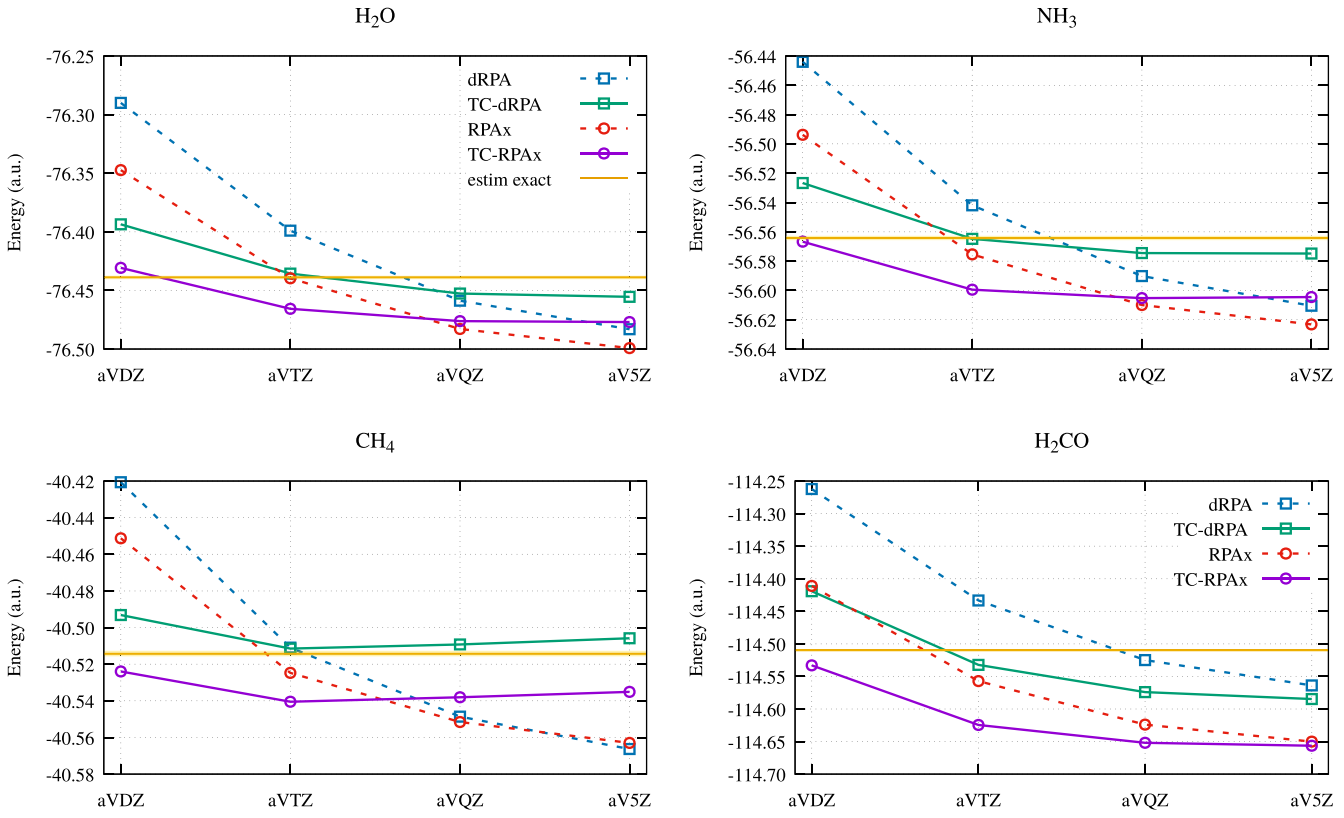


FIG. 2. Basis-set convergence of the total ground-state energies (in a.u.) of H_2O, NH_3, CH_4, and H_2CO as a function of the basis set cardinal number X (aug-cc-pVXZ). Results are shown for dRPA (blue dashed), TC-dRPA (green solid), RPAx (red dashed), and TC-RPAx (purple solid). The horizontal yellow line represents the estimated exact non-relativistic ground-state energy.[192,204] Raw data can be found in the supplementary material.

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quasiboson picture is more appropriate. In this sense, transcorrelation reduces the energetic consequences of the Pauli-violating components of the quasiboson approximation rather than eliminating them.

We now extend our analysis to the ground-state energies of a set of molecules comprising H_2O, NH_3, CH_4, and H_2CO. Figure 2 compares the total energies obtained with conventional RPA and TC-RPA as a function of the basis set cardinal number. Estimated exact non-relativistic ground-state energies are also shown for reference (Ref. 204 for H_2O and Ref. 192 for NH_3, CH_4, and H_2CO).

The molecular results confirm the trends observed for He and Ne. Most notably, the TC-RPA variants converge significantly faster with respect to the one-electron basis than their conventional counterparts, for both DRPA and RPAX. This acceleration is particularly pronounced for TC-RPAX, whose energies are already close to their limiting values at the aVTZ or aVQZ level for most systems. TC-DRPA exhibits a similarly reduced basis set dependence, although the convergence is somewhat more system dependent, especially for H_2CO. In contrast, the conventional DRPA and RPAX energies continue to vary appreciably up to the largest basis sets considered.

In addition to accelerating basis set convergence, the TC treatment also modifies the limiting energies reached by the RPA approximations. At the aV5Z level, the absolute errors of DRPA are 44.2, 46.3, 52.1, and 53.9 mH for H_2O, NH_3, CH_4, and H_2CO, respectively, compared with 16.5, 10.6, 8.4, and 74.7 mH for TC-DRPA. The improvement is, therefore, particularly systematic for TC-DRPA, which yields remarkably accurate energies for H_2O, NH_3, and CH_4. For RPAX, the corresponding errors decrease from 60.2, 59.0, 48.7, and 140.1 to 38.0, 40.3, 20.9, and 146.3 mH upon introducing the TC treatment. Thus, while TC-RPAX substantially improves the energies of H_2O, NH_3, and CH_4, no improvement in absolute accuracy is observed for H_2CO at the aV5Z level.

These comparisons should, however, be interpreted in light of the markedly different basis set convergence rates of the conventional and TC approaches. At aV5Z, the TC-RPA energies are already close to their respective CBS limits, whereas the conventional RPA energies, particularly those of DRPA, still exhibit a noticeable basis set dependence. Consequently, similar errors at a finite basis set level do not necessarily imply similar accuracies at the CBS limit. As discussed above, the conventional and transcorrelated RPA formulations effectively explore different approximate many-body spaces and, therefore, need not converge toward the same CBS energy.

Overall, the molecular results reinforce the two main effects of the transcorrelated treatment already identified for the atomic systems. First, transcorrelation substantially accelerates basis set convergence for both DRPA and RPAX. Second, it modifies the corresponding CBS limits, often bringing them closer to the exact fermionic ground-state energies, although this improvement in absolute accuracy is system- and approximation-dependent. Importantly, these two effects are distinct: faster basis set convergence does not necessarily imply a more accurate CBS limit. Among the systems considered here, the improvement in accuracy is particularly systematic for TC-DRPA, whereas TC-RPAX exhibits a more system-dependent accuracy despite its consistently faster basis set convergence.

C. Excited-state energies

We now turn to vertical excitation energies and investigate whether the benefits of the transcorrelated treatment observed for ground-state energies carry over to excited states. Table I compares DRPA and RPAX with their transcorrelated counterparts for two vertical Rydberg excitations of H_2O. In contrast to the ground-state energies, the TC treatment does not lead to a systematic improvement of the excitation energies.

For the $n \to 3s$ transition (TBE = 7.672 eV), DRPA strongly overestimates the excitation energy, yielding 14.581 eV at the aV5Z level. The TC treatment lowers this value by ~0.3–0.4 eV across the basis set sequence, reaching 14.230 eV at aV5Z. Although this shift is non-negligible, it is far too small to remedy the large intrinsic error of DRPA for this transition. RPAX provides a much more accurate description, with an aV5Z excitation energy of 8.639 eV, but the TC transformation has essentially no effect: RPAX and TC-RPAX are virtually indistinguishable beyond aVDZ.

A similar picture emerges for the $n \to 3p$ transition (TBE = 9.449 eV). The TC transformation lowers the DRPA excitation energy by ~0.3–0.4 eV, from 14.900 to 14.500 eV at the aV5Z level, but the resulting TC-DRPA value remains more than 5 eV above the reference. For RPAX, the effect of the TC treatment is again very small, with changes of only a few hundredths of an eV across the entire basis set sequence. Interestingly, in this case the TC correction slightly increases the RPAX excitation energy and, therefore, does not improve agreement with the TBE.

The analysis is extended to NH_3 and H_2CO in Tables II and III, respectively. These results reinforce the absence of a systematic effect of the TC transformation on vertical excitation energies while also revealing a pronounced dependence on the system and the nature of the transition.

For NH_3, the TC correction has an almost negligible effect on DRPA. At the aV5Z level, the excitation energies change by only −0.018 eV for the $n \to 3s$ transition and +0.002 eV for the $n \to 3p$

TABLE I. Vertical excitation energies (in eV) of the two lowest Rydberg states of H_2O, computed with dRPA, TC-dRPA, RPAx, and TC-RPAx using the aug-cc-pV*X*Z basis sets. The theoretical best estimates (TBEs) at the CBS limit are taken from Ref. 202.

	Cardinal number X			
Method	D	T	Q	5
$1^1A_1 \to 1^1B_1$ ($n \to 3s$), TBE = 7.672				
dRPA	14.909	14.752	14.680	14.581
TC-dRPA	14.601	14.423	14.337	14.230
RPAx	8.625	8.640	8.639	8.639
TC-RPAx	8.638	8.640	8.639	8.639
$1^1A_1 \to 1^1A_2$ ($n \to 3p$), TBE = 9.449				
dRPA	15.455	15.194	15.070	14.900
TC-dRPA	15.122	14.832	14.687	14.500
RPAx	10.306	10.312	10.308	10.306
TC-RPAx	10.345	10.340	10.333	10.333

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TABLE II. Vertical excitation energies (in eV) of the two lowest Rydberg states of NH_3, computed with dRPA, TC-dRPA, RPAx, and TC-RPAx using the aug-cc-pV*X*Z basis sets. The theoretical best estimates (TBEs) at the CBS limit are taken from Ref. 202.

Method	Cardinal number *X*			
	D	T	Q	5
$1^1A_1 \rightarrow 1^1A_2$ ($n \rightarrow 3s$), TBE = 6.627				
dRPA	12.734	12.559	12.476	12.398
TC-dRPA	12.704	12.542	12.453	12.380
RPAx	7.414	7.423	7.427	7.428
TC-RPAx	7.546	7.558	7.554	7.556
$1^1A_1 \rightarrow 1^1E$ ($n \rightarrow 3p$), TBE = 8.190				
dRPA	13.323	13.028	12.896	12.743
TC-dRPA	13.314	13.032	12.894	12.745
RPAx	8.888	8.877	8.875	8.869
TC-RPAx	9.096	9.088	9.078	9.074

TABLE III. Vertical excitation energies (in eV) of the lowest valence and Rydberg states of H_2CO, computed with dRPA, TC-dRPA, RPAx, and TC-RPAx using the aug-cc-pV*X*Z basis sets. The theoretical best estimates (TBEs) at the CBS limit are taken from Ref. 202.

Method	Cardinal number *X*			
	D	T	Q	5
$1^1A_1 \rightarrow 1^1A_2$ ($n \rightarrow \pi^*$), TBE = 3.969				
dRPA	12.988	12.831	12.754	12.689
TC-dRPA	12.288	12.114	11.999	11.911
RPAx	4.379	4.396	4.395	4.394
TC-RPAx	4.250	4.285	4.281	4.280
$1^1A_1 \rightarrow 1^1B_2$ ($n \rightarrow 3s$), TBE = 7.269				
dRPA	13.473	13.247	13.145	13.003
TC-dRPA	12.710	12.460	12.318	12.143
RPAx	8.566	8.588	8.588	8.586
TC-RPAx	8.220	8.248	8.229	8.221
$1^1A_1 \rightarrow 1^1B_1$, TBE = 9.187				
dRPA	15.983	15.727	15.393	14.903
TC-dRPA	15.484	15.016	14.658	14.389
RPAx	9.628	9.586	9.576	9.566
TC-RPAx	9.467	9.442	9.437	9.407

transition. Consequently, the very large DRPA errors remain essentially unchanged, with TC-DRPA overestimating the corresponding TBEs by ~5.7 and 4.5 eV, respectively. The effect is somewhat larger for RPAX, for which the TC transformation increases the aV5Z excitation energies by 0.128 eV for the $n \rightarrow 3s$ transition and 0.205 eV for the $n \rightarrow 3p$ transition. Since the conventional RPAX values already lie above the corresponding TBEs, these shifts slightly deteriorate the agreement with the reference values.

The behavior of H_2CO is more pronounced. For the valence $n \rightarrow \pi^\star$ transition (TBE = 3.969 eV), the TC transformation produces a substantial reduction of the DRPA excitation energy, from 12.689 to 11.911 eV at the aV5Z level. Despite this sizable 0.778 eV shift, TC-DRPA still strongly overestimates the reference value, demonstrating that the TC transformation alone cannot remedy the intrinsic limitations of the DRPA response kernel. For RPAX, the corresponding shift is smaller but favorable, lowering the excitation energy from 4.394 to 4.280 eV and thereby improving agreement with the TBE.

For the Rydberg $n \rightarrow 3s$ transition of H_2CO (TBE = 7.269 eV), the TC transformation also produces appreciable shifts. At the aV5Z level, it lowers the DRPA excitation energy by 0.860 eV, from 13.003 to 12.143 eV, while the RPAX excitation energy decreases by 0.365 eV, from 8.586 to 8.221 eV. The latter represents a noticeable improvement over conventional RPAX, although the TC-RPAX value remains ~0.9 eV above the reference. For the additional valence 1, $^1A_1 \rightarrow 1$, $^1B_1$ transition (TBE = 9.187 eV), the same overall trend is observed, with the TC transformation lowering the excitation energies for both DRPA and RPAX, while TC-RPAX remains closer to the TBE than TC-DRPA.

An important aspect of these results is that most of the excited states considered here are Rydberg states. Their accurate description requires substantial radial flexibility in the one-electron basis and, in particular, the presence of sufficiently diffuse basis functions. The transcorrelated approach employed here is not specifically designed to address this source of basis set incompleteness. Rather, by explicitly incorporating short-range electron correlation through the Jastrow factor, it primarily alleviates the need for the high-angular-momentum components required to describe the electron–electron cusp. Consequently, one should not necessarily expect the TC transformation to eliminate the slow convergence associated with the radial and diffuse character of Rydberg states, and augmented basis sets remain essential for their accurate description.

In this respect, the two valence excitations of H_2CO are particularly noteworthy. Unlike the predominantly Rydberg transitions considered above, these excitations do not rely as strongly on the diffuse radial part of the basis. The more pronounced effect of the TC transformation observed for these transitions may, therefore, indicate that valence excitations benefit differently from the improved description of short-range correlation. However, the present dataset contains too few valence excitations to establish a general trend, and a broader investigation would be required to substantiate this interpretation.

Overall, these results reveal a clear contrast between ground-state and excitation energies. For ground-state energies, the transcorrelated treatment systematically accelerates basis set convergence and substantially modifies the corresponding CBS limits. For vertical excitation energies, however, no similarly systematic improvement is observed. The magnitude and even the sign of the TC-induced shifts depend strongly on the system, the transition, and the underlying RPA approximation. In particular, the TC transformation does not resolve the severe overestimation of excitation energies obtained with DRPA, indicating that the dominant deficiency lies in the approximate response kernel itself. The inclusion of exchange through RPAX is far more consequential, reducing

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errors by several eV in many cases before the TC transformation is even introduced. Once exchange is included, the additional effect of TC ranges from essentially negligible for H_2O to slightly detrimental for NH_3 and beneficial for the transitions considered in H_2CO.

Several factors may contribute to this contrasting behavior. First, excitation energies are energy differences so that substantial TC-induced changes in the absolute ground- and excited-state energies may partially cancel. Second, the Jastrow factor employed in the present calculations is optimized exclusively for the ground state and, therefore, does not explicitly account for the correlation characteristics of the target excited states. Finally, for the predominantly Rydberg states considered here, the dominant basis set requirement is associated with radial diffuseness rather than the short-range correlation effects that the TC transformation is primarily designed to capture. These observations suggest several possible routes for further improvement, including state-specific or state-averaged optimization of the Jastrow factor and the development of improved response kernels tailored to the transcorrelated Hamiltonian.[149,205,206] A more systematic investigation of valence excitations would also be particularly valuable to disentangle the respective roles of short-range correlation and radial basis set incompleteness.

IV. CONCLUSION

In this work, we have derived the RPA equations for a non-Hermitian Hamiltonian containing up to three-body interactions, with particular emphasis on the TC Hamiltonian. This formulation generalizes the standard RPA framework to Jastrow-correlated wave functions and provides a rigorous foundation for computing both ground-state correlation energies and vertical excitation energies within TC-RPA.

For ground-state energies, our results reveal two major benefits of the transcorrelated treatment. First, both TC-DRPA and TC-RPAX exhibit substantially faster basis set convergence than their conventional counterparts, reaching near-asymptotic energies with considerably smaller one-electron basis sets. Second, the TC transformation modifies the limiting energies reached by the RPA approximations, often bringing them significantly closer to the exact non-relativistic ground-state energies. These two effects are distinct: faster basis set convergence does not necessarily imply a more accurate CBS limit. Nevertheless, across the atoms and small molecules considered here, the TC treatment provides a systematic and substantial improvement in basis set convergence, together with generally improved ground-state energetics. These findings demonstrate the effectiveness of explicitly incorporating short-range correlation through the Jastrow factor within the RPA framework.

The picture is more nuanced for vertical excitation energies. Unlike for ground-state energies, the TC transformation does not produce a systematic improvement across the systems and transitions considered. The magnitude and even the sign of the TC-induced shifts depend on the system, the nature of the excitation, and the underlying RPA approximation. In particular, TC does not remedy the severe overestimation of excitation energies obtained with DRPA, indicating that the dominant deficiency lies in the approximate response kernel itself. The inclusion of exchange through RPAX has a much larger impact on the excitation energies, while the additional effect of the TC transformation is strongly system dependent.

Several factors may account for this contrasting behavior. The Jastrow factor employed in the present calculations is optimized exclusively for the ground state and, therefore, does not explicitly account for the specific correlation characteristics of the target excited states. Moreover, most of the excitations considered here are Rydberg in nature and require substantial radial flexibility through diffuse basis functions. By explicitly describing short-range electron correlation, the TC transformation primarily alleviates basis set incompleteness associated with the angular description of the electron–electron cusp, rather than the radial incompleteness that is critical for Rydberg states. Interestingly, the results obtained for the valence excitations of H_2CO suggest that valence excitations may respond differently to the TC treatment, although a broader set of transitions is required to establish whether this represents a general trend.

Overall, this work establishes a general RPA framework for non-Hermitian Hamiltonians with three-body interactions and demonstrates the considerable potential of its application to transcorrelated Hamiltonians. For ground-state energetics, TC-RPA combines substantially accelerated basis set convergence with generally improved accuracy, making it a promising route toward compact and efficient correlated calculations. For excited states, the present results highlight a more complex interplay between the Jastrow factor, the response kernel, and the radial and angular requirements of the one-electron basis. They, therefore, point toward several directions for future developments, including improved response kernels tailored to the TC Hamiltonian, state-specific or state-averaged optimization of the Jastrow factor, and a systematic investigation of valence excitations.

SUPPLEMENTARY MATERIAL

See the supplementary material for additional theoretical details for the derivation and implementation of the TC-RPA formalism, as well as the raw data associated with the figures.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

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Author Contributions

Abdallah Ammar: Data curation (equal); Software (equal); Writing – original draft (equal). **Enzo Monino**: Writing – original draft (equal). **Anthony Scemama**: Software (equal); Writing – review & editing (equal). **Emmanuel Giner**: Software (equal); Writing – review & editing (equal). **Pierre-François Loos**: Funding acquisition (equal); Supervision (equal); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

REFERENCES

[1] T. Kato, "Fundamental properties of Hamiltonian operators of schrödinger type," Trans. Am. Math. Soc. **70**, 195–211 (1951).
[2] T. Kato, "On the eigenfunctions of many-particle systems in quantum mechanics," Commun. Pure Appl. Math. **10**, 151–177 (1957).
[3] C. R. Myers, C. J. Umrigar, J. P. Sethna, and J. D. Morgan III, "Fock's expansion, Kato's cusp conditions, and the exponential ansatz," Phys. Rev. A **44**, 5537–5546 (1991).
[4] J. D. Morgan III and W. Kutzelnigg, "Hund's rules, the alternating rule, and symmetry holes," J. Phys. Chem. **97**, 2425–2434 (1993).
[5] C. Schwartz, "Importance of angular correlations between atomic electrons," Phys. Rev. **126**, 1015–1019 (1962).
[6] R. N. Hill, "Rates of convergence and error estimation formulas for the Rayleigh–Ritz variational method," J. Chem. Phys. **83**, 1173–1196 (1985).
[7] W. Kutzelnigg, I. Morgan, and D. John, "Rates of convergence of the partial-wave expansions of atomic correlation energies," J. Chem. Phys. **96**, 4484–4508 (1992).
[8] C. Hättig, W. Klopper, A. Köhn, and D. P. Tew, "Explicitly correlated electrons in molecules," Chem. Rev. **112**, 4 (2012).
[9] L. Kong, F. A. Bischoff, and E. F. Valeev, "Explicitly correlated R12/F12 methods for electronic structure," Chem. Rev. **112**, 75–107 (2012).
[10] D. Bohm and D. Pines, "A collective description of electron interactions. I. Magnetic interactions," Phys. Rev. **82**, 625–634 (1951).
[11] D. Pines and D. Bohm, "A collective description of electron interactions: II. Collective vs individual particle aspects of the interactions," Phys. Rev. **85**, 338–353 (1952).
[12] D. Bohm and D. Pines, "A collective description of electron interactions: III. Coulomb interactions in a degenerate electron gas," Phys. Rev. **92**, 609–625 (1953).
[13] H. Eshuis and F. Furche, "Basis set convergence of molecular correlation energy differences within the random phase approximation," J. Chem. Phys. **136**, 084105 (2012).
[14] A.-S. Hehn and W. Klopper, "Communication: Explicitly-correlated second-order correction to the correlation energy in the random-phase approximation," J. Chem. Phys. **138**, 181104 (2013).
[15] A.-S. Hehn, D. P. Tew, and W. Klopper, "Explicitly correlated ring-coupled-cluster-doubles theory," J. Chem. Phys. **142**, 194106 (2015).
[16] D. Traore, E. Giner, and J. Toulouse, "Basis-set correction based on density-functional theory: Linear-response formalism for excited-state energies," J. Chem. Phys. **158**, 234107 (2023).
[17] D. L. Freeman, "Coupled-cluster expansion applied to the electron gas: Inclusion of ring and exchange effects," Phys. Rev. B **15**, 5512–5521 (1977).
[18] G. E. Scuseria, T. M. Henderson, and D. C. Sorensen, "The ground state correlation energy of the random phase approximation from a ring coupled cluster doubles approach," J. Chem. Phys. **129**, 231101 (2008).
[19] G. E. Scuseria, T. M. Henderson, and I. W. Bulik, "Particle-particle and quasiparticle random phase approximations: Connections to coupled cluster theory," J. Chem. Phys. **139**, 104113 (2013).
[20] D. Peng, S. N. Steinmann, H. van Aggelen, and W. Yang, "Equivalence of particle-particle random phase approximation correlation energy and ladder-coupled-cluster doubles," J. Chem. Phys. **139**, 104112 (2013).
[21] M. F. Lange and T. C. Berkelbach, "On the relation between equation-of-motion coupled-cluster theory and the *GW* approximation," J. Chem. Theory Comput. **14**, 4224–4236 (2018).
[22] T. C. Berkelbach, "Communication: Random-phase approximation excitation energies from approximate equation-of-motion coupled-cluster doubles," J. Chem. Phys. **149**, 041103 (2018).
[23] V. Rishi, A. Perera, and R. J. Bartlett, "A route to improving RPA excitation energies through its connection to equation-of-motion coupled cluster theory," J. Chem. Phys. **153**, 234101 (2020).
[24] R. Quintero-Monsebaiz, E. Monino, A. Marie, and P.-F. Loos, "Connections between many-body perturbation and coupled-cluster theories," J. Chem. Phys. **157**, 231102 (2022).
[25] J. Tölle and G. Kin-Lic Chan, "Exact relationships between the *GW* approximation and equation-of-motion coupled-cluster theories through the quasi-boson formalism," J. Chem. Phys. **158**, 124123 (2023).
[26] J. Tölle, M.-P. Kitsaras, A. Irmler, A. Grüneis, and P.-F. Loos, "Connection between *GW* and extended coupled cluster," J. Chem. Theory Comput. **22**, 6471–6486 (2026).
[27] F. Furche, "Developing the random phase approximation into a practical post-Kohn–Sham correlation model," J. Chem. Phys. **129**, 114105 (2008).
[28] G. Jansen, R.-F. Liu, and J. G. Ángyán, "On the equivalence of ring-coupled cluster and adiabatic connection fluctuation-dissipation theorem random phase approximation correlation energy expressions," J. Chem. Phys. **133**, 154106 (2010).
[29] J. G. Ángyán, R.-F. Liu, J. Toulouse, and G. Jansen, "Correlation energy expressions from the adiabatic-connection fluctuation-dissipation theorem approach," J. Chem. Theory Comput. **7**, 3116–3130 (2011).
[30] H. Eshuis, J. E. Bates, and F. Furche, "Electron correlation methods based on the random phase approximation," Theor. Chem. Acc. **131**, 1084 (2012).
[31] E. Trushin, A. Thierbach, and A. Görling, "Toward chemical accuracy at low computational cost: Density-functional theory with σ-functionals for the correlation energy," J. Chem. Phys. **154**, 014104 (2021).
[32] E. Trushin, S. Fauser, A. Mölkner, J. Erhard, and A. Görling, "Accurate correlation potentials from the self-consistent random phase approximation," Phys. Rev. Lett. **134**, 016402 (2025).
[33] L. Hedin, "New method for calculating the one-particle Green's function with application to the electron-gas problem," Phys. Rev. **139**, A796 (1965).
[34] F. Aryasetiawan and O. Gunnarsson, "The *GW* method," Rep. Prog. Phys. **61**, 237–312 (1998).
[35] G. Onida, L. Reining, and A. Rubio, "Electronic excitations: Density-functional versus many-body Green's function approaches," Rev. Mod. Phys. **74**, 601–659 (2002).
[36] L. Reining, "The GW approximation: Content, successes and limitations: The GW approximation," WIREs Comput. Mol. Sci. **8**, e1344 (2017).
[37] D. Golze, M. Dvorak, and P. Rinke, "The GW compendium: A practical guide to theoretical photoemission spectroscopy," Front. Chem. **7**, 377 (2019).
[38] A. Marie, A. Ammar, and P.-F. Loos, "Chapter five—The *GW* approximation: A quantum chemistry perspective," in *Novel Treatments of Strong Correlations*, edited by R. A. M. Quintana and J. F. Stanton (Academic Press, 2024), Vol. 90, pp. 157–184.
[39] K. Sawada, K. A. Brueckner, N. Fukuda, and R. Brout, "Correlation energy of an electron gas at high density: Plasma oscillations," Phys. Rev. **108**, 507–514 (1957).
[40] R. Brout, "Correlation energy of a high-density gas: Plasma coordinates," Phys. Rev. **108**, 515–517 (1957).
[41] G. Wentzel, "Diamagnetism of a dense electron gas," Phys. Rev. **108**, 1593–1596 (1957).
[42] M. Gell-Mann and K. A. Brueckner, "Correlation energy of an electron gas at high density," Phys. Rev. **106**, 364–368 (1957).
[43] J. Hubbard and R. E. Peierls, "The description of collective motions in terms of many-body perturbation theory III. The extension of the theory to the non-uniform gas," Proc. R. Soc. London, Ser. A **244**, 199–211 (1958).

23 October 2026 12:05:00

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[44]P. Nozières and D. Pines, "Correlation energy of a free electron gas," Phys. Rev. **111**, 442–454 (1958).
[45]D. J. Thouless, "Stability conditions and nuclear rotations in the Hartree–Fock theory," Nucl. Phys. **21**, 225–232 (1960).
[46]D. J. Thouless, "Vibrational states of nuclei in the random phase approximation," Nucl. Phys. **22**, 78–95 (1961).
[47]G. E. Brown, J. A. Evans, and D. J. Thouless, "Vibrations of spherical nuclei," Nucl. Phys. **24**, 1–17 (1961).
[48]M. A. Ball and A. D. McLachlan, "Time-dependent Hartree–Fock theory," Mol. Phys. **7**, 501–513 (1964).
[49]T. H. Dunning and V. McKoy, "Nonempirical calculations on excited states: The ethylene molecule," J. Chem. Phys. **47**, 1735–1747 (1967).
[50]J. Dunning, H. Thomas, and V. McKoy, "Nonempirical calculations on excited states: The formaldehyde molecule," J. Chem. Phys. **48**, 5263–5270 (1968).
[51]J. Linderberg and M. Ratner, "Geometric approximation to two-particle Green function for ethylene," Chem. Phys. Lett. **6**, 37–40 (1970).
[52]T.-i. Shibuya and V. McKoy, "Application of a higher RPA to a model π-electron system," J. Chem. Phys. **53**, 3308–3314 (1970).
[53]N. Ostlund and M. Karplus, "The self-consistent random phase approximation," Chem. Phys. Lett. **11**, 450–453 (1971).
[54]P. Jørgensen and J. Oddershede, "Self-consistent polarization propagator calculations in the Pariser–Parr–pople model. A modified random phase method," J. Chem. Phys. **57**, 277–285 (1972).
[55]J. C. Ho, G. A. Segal, and H. S. Taylor, "Comparative study of the random-phase approximation, Hartree–Fock and single excited configuration-interaction methods of computing excitation properties of some molecules," J. Chem. Phys. **56**, 1520–1528 (1972).
[56]O. Tanimoto and K. Toyoda, "Calculation of lower excited electronic levels of benzene with the Green's function method," Mol. Phys. **24**, 1257–1264 (1972).
[57]K. D. Jordan, "Use of unrestricted Hartree–Fock wave functions in RPA calculations," Int. J. Quantum Chem. **7**, 491–504 (2009).
[58]X. Ren, P. Rinke, C. Joas, and M. Scheffler, "Random-phase approximation and its applications in computational chemistry and materials science," J. Mater. Sci. **47**, 7447–7471 (2012).
[59]G. P. Chen, V. K. Voora, M. M. Agee, S. G. Balasubramani, and F. Furche, "Random-phase approximation methods," Annu. Rev. Phys. Chem. **68**, 421–445 (2017).
[60]M. Jemaï and P. Schuck, "Symmetry conserving coupled cluster doubles wave function and the self-consistent odd particle number RPA," Eur. Phys. J. A **56**, 268 (2020).
[61]P. Schuck, D. S. Delion, J. Dukelsky, M. Jemaï, E. Litvinova, G. Röpke, and M. Tohyama, "Equation of motion method for strongly correlated Fermi systems and extended RPA approaches," Phys. Rep. **929**, 1–84 (2021).
[62]K. S. Singwi, M. P. Tosi, R. H. Land, and A. Sjölander, "Electron correlations at metallic densities," Phys. Rev. **176**, 589–599 (1968).
[63]H. Jiang and E. Engel, "Random-phase-approximation-based correlation energy functionals: Benchmark results for atoms," J. Chem. Phys. **127**, 184108 (2007).
[64]A. Förster, "Assessment of the second-order statically screened exchange correction to the random phase approximation for correlation energies," J. Chem. Theory Comput. **18**, 5948–5965 (2022).
[65]K. Takayanagi, K. Shimizu, and A. Arima, "A generalized RPA theory of the nuclear response function," Nucl. Phys. A **477**, 205–230 (1988).
[66]K. Takayanagi, K. Shimizu, and A. Arima, "A theoretical study of magnetic dipole transitions in ^{48}Ca," Nucl. Phys. A **481**, 313–332 (1988).
[67]S. Nishizaki, S. Droździ, J. Wambach, and J. Speth, "Ground state correlation effects on the Gamow–Teller strength distribution in ^{48}Ca," Phys. Lett. B **215**, 231–236 (1988).
[68]S. Adachi and E. Lipparini, "Sum rules in extended RPA theories," Nucl. Phys. A **489**, 445–460 (1988).
[69]S. Drozdz, S. Nishizaki, J. Speth, and J. Wambach, "The nuclear response within extended RPA theories," Phys. Rep. **197**, 1–65 (1990).
[70]A. Mariano, F. Krmpotić, and A. F. R. de Toledo Piza, "Ground-state correlation effects in extended random phase approximation calculations," Phys. Rev. C **49**, 2824–2827 (1994).
[71]P. Joshi and V. K. Voora, "Generalized perturbative singles corrections to the random phase approximation method: Impact on noncovalent interaction energies of closed- and open-shell dimers," J. Chem. Phys. **160**, 044104 (2024).
[72]K. Chatterjee and K. Pernal, "Excitation energies from extended random phase approximation employed with approximate one- and two-electron reduced density matrices," J. Chem. Phys. **137**, 204109 (2012).
[73]H. van Aggelen, B. Verstichel, G. Acke, M. Degroote, P. Bultinck, P. W. Ayers, and D. Van Neck, "Extended random phase approximation method for atomic excitation energies from correlated and variationally optimized second-order density matrices," Comput. Theor. Chem. **1003**, 50–54 (2013).
[74]K. Pernal, K. Chatterjee, and P. H. Kowalski, "How accurate is the strongly orthogonal geminal theory in predicting excitation energies? Comparison of the extended random phase approximation and the linear response theory approaches," J. Chem. Phys. **140**, 014101 (2014).
[75]K. Pernal, "Intergeminal correction to the antisymmetrized product of strongly orthogonal geminals derived from the extended random phase approximation," J. Chem. Theory Comput. **10**, 4332–4341 (2014).
[76]I. DePrince and A. Eugene, "Variational optimization of the two-electron reduced-density matrix under pure-state N-representability conditions," J. Chem. Phys. **145**, 164109 (2016).
[77]K. Pernal, "Electron correlation from the adiabatic connection for multireference wave functions," Phys. Rev. Lett. **120**, 013001 (2018).
[78]E. Maradzike and A. Eugene DePrince III, "Modeling core-level excitations with variationally optimized reduced-density matrices and the extended random phase approximation," J. Chem. Phys. **149**, 234101 (2018).
[79]A. K. Kerman and A. Klein, "Generalized Hartree–Fock approximation for the calculation of collective states of a finite many-particle system," Phys. Rev. **132**, 1326–1342 (1963).
[80]K.-j. Hara, "An extended boson approximation in the theory of nuclear structure," Prog. Theor. Phys. **32**, 88–105 (1964).
[81]G. D. Dang and A. Klein, "Theory of the anharmonicity in the vibrational motion of even–even spherical nuclei," Phys. Rev. **133**, B257–B267 (1964).
[82]K. Ikeda, T. Udagawa, and H. Yamaura, "On the effect of Pauli principle on collective vibrations in nuclei," Prog. Theor. Phys. **33**, 22–37 (1965).
[83]J. Da Providência, "Variational approach to the many-body problem," Nucl. Phys. **61**, 87–96 (1965).
[84]D. J. Rowe, "Methods for calculating ground-state correlations of vibrational nuclei," Phys. Rev. **175**, 1283–1292 (1968).
[85]E. R. Marshalek and J. Weneser, "Nuclear rotation and the random-phase approximation," Ann. Phys. **53**, 569–624 (1969).
[86]E. R. Marshalek and J. Weneser, "Nuclear rotation and boson expansions. I," Phys. Rev. C **2**, 1682–1714 (1970).
[87]E. R. Marshalek, "Boson expansions and broken symmetry," Ann. Phys. **143**, 191–238 (1982).
[88]E. R. Marshalek, "Reconstituting rotational band structure from deformed boson expansions: Generic treatment," Phys. Rev. C **35**, 1900–1921 (1987).
[89]F. Catara, P. Chomaz, and N. Van Giai, "High-lying two-phonon states in ^{40}Ca," Phys. Lett. B **233**, 6–10 (1989).
[90]M. Sambataro and F. Catara, "Extended random-phase approximation in a boson formalism with Pauli principle," Phys. Rev. C **51**, 3066–3077 (1995).
[91]M. Sambataro and J. Suhonen, "Quasiparticle random-phase approximation and β-decay physics: Higher-order approximations in a boson formalism," Phys. Rev. C **56**, 782–790 (1997).
[92]D. Gambacurta, M. Sambataro, and F. Catara, "Solvable many-level pairing model in a boson formalism," Phys. Rev. C **73**, 014310 (2006).
[93]N. R. Werthamer and H. Suhl, "Renormalization of many-fermion momentum-space distributions in higher random phase approximations," Phys. Rev. **125**, 1402–1406 (1962).
[94]G. Fano and J. Sawicki, "The higher random phase approximation and the stability of the energy spectrum of the nuclear shell model," Il Nuovo Cimento **25**, 586–602 (1962).
[95]J. Sawicki, "Higher random phase approximation and energy spectra of spherical nuclei," Phys. Rev. **126**, 2231–2238 (1962).

23 October 2026 12:05:00

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[96]T. Tamura and T. Udagawa, "Higher random phase approximation applied to the description of the spherical vibrational nuclei," Nucl. Phys. **53**, 33–53 (1964).
[97]S. Adachi and N. Van Giai, "Spreading effects on the isovector dipole strength distribution in ^{208}Pb," Phys. Lett. B **149**, 447–450 (1984).
[98]S. Drozdz, V. Klemt, J. Speth, and J. Wambach, "Giant Gamow–Teller resonances in nuclei described with realistic two-body interactions," Phys. Lett. B **166**, 18–22 (1986).
[99]D. Gambacurta and F. Catara, "Second random phase approximation studies in metallic clusters," Phys. Rev. B **79**, 085403 (2009).
[100]D. Gambacurta, M. Grasso, and F. Catara, "Collective nuclear excitations with skyrme-second random-phase approximation," Phys. Rev. C **81**, 054312 (2010).
[101]P. Papakonstantinou and R. Roth, "Large-scale second random-phase approximation calculations with finite-range interactions," Phys. Rev. C **81**, 024317 (2010).
[102]D. Peng, Y. Yang, P. Zhang, and W. Yang, "Restricted second random phase approximations and Tamm-Dancoff approximations for electronic excitation energy calculations," J. Chem. Phys. **141**, 214102 (2014).
[103]J. Högaasen-Feldman, "A study of some approximations of the pairing force," Nucl. Phys. **28**, 258–269 (1961).
[104]J. G. Hirsch, A. Mariano, J. Dukelsky, and P. Schuck, "Fully self-consistent RPA description of the many level pairing model," Ann. Phys. **296**, 187–213 (2002).
[105]J. Dukelsky, G. G. Dussel, J. G. Hirsch, and P. Schuck, "Comparison between exact and approximate treatments of the pairing interaction for finite Fermi systems," Nucl. Phys. A **714**, 63–74 (2003).
[106]H. van Aggelen, Y. Yang, and W. Yang, "Exchange-correlation energy from pairing matrix fluctuation and the particle-particle random-phase approximation," Phys. Rev. A **88**, 030501 (2013).
[107]Y. Yang, H. van Aggelen, S. N. Steinmann, D. Peng, and W. Yang, "Benchmark tests and spin adaptation for the particle-particle random phase approximation," J. Chem. Phys. **139**, 174110 (2013).
[108]D. Zhang, D. Peng, P. Zhang, and W. Yang, "Analytic gradients, geometry optimization and excited state potential energy surfaces from the particle-particle random phase approximation," Phys. Chem. Chem. Phys. **17**, 1025–1038 (2015).
[109]J. Toulouse, I. C. Gerber, G. Jansen, A. Savin, and J. G. Ángyán, "Adiabatic-connection fluctuation-dissipation density-functional theory based on range separation," Phys. Rev. Lett. **102**, 096404 (2009).
[110]J. Toulouse, W. Zhu, J. G. Ángyán, and A. Savin, "Range-separated density-functional theory with the random-phase approximation: Detailed formalism and illustrative applications," Phys. Rev. A **82**, 032502 (2010).
[111]W. Kutzelnigg, "r_{12}-dependent terms in the wave function as closed sums of partial wave amplitudes for large l," Theor. Chim. Acta **68**, 445–469 (1985).
[112]W. Kutzelnigg and W. Klopper, "Wave functions with terms linear in the interelectronic coordinates to take care of the correlation cusp. I. General theory," J. Chem. Phys. **94**, 1985–2001 (1991).
[113]J. Noga and W. Kutzelnigg, "Coupled cluster theory that takes care of the correlation cusp by inclusion of linear terms in the interelectronic coordinates," J. Chem. Phys. **101**, 7738–7762 (1994).
[114]S. Ten-no and J. Noga, "Explicitly correlated electronic structure theory from R12/F12 ansatze," WIREs Comput. Mol. Sci. **2**, 114–125 (2012).
[115]E. Giner, B. Pradines, A. Ferté, R. Assaraf, A. Savin, and J. Toulouse, "Curing basis-set convergence of wave-function theory using density-functional theory: A systematically improvable approach," J. Chem. Phys. **149**, 194301 (2018).
[116]P. F. Loos, B. Pradines, A. Scemama, J. Toulouse, and E. Giner, "A density-based basis-set correction for wave function theory," J. Phys. Chem. Lett. **10**, 2931–2937 (2019).
[117]E. Giner, A. Scemama, J. Toulouse, and P. F. Loos, "Chemically accurate excitation energies with small basis sets," J. Chem. Phys. **151**, 144118 (2019).
[118]P. F. Loos, B. Pradines, A. Scemama, E. Giner, and J. Toulouse, "A density-based basis-set incompleteness correction for GW methods," J. Chem. Theory Comput. **16**, 1018–1028 (2020).
[119]E. Giner, A. Scemama, P.-F. Loos, and J. Toulouse, "A basis-set error correction based on density-functional theory for strongly correlated molecular systems," J. Chem. Phys. **152**, 174104 (2020).
[120]J. O. Hirschfelder, "Removal of electron-electron poles from many-electron hamiltonians," J. Chem. Phys. **39**, 3145–3146 (1963).
[121]S. F. Boys and N. C. Handy, "A calculation for the energies and wavefunctions for states of neon with full electronic correlation accuracy," Proc. R. Soc. London, Ser. A **310**, 63–78 (1969).
[122]R. Jastrow, "Many-body problem with strong forces," Phys. Rev. **98**, 1479–1484 (1955).
[123]O. Hino, Y. Tanimura, and S. Ten-no, "Biorthogonal approach for explicitly correlated calculations using the transcorrelated Hamiltonian," J. Chem. Phys. **115**, 7865–7871 (2001).
[124]M. Ochi and S. Tsuneyuki, "Second-order Møller–Plesset perturbation theory for the transcorrelated Hamiltonian applied to solid-state calculations," Chem. Phys. Lett. **621**, 177–183 (2015).
[125]H. J. A. Zweistra, C. C. M. Samson, and W. Klopper, "Similarity-transformed Hamiltonians by means of Gaussian-damped interelectronic distances," Collect. Czech. Chem. Commun. **68**, 374–386 (2003).
[126]S. Tsuneyuki, "Transcorrelated method: Another possible way towards electronic structure calculation of solids," Prog. Theor. Phys. Suppl. **176**, 134–142 (2008).
[127]H. Luo, "Complete optimisation of multi-configuration jastrow wave functions by variational transcorrelated method," J. Chem. Phys. **135**, 024109 (2011).
[128]M. Ochi and S. Tsuneyuki, "Optical absorption spectra calculated from a first-principles wave function theory for solids: Transcorrelated method combined with configuration interaction singles," J. Chem. Theory Comput. **10**, 4098–4103 (2014).
[129]E. Giner, "A new form of transcorrelated hamiltonian inspired by range-separated dft," J. Chem. Phys. **154**, 084119 (2021).
[130]A. Ammar, A. Scemama, and E. Giner, "Extension of selected configuration interaction for transcorrelated methods," J. Chem. Phys. **157**, 134107 (2022).
[131]A. Ammar, E. Giner, and A. Scemama, "Optimization of large determinant expansions in quantum Monte Carlo," J. Chem. Theory Comput. **18**, 5325–5336 (2022).
[132]H. Luo and A. Alavi, "Combining the transcorrelated method with full configuration interaction quantum Monte Carlo: Application to the homogeneous electron gas," J. Chem. Theory Comput. **14**, 1403–1411 (2018).
[133]W. Dobrautz, H. Luo, and A. Alavi, "Compact numerical solutions to the two-dimensional repulsive Hubbard model obtained via nonunitary similarity transformations," Phys. Rev. B **99**, 075119 (2019).
[134]A. J. Cohen, H. Luo, K. Guther, W. Dobrautz, D. P. Tew, and A. Alavi, "Similarity transformation of the electronic Schrödinger equation via Jastrow factorization," J. Chem. Phys. **151**, 061101 (2019).
[135]W. Dobrautz, A. J. Cohen, A. Alavi, and E. Giner, "Performance of a one-parameter correlation factor for transcorrelation: Study on a series of second row atomic and molecular systems," J. Chem. Phys. **156**, 234108 (2022).
[136]P. Jeszenszki, U. Ebling, H. Luo, A. Alavi, and J. Brand, "Eliminating the wave-function singularity for ultracold atoms by a similarity transformation," Phys. Rev. Res. **2**, 043270 (2020).
[137]K. Guther, A. J. Cohen, H. Luo, and A. Alavi, "Binding curve of the beryllium dimer using similarity-transformed FCIQMC: Spectroscopic accuracy with triple-zeta basis sets," J. Chem. Phys. **155**, 011102 (2021).
[138]J. P. Haupt, S. M. Hosseini, P. López Ríos, W. Dobrautz, A. Cohen, and A. Alavi, "Optimizing Jastrow factors for the transcorrelated method," J. Chem. Phys. **158**, 224105 (2023).
[139]O. Hino, Y. Tanimura, and S. Ten-no, "Application of the transcorrelated Hamiltonian to the linearized coupled cluster singles and doubles model," Chem. Phys. Lett. **353**, 317–323 (2002).
[140]S. Ten-no and O. Hino, "New transcorrelated method improving the feasibility of explicitly correlated calculations," Int. J. Mol. Sci. **3**, 459–474 (2002).
[141]K. Liao, T. Schraivogel, H. Luo, D. Kats, and A. Alavi, "Towards efficient and accurate *ab initio* solutions to periodic systems via transcorrelation and coupled cluster theory," Phys. Rev. Res. **3**, 033072 (2021).
[142]T. Schraivogel, A. J. Cohen, A. Alavi, and D. Kats, "Transcorrelated coupled cluster methods," J. Chem. Phys. **155**, 191101 (2021).
[143]A. Baiardi and M. Reiher, "Transcorrelated density matrix renormalization group," J. Chem. Phys. **153**, 164115 (2020).

23 October 2026 12:05:00

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[144]A. Baiardi, M. Lesiuk, and M. Reiher, "Explicitly correlated electronic structure calculations with transcorrelated matrix product operators," J. Chem. Theory Comput. **18**, 4203–4217 (2022).
[145]Y. Imamura and G. E. Scuseria, "A new correlation functional based on a transcorrelated Hamiltonian," J. Chem. Phys. **118**, 2464–2469 (2003).
[146]N. Umezawa, "Extended screened exchange functional derived from transcorrelated density functional theory," J. Chem. Phys. **147**, 104104 (2017).
[147]H. Luo and A. Alavi, "Perturbation calculation of the uniform electron gas with a transcorrelated Hamiltonian," J. Chem. Phys. **157**, 074105 (2022).
[148]H. Luo and A. Alavi, "Transcorrelated approach to the thermodynamic limit," Phys. Rev. B **113**, 165146 (2026).
[149]J. P. Haupt, E. M. C. Christlmaier, P. López Ríos, N. A. Bogdanov, D. Kats, and A. Alavi, "Transcorrelated methods for multireference problems," J. Chem. Phys. **163**, 144113 (2025).
[150]S. McArdle and D. P. Tew, "Improving the accuracy of quantum computational chemistry using the transcorrelated method," arXiv:2006.11181 (2020).
[151]I. O. Sokolov, W. Dobrautz, H. Luo, A. Alavi, and I. Tavernelli, Phys. Rev. Res. **5**, 023174 (2023).
[152]W. Dobrautz, I. O. Sokolov, K. Liao, P. L. Ríos, M. Rahm, A. Alavi, and I. Tavernelli, "Toward real chemical accuracy on current quantum hardware through the transcorrelated method," J. Chem. Theory Comput. **20**, 4146–4160 (2024).
[153]A. Uvarov and A. F. Izmaylov, "Accuracy and resource advantages of quantum eigenvalue estimation with non-Hermitian transcorrelated electronic Hamiltonians," J. Chem. Theory Comput. **22**, 6431–6443 (2026).
[154]A. D. Mclachlan and M. A. Ball, "Time-dependent Hartree–Fock theory for molecules," Rev. Mod. Phys. **36**, 844–855 (1964).
[155]J. Harris and R. O. Jones, "The surface energy of a bounded electron gas," J. Phys. F: Met. Phys. **4**, 1170 (1974).
[156]D. C. Langreth and J. P. Perdew, "The exchange-correlation energy of a metallic surface," Solid State Commun. **17**, 1425–1429 (1975).
[157]O. Gunnarsson and B. I. Lundqvist, "Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism," Phys. Rev. B **13**, 4274–4298 (1976).
[158]D. C. Langreth and J. P. Perdew, "Exchange-correlation energy of a metallic surface: Wave-vector analysis," Phys. Rev. B **15**, 2884–2901 (1977).
[159]B. Mussard, P. Reinhardt, J. G. Ángyán, and J. Toulouse, "Spin-unrestricted random-phase approximation with range separation: Benchmark on atomization energies and reaction barrier heights," J. Chem. Phys. **142**, 154123 (2015).
[160]V. Lotrich and R. J. Bartlett, "External coupled-cluster perturbation theory: Description and application to weakly interaction dimers. Corrections to the random phase approximation," J. Chem. Phys. **134**, 184108 (2011).
[161]W. Klopper, A. M. Teale, S. Coriani, T. B. Pedersen, and T. Helgaker, "Spin flipping in ring-coupled-cluster-doubles theory," Chem. Phys. Lett. **510**, 147–153 (2011).
[162]M. Jemaï, D. S. Delion, and P. Schuck, "Self-consistent random-phase approximation from a coupled-cluster wave function perspective," Phys. Rev. C **88**, 044004 (2013).
[163]Á. Szabados and Á. Margócsy, "Ring coupled-cluster doubles correction to geminal wavefunctions," Mol. Phys. **115**, 2731–2742 (2017).
[164]Á. Margócsy and Á. Szabados, "Ring coupled cluster doubles at the multireference level," J. Chem. Phys. **152**, 204114 (2020).
[165]N. E. Dahlen, R. van Leeuwen, and U. von Barth, "Variational energy functionals of the Green function and of the density tested on molecules," Phys. Rev. A **73**, 012511 (2006).
[166]F. Caruso, D. R. Rohr, M. Hellgren, X. Ren, P. Rinke, A. Rubio, and M. Scheffler, "Bond breaking and bond formation: How electron correlation is captured in many-body perturbation theory and density-functional theory," Phys. Rev. Lett. **110**, 146403 (2013).
[167]T. Ando, "Inter-subband optical absorption in space-charge layers on semiconductor surfaces," Z. Phys. B: Condens. Matter Quanta **26**, 263–272 (1977).
[168]J. Oddershede, P. Jørgensen, and N. H. F. Beebe, "Coupled Hartree–Fock and second order polarization propagator calculations of indirect nuclear spin–spin coupling constants for diatomic molecules," Chem. Phys. **25**, 451–458 (1977).
[169]P. Jørgensen, "Molecular and atomic applications of time-dependent Hartree–Fock theory," Annu. Rev. Phys. Chem. **26**, 359–380 (1975).
[170]J. Oddershede, "Polarization propagator calculations," in *Advances in Quantum Chemistry*, edited by P.-O. Löwdin (Academic Press, 1978), Vol. 11, pp. 275–352.
[171]A. Zangwill and P. Soven, "Density-functional approach to local-field effects in finite systems: Photoabsorption in the rare gases," Phys. Rev. A **21**, 1561–1572 (1980).
[172]M. J. Stott and E. Zaremba, "Linear-response theory within the density-functional formalism: Application to atomic polarizabilities," Phys. Rev. A **21**, 12–23 (1980).
[173]E. Gross and W. Kohn, *Time-Dependent Density-Functional Theory*, *Density Functional Theory of Many-Fermion Systems*, edited by P.-O. Löwdin (Academic Press, 1990), Vol. 21, pp. 255–291.
[174]F. Furche, "Molecular tests of the random phase approximation to the exchange-correlation energy functional," Phys. Rev. B **64**, 195120 (2001).
[175]D. J. Rowe, "An intepretation of time-dependent Hartree–Fock theory," Nucl. Phys. **80**, 209–222 (1966).
[176]D. J. Rowe, "Equations-of-motion method and the extended shell model," Rev. Mod. Phys. **40**, 153–166 (1968).
[177]A. Ammar, A. Scemama, P.-F. Loos, and E. Giner, "Compactification of determinant expansions via transcorrelation," J. Chem. Phys. **161**, 084104 (2024).
[178]M. Moshinsky and T. Seligman, "Group theory and second quantization for nonorthogonal orbitals," Ann. Phys. **66**, 311–334 (1971).
[179]D. C. Brody, "Biorthogonal quantum mechanics," J. Phys. A: Math. Theor. **47**, 035305 (2013).
[180]A. Ammar, A. Scemama, and E. Giner, "Biorthonormal orbital optimization with a cheap core-electron-free three-body correlation factor for quantum Monte Carlo and transcorrelation," J. Chem. Theory Comput. **19**, 4883–4896 (2023).
[181]A. Ammar, A. Scemama, and E. Giner, "Transcorrelated selected configuration interaction in a bi-orthonormal basis and with a cheap three-body correlation factor," J. Chem. Phys. **159**, 114121 (2023).
[182]P.-G. Reinhard and Y. K. Gambhir, "RPA in wavefunction representation," Ann. Phys. **504**, 598–631 (1992).
[183]P. Ring and P. Schuck, *The Nuclear Many-Body Problem* (Springer, 2004).
[184]X. Blase, I. Duchemin, D. Jacquemin, and P.-F. Loos, "The Bethe–Salpeter equation formalism: From physics to chemistry," J. Phys. Chem. Lett. **11**, 7371–7382 (2020).
[185]M. Nooijen and R. J. Bartlett, "A new method for excited states: Similarity transformed equation-of-motion coupled-cluster theory," J. Chem. Phys. **106**, 6441–6448 (1997).
[186]M. Nooijen and R. J. Bartlett, "Similarity transformed equation-of-motion coupled-cluster theory: Details, examples, and comparisons," J. Chem. Phys. **107**, 6812–6830 (1997).
[187]M. Nooijen and R. J. Bartlett, "Similarity transformed equation-of-motion coupled-cluster study of ionized, electron attached, and excited states of free base porphin," J. Chem. Phys. **106**, 6449–6455 (1997).
[188]T. Holstein and H. Primakoff, "Field dependence of the intrinsic domain magnetization of a ferromagnet," Phys. Rev. **58**, 1098–1113 (1940).
[189]S. T. Beliaev and V. G. Zelevinsky, "Anharmonic effects of quadrupole oscillations of spherical nuclei," Nucl. Phys. **39**, 582–604 (1962).
[190]G. Ripka and J. P. Blaizot, *Quantum Theory of Finite Systems* (MIT Press, 1986).
[191]K. E. Schmidt and J. W. Moskowitz, "Correlated monte carlo wave functions for the atoms He through Ne," J. Chem. Phys. **93**, 4172–4178 (1990).
[192]P. T. A. Galek, N. C. Handy, and W. A. Lester, Jr., "Quantum Monte Carlo studies on small molecules," Mol. Phys. **104**, 3069–3085 (2006).
[193]A. D. Becke, "A multicenter numerical integration scheme for polyatomic molecules," J. Chem. Phys. **88**, 2547–2553 (1988).
[194]M. E. Mura and P. J. Knowles, "Improved radial grids for quadrature in molecular density-functional calculations," J. Chem. Phys. **104**, 9848–9858 (1996).
[195]Y. Garniron, T. Applencourt, K. Gasperich, A. Benali, A. Ferté, J. Paquier, B. Pradines, R. Assaraf, P. Reinhardt, J. Toulouse, P. Barbaresco, N. Renon, G. David, J.-P. Malrieu, M. Véril, M. Caffarel, P.-F. Loos, E. Giner, and A. Scemama, "Quantum package 2.0: An open-source determinant-driven suite of programs," J. Chem. Theory Comput. **15**, 3591–3609 (2019).

23 October 2026 12:05:00

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[196]J. Dunning and H. Thom, "Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen," J. Chem. Phys. **90**, 1007–1023 (1989).
[197]R. A. Kendall, T. H. Dunning, Jr., R. J. Harrison, and R. J. Harrison, "Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions," J. Chem. Phys. **96**, 6796–6806 (1992).
[198]D. E. Woon, J. Dunning, and H. Thom, "Gaussian basis sets for use in correlated molecular calculations. V. Core-valence basis sets for boron through neon," J. Chem. Phys. **103**, 4572–4585 (1995).
[199]P.-F. Loos, A. Scemama, A. Blondel, Y. Garniron, M. Caffarel, and D. Jacquemin, "A mountaineering strategy to excited states: Highly accurate reference energies and benchmarks," J. Chem. Theory Comput. **14**, 4360–4379 (2018).
[200]P.-F. Loos, A. Scemama, and D. Jacquemin, "The quest for highly accurate excitation energies: A computational perspective," J. Phys. Chem. Lett. **11**, 2374–2383 (2020).
[201]M. Véril, A. Scemama, M. Caffarel, F. Lipparini, M. Boggio-Pasqua, D. Jacquemin, and P.-F. Loos, "QUESTDB: A database of highly accurate excitation energies for the electronic structure community," WIREs Comput. Mol. Sci. **11**, e1517 (2021).
[202]P.-F. Loos, M. Boggio-Pasqua, A. Blondel, F. Lipparini, and D. Jacquemin, "QUEST database of highly-accurate excitation energies," J. Chem. Theory Comput. **21**, 8010–8033 (2025).
[203]D. P. O'eill and P. M. W. Gill, "Benchmark correlation energies for small molecules," Mol. Phys. **103**, 763–766 (2005).
[204]M. Caffarel, T. Applencourt, E. Giner, and A. Scemama, "Communication: Toward an improved control of the fixed-node error in quantum Monte Carlo: The case of the water molecule," J. Chem. Phys. **144**, 151103 (2016).
[205]K. Simula, M.-A. Filip, and A. Alavi, "Transcorrelated theory for transition-metal atoms," Phys. Rev. A **112**, 032805 (2025).
[206]M. Dash, J. Feldt, S. Moroni, A. Scemama, and C. Filippi, "Excited states with selected configuration interaction-quantum Monte Carlo: Chemically accurate excitation energies and geometries," J. Chem. Theory Comput. **15**, 4896–4906 (2019).

23 October 2026 12:05:00

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