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ABSTRACT

The accurate prediction of ionization potentials (IPs) is central to understanding molecular reactivity, redox behavior, and spectroscopic properties. While vertical IPs can be accessed directly from electronic excitations at fixed nuclear geometries, the computation of adiabatic IPs requires nuclear gradients of the ionized states, posing a major theoretical and computational challenge, especially within correlated frameworks. Among the most promising approaches for IP calculations is the many-body Green's function GW method, which provides a balanced compromise between accuracy and computational efficiency. Furthermore, it is applicable to both finite and extended systems. Recent work has established formal connections between GW and coupled-cluster doubles (CCD) theory, leading to the first derivation of analytic GW nuclear gradients via a unitary CCD framework. In this work, we present an alternative, fully analytic formulation of GW nuclear gradients based on a modified version of the traditional equation-of-motion CCD formalism, enabling the inclusion of missing correlation effects in the traditional CCD methods.

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I. INTRODUCTION

The ionization potential (IP) of a molecule, defined as the minimum energy required to remove an electron from a neutral species in its ground state, is a fundamental property that governs its reactivity, redox behavior, and spectroscopic signatures. Two main types of IPs are commonly distinguished: the vertical ionization potential (VIP) and the adiabatic ionization potential (AIP). These differ in whether or not nuclear relaxation of the ionic state is considered.

The VIP refers to the energy required to remove an electron without allowing the nuclei to move. In other words, the ionized state is constrained to the equilibrium geometry of the neutral molecule. This vertical transition approximates the Franck–Condon principle and is representative of ultrafast ionization events, where the nuclei remain effectively frozen during the electronic transition.

Experimentally, VIPs manifest as sharp, intense peaks in photoelectron spectroscopy (PES), particularly when probed using ultraviolet or x-ray photons for valence and core levels, respectively.

In contrast, the AIP accounts for full nuclear relaxation in both the neutral and ionized states. It represents the true thermodynamic threshold for ionization, corresponding to the energy difference between the neutral ground state and the fully relaxed ionic ground state. As such, AIPs are directly linked to gas-phase thermochemistry and redox potentials. In PES experiments, AIPs appear as the onset of a given ionization band, while the corresponding VIP aligns with the maximum of the corresponding band. High-resolution PES, and in particular threshold photoelectron spectroscopy (TPES), are capable of resolving this onset with sufficient precision to extract both AIP and VIP from a single measurement.¹

The energy difference between VIP and AIP, known as the relaxation energy, provides insight into the structural reorganization

of the molecule upon ionization. A large relaxation energy indicates a significant geometric change, whereas a small value suggests that the neutral and ionic states share similar geometries. The simultaneous analysis of AIP and VIP in high-resolution PES thus enables a detailed understanding of the interplay between electronic structure and nuclear dynamics during ionization.

From a theoretical standpoint, the evaluation of VIPs is relatively straightforward. It requires knowledge of the ground-state equilibrium geometry and the ability to compute total energies of the neutral and cationic species at this fixed geometry. This can be achieved using standard electronic structure methods or, more efficiently, by computing excitation energies corresponding to electron removal (i.e., ionization) from the reference neutral ground state.

In contrast, the calculation of AIPs is more demanding as it involves geometry optimization of the ionized species. This requires access to nuclear gradients of the ionized state, i.e., the first derivatives of the cationic energy with respect to the nuclear coordinates. Unlike ground-state gradients, which are routinely available in most quantum chemistry packages,^{2–5} analytic gradients for charged excited states are significantly more challenging to derive and implement,⁶ especially within correlated or many-body frameworks.^{7–10} Nonetheless, these gradients are essential to perform geometry optimization, typically using a Newton–Raphson procedure, until a stationary point corresponding to the relaxed ionic minimum is reached.

While various computational approaches exist for accessing charged excitations, ranging from state-specific (e.g., ΔSCF) to equation-of-motion/linear-response formalisms,^{11,12} one particularly promising method is the *GW* approximation^{13–17} from many-body Green's function theory.^{18,19} The *GW* formalism provides a robust framework to compute IPs^{20–33} and electron affinities (EAs)^{20–22,34–37} by approximating Hedin's equations.^{13,38} It gained popularity due to its favorable balance between accuracy and computational cost. Its results often rival those of high-level wavefunction-based approaches, while remaining applicable to much larger molecular systems^{38,33,39–55} and, importantly, periodic materials.^{18,19} Although traditionally limited to finite systems, equation-of-motion coupled-cluster (EOM-CC) has very recently been extended to periodic systems as well, using both Gaussian and plane-wave basis sets.^{56,57}

Recently, based on the established theoretical connections^{58–60} between *GW* and coupled-cluster doubles (CCD) theory,^{61–66} Tölle derived and implemented the first fully analytic *GW* nuclear gradients⁶⁷ (also see Refs. 68–73). His work has subsequently been extended to the first fully analytic Bethe–Salpeter equation (BSE)^{74,75} nuclear gradients,^{76–83} effectively generalizing the present formalism to neutral (optical) excited states.^{84,85} These pioneering results exploit theoretical connections between *GW* and the unitary CCD (UCCD)^{86–92} framework.⁶⁰ However, this approach necessitates the numerical evaluation of an infinite series of nested (anti)commutators, which is a non-standard numerical technique in traditional CCD implementations.

It would be, therefore, desirable to reformulate the *GW* nuclear gradients to leverage the well-established traditional EOM-CCD framework, as well as its extension to analytic properties. Unfortunately, a direct application of the traditional EOM-CCD formalism to *GW* is hindered by the missing correlation effects, as analyzed

in detail in Refs. 60 and 93. In this work, we demonstrate how this obstacle can be overcome by introducing a modified version of the traditional EOM-CCD formalism, which we refer to as IP/EA-EOM-λ-direct-ring CCD. This approach allows (i) for the inclusion of missing correlation effects and (ii) the derivation of analytic *GW* nuclear gradients within a more standard CC Lagrangian framework.

II. THEORY

A. The *GW* approximation

Similar to other Green's function approaches, the *GW* one-body Green's function *G* is expressed using the recursive Dyson equation,

$$G = G_0 + G_0 \Sigma G. \quad (1)$$

The mean-field reference one-body Green's function, *G*₀, which, for the current study, corresponds to the Hartree–Fock (HF) approximation, is given by

$$G_0(\mathbf{x}_1 \mathbf{x}_2; \omega) = \sum_i \frac{\phi_i^*(\mathbf{x}_1) \phi_i(\mathbf{x}_2)}{\omega - \epsilon_i^{\text{HF}}} + \sum_a \frac{\phi_a^*(\mathbf{x}_1) \phi_a(\mathbf{x}_2)}{\omega - \epsilon_a^{\text{HF}}}, \quad (2)$$

where $\phi_p(\mathbf{x})$ and ϵ_p^{HF} are the canonical HF orbitals and their corresponding energies, respectively. Similarly, the exact one-body Green's function is expressed as

$$G(\mathbf{x}_1 \mathbf{x}_2; \omega) = \sum_I \frac{\psi_I^*(\mathbf{x}_1) \psi_I(\mathbf{x}_2)}{\omega - \epsilon_I} + \sum_A \frac{\psi_A^*(\mathbf{x}_1) \psi_A(\mathbf{x}_2)}{\omega - \epsilon_A}, \quad (3)$$

where $\psi_I(\mathbf{x})$ and $\psi_A(\mathbf{x})$ are the so-called Dyson orbitals. The exact Green's function has poles at the energy differences associated with the electron-detached (hole states) and electron-attached (particle states) processes, namely, $\epsilon_I = E_0^N - E_I^{N-1}$ and $\epsilon_A = E_A^{N+1} - E_0^N$, where E_0^N is the ground-state energy of the neutral *N*-electron system and E_I^{N-1} and E_A^{N+1} are the energies of the corresponding (*N*–1)- and (*N*+1)-electron states, respectively. Within the quasiparticle approximation, where only ionized and electron-attached states with a dominant single-particle character are retained, the Green's function reduces to the quasiparticle form

$$G(\mathbf{x}_1 \mathbf{x}_2; \omega) = \sum_i \frac{\psi_i^*(\mathbf{x}_1) \psi_i(\mathbf{x}_2)}{\omega - \epsilon_i} + \sum_a \frac{\psi_a^*(\mathbf{x}_1) \psi_a(\mathbf{x}_2)}{\omega - \epsilon_a}, \quad (4)$$

where ϵ_i and ϵ_a denote the hole and particle quasiparticle energies, respectively. In the following, the standard convention is used for the orbital indices, with i, j, k, \dots denoting hole states, a, b, c, \dots denoting particle states, and p, q, r, \dots indicating either occupied or virtual orbitals.

The dynamical self-energy Σ describes correlation effects beyond the mean-field approximation. In *GW*, the self-energy is constructed using the dynamically screened Coulomb interaction computed at the random-phase approximation (RPA) level of theory^{94–100} and is given by

$$\Sigma_{pq}(\omega) = \sum_{i\mu} \frac{(pi|\mu)(\mu|qi)}{\omega - \epsilon_i + \Omega_\mu} + \sum_{a\mu} \frac{(ap|\mu)(\mu|aq)}{\omega - \epsilon_a - \Omega_\mu}. \quad (5)$$

The quasiparticle energies and the effective two-electron integrals,

$$\langle pq|\mu \rangle = \sum_{ia} [\langle pa|qi\rangle x_{i,\mu}^a + \langle pi|qa\rangle y_{a,\mu}^i], \quad (6a)$$

$$\langle \mu|pq \rangle = \sum_{ia} [\langle q i|pa\rangle x_{i,\mu}^{a*} + \langle qa|pi\rangle y_{a,\mu}^{i*}], \quad (6b)$$

are required to construct the elements of the self-energy. The index μ enumerates the solutions to the RPA problem where $x_{i,\mu}^a$ and $y_{a,\mu}^i$ are the elements of the eigenvector solutions corresponding to the excitation energy Ω_μ (see Sec. II B 1). The two-electron integrals $\langle pq|rs \rangle$ are given in Dirac notation, i.e., $\langle 12|12 \rangle$.

By substituting Eqs. (2) and (5) into Eq. (1), one finds that the quasiparticle energies ϵ_p and corresponding Dyson orbitals $\psi_p(\mathbf{x})$ are obtained as the eigenvalues and eigenvectors of the following non-linear, frequency-dependent Fock-like operator,

$$[\hat{F} + \Sigma(\omega = \epsilon_p)]\psi_p(\mathbf{x}) = \epsilon_p \psi_p(\mathbf{x}). \quad (7)$$

Here, \hat{F} is the usual Fock operator, including Hartree and exchange contributions, and the self-energy accounts for correlation effects. Although the so-called quasiparticle equation defined in Eq. (7) acts as the working equation for GW, its non-linear and dynamical nature makes it difficult to solve. In practice, it is solved iteratively due to the dependence of the self-energy on the quasiparticle energies [see Eq. (5)]. A hierarchy of approximations has been developed to address this issue, each defined by how the self-energy is constructed and updated at each iteration, leading to various levels of self-consistency (e.g., evGW^{101–105} and qSGW^{50,106–112}). Further details can be found in Ref. 17. The widely used G_0W_0 approximation corresponds to a single-shot calculation in which both the Green's function and the screened interaction are fixed.^{113–119} When combined with the diagonal approximation, the G_0W_0 quasiparticle energies are commonly obtained by solving the following one-dimensional, nonlinear equation for each state p :

$$\epsilon_p = \epsilon_p^{\text{HF}} + \Sigma_{pp}(\omega = \epsilon_p). \quad (8)$$

Green's function approaches are designed to describe properties of the many-body electronic state. In the case of G_0W_0 , the quasiparticle energies, associated with IPs in the hole space and EAs in the particle space, are improved relative to the mean-field reference. However, the total energy of the reference state is not uniquely defined. Various functionals have been proposed to calculate the correlation energy, including the Klein functional,¹²⁰ which is based on G , the Luttinger–Ward functional,^{121–123} which is based on Σ , and the Galitskii–Migdal functional.^{124,125} These expressions yield identical results only when a fully self-consistent Green's function (beyond the quasiparticle approximation) is used.^{126–134} In other words, for non-self-consistent schemes, such as G_0W_0 , they generally differ. Consequently, the total energy for the electron-detached or electron-attached state is also not uniquely defined within the G_0W_0 approximation. In the present work, the correlation energy of the ground state is evaluated at the RPA level (see Sec. II B), which can be shown to be equivalent to the Klein functional.

By analogy with the extended Koopmans' theorem (EKT), in which the total energy of a charged state is approximated as

$$E_p^{\text{EKT}} = E_0^{\text{HF}} \mp \epsilon_p^{\text{HF}}, \quad (9)$$

where E_0^{HF} is the HF energy of the reference state, we define the G_0W_0 total energy as

$$E_p^{G_0W_0} = E_0^{G_0W_0} \mp \epsilon_p^{G_0W_0}, \quad (10)$$

where $E_0^{G_0W_0}$ consists of the mean-field HF energy and the RPA correlation energy, that is,

$$E_0^{G_0W_0} = E_0^{\text{HF}} + E_c^{\text{RPA}}. \quad (11)$$

Furthermore, Eq. (8) is not well-suited for deriving analytic derivatives. Unlike in standard Lagrangian formulations for non-variational ansätze, the identification of wavefunction parameters is obscured by the frequency dependence of the self-energy. In this work, we derive a Lagrangian formulation that correctly reproduces the electronic energy of the charged states at the G_0W_0 level [see Eq. (10)]. This formulation exploits the connection between the RPA and a particular approximation to the CC expansion, as discussed in Sec. II B. Through this connection, an exact block-diagonalization of the RPA matrix is achieved. In Sec. II C, this block-diagonalization is used to reformulate the nonlinear, frequency-dependent G_0W_0 problem into an EOM-CC problem. The resulting formalism not only provides a clear definition of the electron-detached (or-attached) energies but also enables a standard Lagrangian construction for computing analytic derivatives.

B. Connection between RPA and drCCD

1. RPA

The RPA equations can be cast as a linear eigenvalue problem, $\mathbf{H}_{\text{RPA}} \cdot \mathbf{R} = \mathbf{R} \cdot \mathbf{E}$, which takes the form of Casida's equations,¹³⁵

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & -\mathbf{A}^* \end{pmatrix} \cdot \begin{pmatrix} \mathbf{X} & \mathbf{Y}^* \\ \mathbf{Y} & \mathbf{X}^* \end{pmatrix} = \begin{pmatrix} \mathbf{X} & \mathbf{Y}^* \\ \mathbf{Y} & \mathbf{X}^* \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{\Omega} & \mathbf{0} \\ \mathbf{0} & -\boldsymbol{\Omega} \end{pmatrix}, \quad (12)$$

where the elements of matrices \mathbf{A} and \mathbf{B} are given by

$$A_{ia,jb} = \langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle, \quad (13a)$$

$$B_{ia,jb} = \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_0 \rangle. \quad (13b)$$

The determinants $|\Phi_0\rangle$, $|\Phi_i^a\rangle$, and $|\Phi_{ij}^{ab}\rangle$ are the reference, singly, and doubly excited determinants constructed within the mean-field orbital space. The matrices \mathbf{X} and \mathbf{Y} are associated with single excitations and de-excitations, respectively, and gather the elements of the eigenvectors, $x_{i,\mu}^a$ and $y_{a,\mu}^i$, previously defined in Sec. II A. The diagonal matrix $\boldsymbol{\Omega}$ contains the positive excitation energy eigenvalues Ω_μ .

For the purposes of the GW approximation, the so-called direct version of RPA is considered. This approximation only affects the two-electron part of the normal-ordered Hamiltonian $\hat{H}_N = \hat{F}_N + \hat{V}_N$, with $\hat{F}_N = \sum_{pq} f_{pq} \{a_p^\dagger a_q\}$ being the normal-ordered Fock operator. In particular, the exchange contribution in the fluctuation potential,

$$\begin{aligned} \hat{V}_N &= \frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \{a_p^\dagger a_q^\dagger a_s a_r\} \\ &= \frac{1}{4} \sum_{pqrs} (\langle pq|rs \rangle - \langle pq|sr \rangle) \{a_p^\dagger a_q^\dagger a_s a_r\}, \end{aligned} \quad (14)$$

is neglected. In this form, only the direct (Coulomb) component of the electron–electron interaction is retained, while the exchange term is omitted, consistent with the assumptions underlying the *GW* and direct RPA formalisms. Operators a_p^\dagger and a_p are the usual fermionic creators and annihilators, respectively, and the curly braces denote normal ordering with respect to the Fermi vacuum. Under this approximation, the matrix elements defined in Eq. (13) reduce to

$$A_{ia,jb} = (\epsilon_a^{\text{HF}} - \epsilon_i^{\text{HF}}) \delta_{ij} \delta_{ab} + \langle aj|ib\rangle, \quad (15\text{a})$$

$$B_{ia,jb} = \langle ab|ij\rangle, \quad (15\text{b})$$

and the direct RPA correlation energy is given by the plasmon (or trace) formula,^{98,136–138}

$$E_c^{\text{RPA}} = \frac{1}{2} \left[\sum_\mu \Omega_\mu - \text{Tr}(A) \right]. \quad (16)$$

In the remainder of this article, we will drop the term “direct” when referring to RPA, as it is always implied.

2. drCCD

It has been previously shown that RPA is equivalent to the direct-ring (dr) CCD (drCCD) truncation.^{93,139–144} This approach constitutes an approximation to standard CCD, where the cluster operator includes all double excitations,

$$\hat{T}_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i. \quad (17)$$

Within the “ring” approximation, only those terms of the similarity-transformed Hamiltonian that correspond to loop (ring) diagrams are retained. It is well known that the ring approximation comes at the cost of breaking the fundamental antisymmetry of the electronic wavefunction.¹⁴⁰ A bosonic character is introduced to a fundamentally fermionic system and certain contractions among individual fermionic particle operators are ignored. As a result, the wavefunction fails to remain fully antisymmetric under electron exchange. In addition, only the direct Coulomb contribution of the fluctuation potential contributes, that is, excluding exchange. A modified set of rules for computing the drCCD Hamiltonian,

$$\tilde{H}_{\text{CCD}} = e^{-\hat{T}_2} \hat{H}_{\text{NE}} e^{\hat{T}_2} \approx \tilde{H}_{\text{dr}} \quad (18)$$

using diagrammatic techniques is presented in [supplementary material](#), Sec. I.

The drCCD amplitude equations are given by projections of the drCCD Hamiltonian onto doubly excited determinants,

$$\begin{aligned} \langle \Phi_{ij}^{ab} | \tilde{H}_{\text{dr}} | \Phi_0 \rangle &\stackrel{!}{=} 0 \\ \mathbf{B} + \mathbf{A} \cdot \mathbf{t} + \mathbf{t} \cdot \mathbf{A}^* + \mathbf{t} \cdot \mathbf{B}^* \cdot \mathbf{t} &= \mathbf{0}, \end{aligned} \quad (19)$$

with a formal scaling of $\mathcal{O}(M^6)$, where M denotes the system size. The matrix \mathbf{t} collects the drCCD amplitudes $t_{ia,jb} = t_{ij}^{ab}$. Within a standard CCD treatment, the correlation energy is given by

$$\begin{aligned} E_c^{\text{CCD}} &= \langle \Phi_0 | \tilde{H}_{\text{CCD}} | \Phi_0 \rangle = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \langle ij || ab \rangle \\ &= \frac{1}{2} \sum_{ijab} t_{ij}^{ab} \langle ij | ab \rangle, \end{aligned} \quad (20)$$

where the antisymmetric form of the CCD amplitudes ($t_{ij}^{ab} = -t_{ji}^{ab} = t_{ji}^{ba}$) has been exploited. Applying the direct treatment within drCCD (where the amplitudes are not antisymmetric) is equivalent to using the last line of Eq. (20) for the correlation energy expression,¹⁴⁰

$$E_c^{\text{drCCD}} = \langle \Phi_0 | \tilde{H}_{\text{dr}} | \Phi_0 \rangle = \frac{1}{2} \sum_{ijab} t_{ij}^{ab} \langle ij | ab \rangle = \frac{1}{2} \text{Tr}(\mathbf{B}^* \cdot \mathbf{t}). \quad (21)$$

Thus, an effective factor of 2 arises in the calculation of the expectation values of the drCCD Hamiltonian.

It can be further shown¹⁴⁰ that the drCCD correlation energy coincides with the RPA correlation energy,

$$E_c^{\text{drCCD}} = E_c^{\text{RPA}}. \quad (22)$$

The latter becomes apparent when the term $\sum_\mu \Omega_\mu$ in Eq. (16) is rewritten as the trace of a block-diagonal RPA matrix, as seen in Eq. (40).

In order to obtain analytic derivatives of the RPA correlation energy, which is part of the total $G_0 W_0$ electronic energy [see Eq. (10)], the method of Lagrange multipliers is employed.^{145,146} Using the established connection to the drCCD approximation,¹⁴⁷ the corresponding Lagrangian is defined as

$$\mathcal{L}_c^{\text{drCCD}} = \langle \Phi_0 | (1 + \hat{\Lambda}_2) \tilde{H}_{\text{dr}} | \Phi_0 \rangle, \quad (23)$$

with the λ -amplitude equations obtained by enforcing the following stationarity conditions:

$$\frac{\partial \mathcal{L}_c^{\text{drCCD}}}{\partial t_{ij}^{ab}} = \langle \Phi_0 | (1 + \hat{\Lambda}_2) \frac{\partial \tilde{H}_{\text{dr}}}{\partial t_{ij}^{ab}} | \Phi_0 \rangle \stackrel{!}{=} 0. \quad (24)$$

The de-excitation operator $\hat{\Lambda}_2$ is given by

$$\hat{\Lambda}_2 = \frac{1}{4} \sum_{abij} \lambda_{ab}^{ij} a_i^\dagger a_j^\dagger a_b a_a. \quad (25)$$

The λ Lagrange multipliers can also be viewed as wavefunction parameters of the CC bra state within the bivariational formulation of CC.^{148–150} Equation (24) can then be recast in matrix form as

$$\mathbf{B}^* + \boldsymbol{\lambda} \cdot (\mathbf{A} + \mathbf{A}^* + \mathbf{B}^* \cdot \mathbf{t} + \mathbf{t} \cdot \mathbf{B}^*) = \mathbf{0}, \quad (26)$$

exhibiting a formal scaling of $\mathcal{O}(M^6)$. The λ amplitude equations are linear in λ , which collects the elements of the λ amplitudes as $\lambda_{ia,jb} = \lambda_{ab}^{ij}$. A diagrammatic derivation accompanied by working equations can be found in [supplementary material](#), Sec. II.

3. Block diagonalization of the RPA Hamiltonian

Previously, it has been shown that the exact correspondence between $G_0 W_0$ and EOM-CC requires the block diagonalization of the RPA matrix,⁶⁰

$$U^\dagger \cdot H_{\text{RPA}} \cdot U = \begin{pmatrix} \tilde{A} & \mathbf{0} \\ \mathbf{0} & -\tilde{A}^* \end{pmatrix}. \quad (27)$$

This can be achieved either through a Bogoliubov transformation or through an alternative unitary transformation, e.g., a unitary drCCD (drUCCD) treatment.⁶⁰ In contrast, the *similarity-transformed* drCCD Hamiltonian is not equivalent to a *unitary transformation* even if it manages to reproduce the correlation energy E_c^{RPA} . The differences stem from the fact that the similarity transformation only treats the excitation part of Eq. (12) and does not fully account for both forward- and backward-time-ordered bubble diagrams present in GW , as first discussed in Ref. 58.

More precisely, the drCCD Hamiltonian corresponds to the following treatment of the RPA matrix:

$$\tilde{H}_{\text{RPA}} = M^{-1} \cdot H_{\text{RPA}} \cdot M, \quad (28)$$

with

$$M = \begin{pmatrix} 1 & t \\ 0 & 1 \end{pmatrix}, \quad M^{-1} = \begin{pmatrix} 1 & -t \\ 0 & 1 \end{pmatrix}. \quad (29)$$

This transformation leads to a new eigenvalue equation of the form $\tilde{H}_{\text{RPA}} \cdot \tilde{R} = \tilde{R} \cdot E$ with

$$\begin{aligned} \tilde{H}_{\text{RPA}} &= \begin{pmatrix} A + t \cdot B^* & B + A \cdot t + t \cdot A^* + t \cdot B^* \cdot t \\ -B^* & -B^* \cdot t - A^* \end{pmatrix} \\ &= \begin{pmatrix} A + t \cdot B^* & \mathbf{0} \\ -B^* & -B^* \cdot t - A^* \end{pmatrix} \end{aligned} \quad (30)$$

and

$$\tilde{R} = M^{-1} \cdot R = \begin{pmatrix} X - t \cdot Y & Y^* - t \cdot X^* \\ Y & X^* \end{pmatrix} = \begin{pmatrix} \bar{X} & \mathbf{0} \\ Y & X^* \end{pmatrix}, \quad (31)$$

where $\bar{X} = X - t \cdot Y$. The upper right block of \tilde{H}_{RPA} vanishes as it represents the drCCD amplitude equations given by Eq. (19). In addition, it can be shown that

$$t = Y^* \cdot X^{-1}. \quad (32)$$

We note that the formulation presented here to connect RPA to drCCD differs from those found in the literature by a complex conjugation.^{93,140,142} In particular, other studies introduce the following parameterization:

$$T = Y \cdot X^{-1} \quad (33)$$

as a first step to block-diagonalize the RPA matrix. The resulting matrix T corresponds to the deexcitation operator \hat{T}_2^\dagger rather than the excitation operator \hat{T}_2 [see Eq. (17)]. Numerical differences between the common derivations Eqs. (32) and (33) arise only when complex

orbitals are employed, as the two formulations differ only in a complex conjugation. This is the case, for example, in the presence of a magnetic field as used in Ref. 151. Formally, however, the current derivation is consistent in defining \hat{T}_2 as an excitation operator and not as a de-excitation operator.

In order to account for the contributions necessary to replicate the block diagonal structure of Eq. (28), a second similarity transformation is introduced,

$$\bar{M} = \begin{pmatrix} 1 & \mathbf{0} \\ \lambda & 1 \end{pmatrix}, \quad \bar{M}^{-1} = \begin{pmatrix} 1 & \mathbf{0} \\ -\lambda & 1 \end{pmatrix}. \quad (34)$$

The transformed problem reads $\tilde{H}_{\text{RPA}} \cdot \tilde{R} = \tilde{R} \cdot E$, with

$$\begin{aligned} \tilde{H}_{\text{RPA}} &= \bar{M}^{-1} \cdot \tilde{H}_{\text{RPA}} \cdot \bar{M} \\ &= \begin{pmatrix} A + t \cdot B^* & \mathbf{0} \\ -[B^* + \lambda \cdot (A + A^* + B^* \cdot t + t \cdot B^*)] & -B^* \cdot t - A^* \end{pmatrix} \end{aligned} \quad (35)$$

and

$$\tilde{R} = \bar{M}^{-1} \cdot \tilde{R} = \begin{pmatrix} \bar{X} & \mathbf{0} \\ -\lambda \cdot \bar{X} + Y & X^* \end{pmatrix}. \quad (36)$$

The lower left block of Eq. (35) vanishes as it is simply the negative of the λ -amplitude equations given by Eq. (26). Accordingly, it can be shown that the λ amplitudes are connected to the RPA parameters using $\lambda = Y \cdot \bar{X}^{-1}$. The final form for the doubly similarity-transformed RPA matrix in a block-diagonal form is given by

$$\tilde{H}_{\text{RPA}} = \begin{pmatrix} A + t \cdot B^* & \mathbf{0} \\ \mathbf{0} & -(A^* + B^* \cdot t) \end{pmatrix}, \quad (37a)$$

$$\tilde{R} = \begin{pmatrix} \bar{X} & \mathbf{0} \\ \mathbf{0} & X^* \end{pmatrix}. \quad (37b)$$

We note that the matrix A is Hermitian ($A^* = A^\top$, where the superscript \top denotes the transpose of the matrix) and the matrices B and t are symmetric ($B = B^\top$ and $t = t^\top$). The de-excitation block can thus be rewritten as

$$A^* + B^* \cdot t = (A + t \cdot B^*)^\top. \quad (38)$$

As a result, the similarity-transformed RPA problem can be recast in the form of an expectation value,

$$\begin{pmatrix} X^* & \mathbf{0} \\ \mathbf{0} & \bar{X} \end{pmatrix}^\top \cdot \begin{pmatrix} A + t \cdot B^* & \mathbf{0} \\ \mathbf{0} & -(A + t \cdot B^*)^\top \end{pmatrix} \cdot \begin{pmatrix} \bar{X} & \mathbf{0} \\ \mathbf{0} & X^* \end{pmatrix} = \begin{pmatrix} \Omega & \mathbf{0} \\ \mathbf{0} & -\Omega \end{pmatrix}, \quad (39)$$

which can be further simplified to

$$X^\dagger \cdot (A + t \cdot B^*) \cdot \bar{X} = \Omega. \quad (40)$$

This equation demonstrates that \bar{X} is the right eigenvector of the transformed RPA problem corresponding to the left eigenvector X^\dagger , where the superscript \dagger denotes the Hermitian conjugate.

This block-diagonalization reduces the dimensionality of the original RPA problem by eliminating the coupling between excitations and de-excitations. In addition, it establishes an exact relationship between the original RPA eigenvectors, X and Y , the left and right eigenvectors, X and \hat{X} of the resulting non-Hermitian matrix, and the drCCD parameters, t and λ .

It should be noted that the second similarity transformation is only needed to fully block diagonalize the RPA matrix, but the RPA problem can be represented in a reduced dimensionality using only the drCCD amplitudes [see Eqs. (30) and (31)]. In particular, Eq. (40) can be alternatively derived using an excitation-energy EOM-CC treatment.^{93,144} An EOM-singles (EOM-S) ansatz is used on the drCCD Hamiltonian, which yields the following right and left eigenvalue problems:

$$\langle \Phi_i^a | [\tilde{H}_{\text{dr}}, \hat{R}_{1,\mu}] | \Phi_0 \rangle = \Omega_\mu \langle \Phi_i^a | \hat{R}_{1,\mu} | \Phi_0 \rangle, \quad (41\text{a})$$

$$\langle \Phi_0 | \hat{L}_{1,\mu} (\tilde{H}_{\text{dr}} - E_c^{\text{drCCD}}) | \Phi_i^a \rangle = \langle \Phi_0 | \hat{L}_{1,\mu} | \Phi_i^a \rangle \Omega_\mu. \quad (41\text{b})$$

These can be rewritten in matrix form as

$$(A + t \cdot B^*) \cdot R_1 = R_1 \cdot \Omega, \quad (42\text{a})$$

$$L_1 \cdot (A + t \cdot B^*) = \Omega \cdot L_1. \quad (42\text{b})$$

In this way, the right-EOM operator, $\hat{R}_{1,\mu} = \sum_{ia} r_{i,\mu}^a a_a^\dagger a_i$, can be identified to the matrix \hat{X} , and the left-EOM operator, $\hat{L}_{1,\mu} = \sum_{ia} l_{a,\mu}^i a_i^\dagger a_a$, to the matrix X^\dagger . Note that the parameterization in Eq. (32) directly influences the identification of the EOM eigenvectors to the RPA parameters. Previous formulations in the literature^{93,144} are unclear whether \hat{T}_2^\dagger is used instead of \hat{T}_2 . This hinders the correct identification of left and right eigenvectors, and numerical differences are not limited to a complex conjugation. In particular, the right-EOM vector is associated with X instead of \hat{X} and the other way around for the left-EOM vector, when \hat{T}_2^\dagger is employed.

C. $G_0 W_0$ through the EOM-CC lens

As we shall discuss in detail in a forthcoming publication, the double similarity transformation described in Sec. II B 3 corresponds to the direct-ring approximation of an extended coupled-cluster doubles (ECCD) treatment,^{152–155}

$$\tilde{H}_{\text{ECCD}} = e^{\hat{\Lambda}_2} e^{-\hat{T}_2} \hat{H}_{\text{NE}} e^{\hat{T}_2} e^{-\hat{\Lambda}_2}. \quad (43)$$

The resulting approximated Hamiltonian, referred to here as the λ -drCCD transformation, is given by

$$\tilde{H}_{\text{ECCD}} \approx \tilde{H}_{\lambda-\text{dr}} = \tilde{H}_{\text{dr}} + [\hat{\Lambda}_2, \tilde{H}_{\text{dr}}], \quad (44)$$

where the second similarity-transformation truncates exactly after the first-order commutator within the direct-ring approximation. The λ -direct-ring transformation includes all de-excitations (i.e., backward time-ordered bubble diagrams) that are missing in the standard drCCD similarity transformation compared to a unitary transformation, as discussed in Sec. II B 3.

1. The IP/EA-EOM- λ -drCCD expectation value

It has been shown that the quasiparticle equation [see Eq. (8)] can be recast as an eigenvalue problem resulting from an IP/EA equation-of-motion (IP/EA-EOM) approach acting on a block-diagonalized Hamiltonian, as mentioned in Sec. II B 3.^{59,156} Here, we make use of $\tilde{H}_{\lambda-\text{dr}}$, as defined in Eq. (44). In particular, the excitation space is chosen as the singles and doubles IP excitations (i.e., 1h and 2h1p, respectively) and EA de-excitations (i.e., 1p and 2p1h, respectively),

$$\begin{aligned} \hat{R}^{\text{IP/EA}} &= \sum_I R_I^{\text{IP/EA}} \hat{c}_I^{\text{IP/EA}} = \sum_I R_I^{\text{IP}} \hat{c}_I^{\text{IP}} + \sum_I R_I^{\text{EA}} (\hat{c}_I^{\text{EA}})^\dagger \\ &= R_1^{\text{IP}} \hat{c}_1^{\text{IP}} + R_2^{\text{IP}} \hat{c}_2^{\text{IP}} + R_1^{\text{EA}} (\hat{c}_1^{\text{EA}})^\dagger + R_2^{\text{EA}} (\hat{c}_2^{\text{EA}})^\dagger \\ &= \sum_i r_i a_i + \sum_{ijb} r_{ji}^b a_b^\dagger a_j a_i + \sum_a r_a a_a + \sum_{ajb} r_{ba}^j a_b^\dagger a_b a_a. \end{aligned} \quad (45)$$

Here, the collective operator $\hat{c}_I^{\text{IP/EA}}$ correspond to either the IP excitation operator, \hat{c}_I^{IP} , or EA de-excitation operator, $(\hat{c}_I^{\text{EA}})^\dagger$. They create the determinants involved in the IP/EA-EOM formalism when acting on the reference determinant, $\hat{c}_I |\Phi_0\rangle = |\Phi_I\rangle$, with

$$\{|\Phi_I\rangle\} = \{|\Phi_i\rangle, |\Phi^a\rangle, |\Phi_j^{ba}\rangle, |\Phi_{ji}^b\rangle\}. \quad (46)$$

In addition, the index pair bj in the doubles amplitudes r_{ji}^b and r_{ba}^j follows the ring approximation, whereas the remaining index does not. As a result, these indices are formally nonequivalent, in contrast to the standard EOM-CC formulation. The resulting right and left non-Hermitian eigenvalue problems read

$$\begin{aligned} \langle \Phi_0 | [\hat{c}_I^{\text{IP/EA},\dagger}, [\tilde{H}_{\lambda-\text{dr}}, \hat{R}^{\text{IP/EA}}]]_+ | \Phi_0 \rangle \\ = \epsilon^{\text{IP/EA}} \langle \Phi_0 | [\hat{c}_I^{\text{IP/EA},\dagger}, \hat{R}^{\text{IP/EA}}]_+ | \Phi_0 \rangle \end{aligned} \quad (47)$$

and

$$\begin{aligned} \langle \Phi_0 | [\hat{L}^{\text{IP/EA}}, [\tilde{H}_{\lambda-\text{dr}}, \hat{c}_I^{\text{IP/EA}}]]_+ | \Phi_0 \rangle \\ = \epsilon^{\text{IP/EA}} \langle \Phi_0 | [\hat{L}^{\text{IP/EA}}, \hat{c}_I^{\text{IP/EA}}]_+ | \Phi_0 \rangle. \end{aligned} \quad (48)$$

The anticommutator is represented by $[\cdot, \cdot]_+$ and the eigenvalues by $\{\epsilon^{\text{IP/EA}}\}$. Finding one root of the eigenvalue problems formally scales as $\mathcal{O}(M^5)$.

The total energy of the electron-attached or-detached state is expressed as the sum of the HF reference energy and the correlation energy at the drCCD level, augmented by the corresponding quasiparticle energy,

$$E_p^{\text{IP/EA}} = E_0^{\text{HF}} + E_c^{\text{drCCD}} \pm \epsilon^{\text{IP/EA}}. \quad (49)$$

This result follows naturally from the EOM-CC formalism and coincides exactly with the definition given in Eq. (10).

The eigenvalues can also be expressed in an expectation-value form, as follows:

$$\epsilon^{\text{IP/EA}} = \langle \Phi_0 | [\hat{L}^{\text{IP/EA}}, [\tilde{H}_{\lambda-\text{dr}}, \hat{R}^{\text{IP/EA}}]]_+ | \Phi_0 \rangle. \quad (50)$$

By enforcing a decoupling in the 1h and 1p spaces, the EOM vector for the collective IP and EA singles block reduces to having only one non-zero component,

$$\hat{R}_{1,p}^{\text{IP/EA}} \approx \sum_q r_q a_q \delta_{pq} = r_p a_p. \quad (51)$$

This treatment corresponds to the diagonal approximation of $G_0 W_0$. The index p explicitly enumerates the solution for clarity. Within this approximation, the $G_0 W_0$ quasiparticle energies exactly correspond to the IP/EA-EOM eigenvalues as $\epsilon_p^{\text{IP/EA}} = -\epsilon_p^{G_0 W_0}$.

It is again noted that the use of \tilde{H}_{dr} instead of $\tilde{H}_{\lambda-\text{dr}}$ would not reproduce the $G_0 W_0$ quasiparticle energies, as it omits certain contributions from the de-excitation space.⁶⁰ These missing terms are recovered through the second similarity transformation involving the de-excitation operator $\hat{\Lambda}_2$, which effectively eliminates the remaining off-diagonal block of the RPA matrix.

Details regarding the working equations can be found in supplementary material Sec. III. In addition, exact relations between the $G_0 W_0$ and IP/EOM- λ -drCCD parameters can be found in the supplementary material, Sec. IV as well.

2. The Lagrangian treatment of $G_0 W_0$

To derive an analytic expression for the derivatives of the IP/EA-EOM eigenvalues, we introduce the following Lagrangian:

$$\begin{aligned} \mathcal{L}^{\text{IP/EA}} = & \pm \langle \Phi_0 | [\hat{L}^{\text{IP/EA}}, [\tilde{H}_{\lambda-\text{dr}}, \hat{R}^{\text{IP/EA}}]]_+ | \Phi_0 \rangle \\ & \mp \epsilon^{\text{IP/EA}} (\langle \Phi_0 | [\hat{L}^{\text{IP/EA}}, \hat{R}^{\text{IP/EA}}]_+ | \Phi_0 \rangle - 1) \\ & + \langle \Phi_0 | (1 + \hat{Z}_2) \tilde{H}_{\text{dr}} | \Phi_0 \rangle + \langle \Phi_0 | (1 + \hat{\Lambda}_2) [\tilde{H}_{\text{dr}}, \hat{\Xi}_2] | \Phi_0 \rangle, \end{aligned} \quad (52)$$

which, by construction, reproduces the total correlation energy of the electron-detached or-attached state,

$$E_c^{\text{IP/EA}} = E_c^{\text{drCCD}} \pm \epsilon^{\text{IP/EA}} \quad (53)$$

from Eq. (49). The reference correlation energy contribution is contained in the third term of the Lagrangian. Regarding the sign of the first term in the Lagrangian, the EOM expectation value is derived as an excitation and, as such, is added for the IP case. For the EA case, on the other hand, the expectation value corresponds to a de-excitation and must be subtracted.

The Lagrange multipliers introduced in Eq. (52) are as follows: (i) the EOM eigenvalue $\epsilon^{\text{IP/EA}}$ enforces the biorthonormality condition between the left- and right-EOM vectors in the second term; (ii) the de-excitation operator,

$$\hat{Z}_2 = \frac{1}{4} \sum_{ijab} \zeta_{ab}^{ij} a_i^\dagger a_j^\dagger a_b a_a \quad (54)$$

includes the drCCD-amplitude equations for \hat{T}_2 [see Eq. (19)] in the third term; and (iii) the excitation operator,

$$\hat{\Xi}_2 = \frac{1}{4} \sum_{ijab} \xi_{ij}^{ab} a_i^\dagger a_a^\dagger a_b a_j \quad (55)$$

includes the λ -amplitude equations for $\hat{\Lambda}_2$ [see Eq. (24)] in the fourth term.

Enforcing the stationarity conditions on the Lagrangian [see Eq. (52)] results in the following set of equations.

1. Stationarity with respect to the Lagrange multipliers ζ_{ab}^{ij} ,

$$\frac{\partial \mathcal{L}^{\text{IP/EA}}}{\partial \zeta_{ab}^{ij}} \stackrel{!}{=} 0 \quad (56)$$

reproduces the pseudo-linear drCCD amplitude equations [see Eq. (19)].

2. Stationarity with respect to the Lagrange multipliers ξ_{ij}^{ab} ,

$$\frac{\partial \mathcal{L}^{\text{IP/EA}}}{\partial \xi_{ij}^{ab}} \stackrel{!}{=} 0 \quad (57)$$

reproduces the linear drCCD λ -amplitude equations [see Eq. (24)].

3. Stationarity with respect to the left-EOM amplitudes l_I ,

$$\frac{\partial \mathcal{L}^{\text{IP/EA}}}{\partial l_I} \stackrel{!}{=} 0 \quad (58)$$

reproduces the right eigenvalue problem [see Eq. (47)].

4. Stationarity with respect to the right-EOM amplitudes r_I ,

$$\frac{\partial \mathcal{L}^{\text{IP/EA}}}{\partial r_I} \stackrel{!}{=} 0 \quad (59)$$

reproduces the left eigenvalue problem [Eq. (48)].

5. Stationarity with respect to the Lagrange multiplier $\epsilon^{\text{IP/EA}}$,

$$\frac{\partial \mathcal{L}^{\text{IP/EA}}}{\partial \epsilon^{\text{IP/EA}}} \stackrel{!}{=} 0 \quad (60)$$

reproduces the biorthonormality condition,

$$\langle \Phi_0 | [\hat{L}^{\text{IP/EA}}, \hat{R}^{\text{IP/EA}}]_+ | \Phi_0 \rangle = 1. \quad (61)$$

6. Stationarity with respect to the λ -amplitudes,

$$\frac{\partial \mathcal{L}^{\text{IP/EA}}}{\partial \lambda_{ab}^{ij}} \stackrel{!}{=} 0 \quad (62)$$

yields the inhomogeneous linear ξ amplitude equations,

$$\mp \langle \Phi_0 | \left[\hat{L}^{\text{IP/EA}}, \left[\frac{\partial \tilde{H}_{\lambda-\text{dr}}}{\partial \lambda_{ab}^{ij}}, \hat{R}^{\text{IP/EA}} \right] \right]_+ | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | [\tilde{H}_{\text{dr}}, \hat{\Xi}_2] | \Phi_0 \rangle. \quad (63)$$

7. Stationarity with respect to the drCCD amplitudes,

$$\frac{\partial \mathcal{L}^{\text{IP/EA}}}{\partial t_{ij}^{ab}} \stackrel{!}{=} 0 \quad (64)$$

yields the inhomogeneous linear ζ amplitude equations,

$$\begin{aligned} \mp \langle \Phi_0 | \left[\hat{L}^{\text{IP/EA}}, \left[\frac{\partial \tilde{H}_{\lambda-\text{dr}}}{\partial t_{ij}^{ab}}, \hat{R}^{\text{IP/EA}} \right] \right]_+ | \Phi_0 \rangle \\ - \langle \Phi_0 | (1 + \hat{\Lambda}_2) \left[\frac{\partial \tilde{H}_{\text{dr}}}{\partial t_{ij}^{ab}}, \hat{\Xi}_2 \right] | \Phi_0 \rangle = \langle \Phi_0 | (1 + \hat{Z}_2) \frac{\partial \tilde{H}_{\text{dr}}}{\partial t_{ij}^{ab}} | \Phi_0 \rangle. \end{aligned} \quad (65)$$

Since Eq. (65) includes contributions from the ξ amplitudes, the set of linear equations in Eq. (63) has to be solved first and is thus decoupled. The diagrammatic representation and the derivation of working equations are presented in the [supplementary material](#), Sec. III.

Compared to the drUCCD approach employed in Ref. 67, the λ -drCCD formulation avoids the need for a numerical truncation of the otherwise non-terminating Baker–Campbell–Hausdorff (BCH) expansion inherent to the unitary CC framework, while retaining the same $\mathcal{O}(M^6)$ formal scaling. This advantage, however, comes at the cost of introducing additional sets of wavefunction parameters, namely, the left-EOM vector, the λ amplitudes, and the ξ amplitudes.

After recasting Eq. (52) as a function of the contributions of the one- and two-electron reduced density matrices,

$$\mathcal{L}^{\text{IP/EA}} = \sum_{pq} \gamma_{pq} f_{pq} + \frac{1}{2} \sum_{pqrs} \Gamma_{pqrs} \langle pq | rs \rangle, \quad (66)$$

and a subsequent Hermitization, i.e.,

$$\tilde{\mathcal{L}}^{\text{IP/EA}} = \frac{\mathcal{L}^{\text{IP/EA}} + (\mathcal{L}^{\text{IP/EA}})^*}{2}, \quad (67)$$

to derive Hermitian reduced densities,

$$\bar{\gamma}_{pq} = \frac{\gamma_{pq} + \gamma_{qp}^*}{2}, \quad \bar{\Gamma}_{pqrs} = \frac{\Gamma_{pqrs} + \Gamma_{rspq}^*}{2}, \quad (68)$$

the z -vector method can be applied to account for the orbital relaxation.² The resulting Lagrangian is

$$\mathcal{L}_{\text{rel}}^{\text{IP/EA}} = \tilde{\mathcal{L}}^{\text{IP/EA}} + \sum_{pq} w_{pq} (f_{pq} - \delta_{pq} \epsilon_p) + \sum_{pq} I_{pq} (S_{pq} - \delta_{pq}). \quad (69)$$

The Lagrange multipliers w_{pq} and I_{pq} are introduced for the diagonal form of the Fock matrix and the orbital orthonormality $S_{pq} = \langle \phi_p | \phi_q \rangle = \delta_{pq}$, respectively. They can be assumed Hermitian with no loss of generality. The diagonal approximation that results in the decoupling of the singles–singles block in the EOM problem implies that the method is not invariant under rotations within the occupied–occupied and virtual–virtual orbital subspaces. As a consequence, the w_{pq} amplitudes acquire non-zero components in these blocks, even in the absence of a frozen-core approximation. Working equations for the evaluation of w_{pq} and I_{pq} are provided in Ref. 157.

Incorporating the w_{pq} contributions in the one-body reduced density matrix, $\gamma_{pq}^{\text{rel}} = \bar{\gamma}_{pq} + w_{pq}$, yields a final expression for the derivative of the energy with respect to a parameter κ that depends only on the partial derivatives of the mean-field Fock matrix elements, the two-electron integrals, and the overlap integrals,

$$\begin{aligned} \frac{dE^{\text{IP/EA}}}{d\kappa} &= \frac{\partial \mathcal{L}^{\text{IP/EA}}}{\partial \kappa} = \sum_{pq} \gamma_{pq}^{\text{rel}} \frac{\partial f_{pq}}{\partial \kappa} + \sum_{pq} I_{pq} \frac{\partial S_{pq}}{\partial \kappa} \\ &+ \frac{1}{2} \sum_{pqrs} \bar{\Gamma}_{pqrs} \frac{\partial \langle pq | rs \rangle}{\partial \kappa}. \end{aligned} \quad (70)$$

Different choices for the parameter κ lead to expressing first-order properties as analytic first-order derivatives of the energy. In the case

of κ being nuclear displacements, geometrical gradients are derived to use in a geometry optimization calculation.

While the present derivation makes use of HF orbitals in combination with the underlying Fock matrix throughout, this can be generalized to a Kohn–Sham (KS) scheme with only minor modifications. The Fock operator at the HF level is built using the KS orbitals for the construction of the ring-similarity transformed Hamiltonian Eq. (18) and the λ -direct-ring Hamiltonian Eq. (44). The main modification concerns the orbital-relaxation terms in Eq. (69) where the KS Fock matrix has to be used in place of the standard Fock matrix. The modified contributions within the z -vector equations concern the calculation of the derivative of the KS Fock matrix f_{pq}^{KS} with respect to orbital rotations. Further details on the z -vector approach in the case of KS orbitals can be found in Ref. 158. Generalizations to other GW variants could be formulated in the current setting, but are beyond the scope of this work.

III. COMPUTATIONAL DETAILS

For the purpose of the current work, the drCCD approximation (energy and fully analytic properties) and the G_0W_0 approximation through the IP/EA-EOM- λ -drCCD formulation (energy and fully analytic properties) were implemented in the QCUMBRE program package.¹⁵⁹ The integrals and the SCF solution are provided by the MINT module¹⁶⁰ of the CFOUR program package.^{161,162} The geometry optimizer of CFOUR was also used to get the equilibrium geometries.

The verification of the RPA and G_0W_0 energies was achieved through comparison with the QUACK program package.¹⁶³ Analytic one-electron properties were tested in the case of dipole moments against numerical derivatives with finite electric-field calculations. Accordingly, analytic geometric gradients were tested against numerical differentiation by finite displacements of the nuclear coordinates, as well as the implementation reported in Ref. 67.

The implemented method was applied on the GW20 set^{23,25,164} (composed by the 20 smallest systems of the GW100 set²⁰), where the He, Ne, and Ar atomic systems were excluded. The results were generated in different levels of theory for comparison and benchmarking purposes. In particular, the optimal geometry of the neutral system was calculated at the ground-state ADC(2), CC2, G_0W_0 , CCSD, and CC3 levels of theory. For the purposes of the current study, only closed-shell configurations were targeted, even if for some systems a triplet state may be lower in energy. To target the lowest electronic state of the cationic systems, calculations were performed at the excited-state ADC(2), EOM-CC2, G_0W_0 , EOM-CCSD, and EOM-CC3 levels of theory. The methods are presented in ascending computational cost. Formally, ADC(2) and CC2 scale as $\mathcal{O}(M^5)$, G_0W_0 and CCSD as $\mathcal{O}(M^6)$, and CC3 as $\mathcal{O}(M^7)$, where M denotes the system size. This formal scaling may be reduced by using an auxiliary basis or a Cholesky decomposition of the two-electron integrals for some of these approaches. For EOM-CCSD, the corresponding IP-EOM-CC implementation was used, while excitations in continuum orbitals were probed to target the respective cationic states in the case of ADC(2), EOM-CC2, and EOM-CC3.¹⁶⁵ All electrons were included for the calculation of correlation effects using the aug-cc-pVTZ basis set.^{166–169} The scheme to generate G_0W_0 quasiparticle energies, as described in the previous

TABLE I. Vertical and adiabatic ionization potentials (in eV) using the aug-cc-pVTZ basis set. The IRREP of the HOMO is reported. For the vertical IPs, the optimal geometry of the neutral molecule at the respective level of theory has been used. For the adiabatic IPs, the energy of the ionized state at the optimal geometry calculated at the respective level of theory has been subtracted from the optimal energy of the neutral molecule at the respective level of theory. The MAE and MSE are reported with respect to the IP-EOM-CC3 results.

System	HOMO	Vertical IPs					Adiabatic IPs				
		ADC(2)	CC2	$G_0 W_0$	CCSD	CC3	ADC(2)	CC2	$G_0 W_0$	CCSD	CC3
H ₂	σ_g^+	16.350	16.330	18.036	16.397	16.397	15.415	15.387	15.621	15.520	15.520
LiH	σ_g^+	8.024	8.002	8.233	8.005	8.005	7.783	7.757	8.024	7.728	7.729
BH ₃	e'	13.290	13.251	13.716	13.353	13.314	12.223	12.193	12.620	12.315	12.285
Li ₂	σ_g^+	5.178	5.155	5.348	5.235	5.235	5.073	5.057	5.240	5.121	5.121
CH ₄	t_2	14.115	14.056	14.797	14.404	14.369	12.490	12.428	13.110	12.825	12.758
NH ₃	a'	10.185	10.163	11.162	10.857	10.891	9.441	9.416	10.414	10.121	10.135
H ₂ O	b_1	11.519	11.542	12.916	12.615	12.666	11.328	11.347	12.841	12.516	12.565
HF	π	14.643	14.719	16.273	16.045	16.132	14.320	14.389	16.154	15.896	15.976
BN	π	10.812	10.856	11.769	12.005	12.071	10.700	10.730	11.722	11.892	11.914
BeO	π	8.237	7.784	9.976	10.041	9.744	7.472	6.982	9.768	9.897	8.755
LiF	π	9.665	9.773	11.432	11.427	11.391 ^a	8.785	^b	10.965	10.980	10.892 ^a
CO	σ_g^+	14.000	13.766	14.721	14.179	13.866	13.990	13.762	14.685	14.159	13.860
N ₂	π_u	17.108	16.999	17.267	17.314	16.851	16.899	16.771	16.963	17.051	16.461
BF	σ_g^+	11.024	10.955	11.266	11.235	11.102	10.931	10.864	11.165	11.130	11.012
H ₂ S	b_1	10.179	10.148	10.508	10.414	10.381	10.164	10.132	10.503	10.404	10.370
HCl	π	12.408	12.389	12.789	12.704	12.664	12.373	12.355	12.772	12.680	12.641
F ₂	π_g	14.124	14.156	16.122	15.562	15.756	14.101	14.149	15.854	15.397	15.591
MAE		0.635	0.652	0.359	0.107		0.667	0.603	0.307	0.163	
MSE		-0.587	-0.635	0.323	0.056		-0.594	-0.561	0.284	0.120	

^aPredictions at the IP-EOM-CC3 level for the LiF⁺ are non-consistent. For this reason, predictions at the CCSDT level were used. Further details can be found in the supplementary material Sec. V.

^bA geometry optimization for LiF⁺ at the IP-EOM-CC2 level was not possible due to the deteriorating quality of the reference CC2 wavefunction for interatomic distances near the expected optimal geometry for the LiF⁺ cation. In addition, the LiF results have been excluded when calculating the MAE and MSE in all cases due to apparent qualitative differences between the different levels of theory.

TABLE II. Interatomic distance (in Å) in the optimal geometry for the neutral R_{neu} and cationic R_{cat} linear molecules using the aug-cc-pVTZ basis set. The MAE and MSE are reported with respect to the CC3 and IP-EOM-CC3 results.

System	R_{neu}					R_{cat}				
	ADC(2)	CC2	$G_0 W_0$ ^a	CCSD	CC3	ADC(2)	CC2	$G_0 W_0$	CCSD	CC3
H ₂	0.7374	0.7377	0.7354	0.7430	0.7430	1.0627	1.0657	1.0578	1.0581	1.0581
LiH	1.5879	1.5883	1.5719	1.5924	1.5922	2.0544	2.0599	1.9661	2.1635	2.1633
Li ₂	2.7125	2.7117	2.6725	2.6623	2.6600	3.1636	3.1431	3.1278	3.1076	3.1030
HF	0.9201	0.9225	0.9097	0.9164	0.9196	1.0671	1.0753	0.9799	0.9989	1.0075
BN	1.3212	1.2972	1.2700	1.2713	1.2765	1.3691	1.3657	1.3058	1.3362	1.3489
BeO	1.3452	1.4101	1.3077	1.3200	1.3621	1.6012	1.6097	1.4026	1.3975	1.6061
LiF	1.5817	1.5880	1.5641	1.5722	1.5762 ^b	2.7302	^c	1.9711	1.9600	2.0344 ^b
CO	1.1342	1.1442	1.1150	1.1241	1.1335	1.1203	1.1351	1.0923	1.1067	1.1234
N ₂	1.1097	1.1167	1.0830	1.0929	1.1007	1.1712	1.1853	1.1489	1.1560	1.1869
BF	1.2640	1.2699	1.2521	1.2629	1.2686	1.2109	1.2163	1.1994	1.2075	1.2160
HCl	1.2710	1.2717	1.2649	1.2728	1.2751	1.3212	1.3222	1.2979	1.3138	1.3156
F ₂	1.3977	1.4152	1.3641	1.3918	1.4137	1.3545	1.3872	1.2608	1.2997	1.3145
MAE	0.0137	0.0148	0.0196	0.0087		0.0853	0.0302	0.0597	0.0318	
MSE	0.0051	0.0127	-0.0176	-0.0083		0.0624	0.0111	-0.0556	-0.0310	

^aRPA results are used for the neutral system at the $G_0 W_0$ level of theory.

^bPredictions at the IP-EOM-CC3 level for the LiF⁺ are non-consistent. For this reason, predictions at the CCSDT level were used. Further details can be found in the supplementary material Sec. V.

^cA geometry optimization for LiF⁺ at the IP-EOM-CC2 level was not possible due to the deteriorating quality of the reference CC2 wavefunction for interatomic distances near the expected optimal geometry for the LiF⁺ cation. In addition, the LiF results have been excluded when calculating the MAE and MSE in all cases due to apparent qualitative differences between the different levels of theory.

paragraphs, corresponds to an η parameter of 0 on top of canonical restricted HF orbitals. In the following discussion, the RPA ground-state energy for the neutral system calculated via the drCCD scheme can be assumed when referring to $G_0 W_0$ results.

All calculations were performed using the QCUMBRE¹⁵⁹ and CFOUR program packages.^{160–162} A double convergence criterion of $10^{-7} E_h$ for the energy difference and 10^{-7} for the DIIS error was used for the HF calculation. Accordingly, a 10^{-7} criterion was used for the norm of the residual vector in the linear solver for the drCCD and λ amplitudes and in the Davidson algorithm for the excited-state calculations. For the geometry optimizations, a convergence criterion of $10^{-6} E_h a_0^{-1}$ was used for the gradient norm in the quasi-Newton algorithm.

IV. RESULTS

In the following paragraphs, results regarding the closed-shell states of the neutral systems and the corresponding lowest in energy states of the cationic systems in the molecular subset of the GW20 set

are presented. Vertical IPs were calculated as the energy difference between the ionized-state and ground-state energy at the geometry optimized for the neutral system at the corresponding level of theory. Instead, for the calculation of the adiabatic IPs, the same ground-state energy was used in combination with the ionized-state energy calculated at the geometry optimized for the cationic system at the corresponding level of theory. The IPs are collected in Table I, where the irreducible representation (IRREP) of the highest occupied molecular orbital (HOMO) is also reported. In the present calculation, the lowest-energy cationic state consistently corresponds to removing an electron from the HOMO. In Tables II and III, the geometric parameters of the optimal geometries of the neutral and the cationic systems are presented. Intermolecular distances for diatomic molecules are reported in Table II. The point group (PG) of the neutral and cationic systems in the case of polyatomic molecules, accompanied by a description of the reported geometrical parameters, can be found in Table III. In Tables I and II, the mean absolute error (MAE) and mean signed error (MSE) have been calculated with respect to the CC3 and IP-EOM-CC3 results. The only

TABLE III. Geometric parameters in the optimal geometry for the neutral and cationic polyatomic molecules using the aug-cc-pVTZ basis set. Distances are given in Å and angles in °. The point group (PG) of the molecular symmetry is reported in the last column.

System	ADC(2)	CC2	$G_0 W_0$ ^a	CCSD	CC3	Param.	PG
BH ₃	1.1811	1.1814	1.1756	1.1840	1.1848	<i>R</i>	D_{3h} ^b
BH ₃ ⁺	1.4140	1.4096	1.4420	1.4395	1.4365	<i>R</i> ₁	C_{2v} ^c
...	1.1749	1.1765	1.1636	1.1776	1.1801	<i>R</i> ₂	
...	164.62	164.71	163.07	163.07	163.38	ω	
CH ₄	1.0841	1.0846	1.0808	1.0863	1.0879	<i>R</i>	T_d ^d
CH ₄ ⁺	1.1760	1.1781	1.1746	1.1782	1.1838	<i>R</i> ₁	C_{2v} ^e
...	55.15	55.04	56.08	56.14	55.34	ω ₁	
...	1.0796	1.0812	1.0670	1.0783	1.0805	<i>R</i> ₂	
...	125.43	125.42	125.33	125.01	125.54	ω ₂	
NH ₃	1.0095	1.0107	1.0024	1.0095	1.0122	<i>R</i>	C_{3v} ^f
...	111.80	111.94	111.49	111.90	112.15	ω	
NH ₃ ⁺	1.0275	1.0293	1.0068	1.0187	1.0209	<i>R</i>	D_{3h} ^g
H ₂ O	0.9588	0.9607	0.9484	0.9561	0.9591	<i>R</i>	C_{2v} ^h
...	104.27	104.06	105.01	104.59	104.33	ω	
H ₂ O ⁺	1.0245	1.0285	0.9798	0.9972	1.0009	<i>R</i>	C_{2v} ^b
...	108.73	108.20	110.59	109.38	109.38	ω	
H ₂ S	1.3319	1.3326	1.3264	1.3351	1.3375	<i>R</i>	C_{2v} ⁱ
...	91.93	91.87	92.51	92.27	92.00	ω	
H ₂ S ⁺	1.3558	1.3575	1.3394	1.3550	1.3579	<i>R</i>	C_{2v} ⁱ
...	92.69	92.63	93.29	92.99	92.71	ω	

^aRPA results are used for the neutral system at the $G_0 W_0$ level of theory.

^bPlanar symmetric. *R* is the B–H distance.

^cPlanar with one non-equivalent B–H bond. *R*₁ is the nonequivalent B–H distance; *R*₂ is the B–H distance of the equivalent H atomic centers; and ω is the angle H–B–H angle between the equivalent H atomic centers.

^dTetrahedral symmetric. *R* is the C–H distance.

^eTwo pairs of equivalent H atomic centers. *R*₁ is the C–H distance of the first pair; ω ₁ is the H–C–H angle of the first pair; *R*₂ is the C–H distance of the second pair; and ω ₂ is the H–C–H angle of the second pair.

^f*R* is the N–H distance and ω is the angle of the N–H with respect to the C_3 rotational axis.

^gPlanar symmetric. *R* is the N–H distance.

^h*R* is the O–H distance; ω is the H–O–H angle. The symmetry does not change between the neutral and cationic systems.

ⁱ*R* is the S–H distance; ω is the H–S–H angle. The symmetry does not change between the neutral and cationic systems.

exception is LiF for which we employed CCSDT reference values. This point is discussed in detail in the [supplementary material](#), Secs. V and VI.

Regarding the IPs ([Table I](#)), the relative performance of the methods remain essentially consistent between vertical and adiabatic values. ADC(2) and CC2 yield comparable results, with MAEs of $\sim 0.6\text{--}0.7$ eV and negative MSEs of similar magnitude. The G_0W_0 approximation performs noticeably better, producing MAEs in the range of 0.3–0.4 eV and positive MSEs of comparable size. Similar superior performance of G_0W_0 compared to ADC(2) has also been observed in Ref. 67 without employing the diagonal approximation as used in the current work. CCSD delivers the most accurate results, with small positive MSEs and MAEs between 0.1 and 0.2 eV. The VIP of H₂, however, is known to be poorly described, likely due to the self-screening problem inherent to the GW approximation.^{170–173} In contrast, the AIP appears largely unaffected.

For the equilibrium geometries of the diatomic molecules ([Table II](#)), ADC(2), CC2, and CCSD all outperform G_0W_0 (and RPA for the neutral system). While the errors in the ground-state bond lengths are generally small (0.01 to 0.02 Å), the deviations in the equilibrium geometries of the corresponding cations are larger by a factor of two to three for all methods. Consistent with observations for neutral excited states,^{174,175} CCSD tends to underestimate bond lengths in the cationic states, whereas ADC(2) and CC2 systematically overestimate them. Similarly, G_0W_0 exhibits a systematic underestimation of cationic bond lengths, in contrast to BSE@ G_0W_0 , which has been shown to overestimate bond-length changes upon excitation in the case of neutral excitations.⁸³ Analogous trends are observed for the larger polyatomic species in the test set ([Table III](#)).

V. CONCLUSION

In this work, we have presented the implementation of the ionization-potential and electron-affinity equation-of-motion λ -direct-ring coupled-cluster doubles (IP/EAO-EOM- λ -drCCD) formalism, enabling the computation of fully analytic G_0W_0 energies and nuclear gradients within a standard CC Lagrangian framework. The approach has been implemented in the QCUMBRE program package and rigorously verified against numerical derivatives, as well as existing analytic implementations of GW gradients.⁶⁷

Benchmark calculations were performed on the molecular subset of the GW20 test set. Both vertical and adiabatic IPs were obtained at various levels of theory and compared to CC3 and IP-EOM-CC3 reference data. The results confirm that the newly implemented G_0W_0 formalism yields IPs with MAEs in the range of 0.3–0.4 eV, thereby outperforming second-order methods, such as ADC(2) and CC2. The equilibrium geometries of both neutral and cationic species are accurately reproduced, with typical bond-length deviations on the order of 0.01 Å for neutrals and slightly larger discrepancies for cations. Systematic trends were observed across methods: CCSD and G_0W_0 tend to underestimate bond lengths in cationic states, whereas ADC(2) and CC2 systematically overestimate them.

These results demonstrate that the IP/EAO-EOM- λ -drCCD formulation provides a new route for obtaining fully analytic G_0W_0 properties, by leveraging the connection between Green's

function and coupled-cluster theories. The achieved agreement with high-level wavefunction benchmarks highlights the accuracy and robustness of the approach, while its analytic nature opens the door to geometry optimization and property evaluation for larger and more complex systems. In future work, we plan to conduct a more extensive benchmark study on a broader set of IPs and EAs, in order to further assess the transferability and accuracy of the present formulation across diverse chemical environments. Extensions toward self-consistent GW variants and BSE within the same analytic formulation are also under active development.

SUPPLEMENTARY MATERIAL

The [supplementary material](#) includes rules for the diagrammatic derivation within the direct-ring approximation, a complete diagrammatic derivation of the drCCD and EA/IP-EOM- λ -drCCD working equations, and a guide connecting the G_0W_0 non-linear equations to the EA/IP-EOM- λ -drCCD parameters. Finally, it gathers additional calculations and potential energy curves for the LiF molecule and its cation, as well as a limited comparison of the CC3 with the CCSDT predictions.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Marios-Petros Kitsaras: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Methodology (lead); Software (lead); Validation (lead); Writing – original draft (lead); Writing – review & editing (equal). **Johannes Tölle:** Conceptualization (equal); Methodology (supporting); Writing – review & editing (equal). **Pierre-François Loos:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (lead); Methodology (supporting); Resources (lead); Supervision (equal); Writing – original draft (supporting); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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