

A route to improving RPA excitation energies through its connection to equation-of-motion coupled cluster theory

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(Dated: 4 August 2020)

We revisit the connection between equation-of-motion coupled cluster (EOM-CC) and random phase approximation (RPA) explored recently by Berkelbach [J. Chem. Phys. **149**, 041103 (2018)]. We bring together various methodological aspects of these diverse treatment of ground and excited states and present a unified outlook. We present numerical results showing the equivalence that was previously proved on theoretical grounds. We then introduce new approximations in EOM-CC (and RPA) family of methods, assess their numerical performance and explore a way to reap the benefits of such a connection to improve on excitation energies. Our results suggest that addition of perturbative corrections to account for double excitations and missing exchange effects could result in significantly improved estimates.

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I. INTRODUCTION

The random phase approximation (RPA)¹⁻³, in its various flavors, holds a historical place in the development of theoretical models in condensed matter physics and quantum chemistry⁴⁻⁸. From the viewpoint of quantum chemistry RPA has offered a dilemma. RPAs primary role in quantum chemistry before its recent resurgence through use in density functional theory(DFT),⁹ had been to describe *non-correlated* approximations to excitation energies of molecules as an effective one-particle theory. This is unlike *ab-initio* theory such as coupled cluster (CC) or configuration interaction (CI) whose focus has been the correlation problem and its subsequent effect on all other properties including excited states. So, in the context of excited states, RPA is a pseudonym for time-dependent Hartree-Fock (TDHF)^{8,10,11} and as Hartree-Fock(HF) for ground states, does not include correlation explicitly. In TDHF, the perturbation might be time-dependent but still only *orbital relaxation* is obtained. In its time (or frequency)-independent form it becomes coupled-perturbed HF (CPHF) whose solutions introduce the *orbital relaxation* in a set of HF orbitals under the influence of a perturbation. Thus, the solution is *relaxed* but not correlated. It is true that in many-body physics the term RPA also corresponds to the well-known infinite sum of ring diagrams^{12,13} that describes the correlation energy of the high-density electron gas.¹⁻³ Similarly, an equivalence has been known for the ground state energy for RPA and a particular approximation to coupled cluster doubles (ring CCD) method¹³⁻¹⁵. But this is the origin of the RPA dilemma. RPA solutions for excited states have no correlation, but RPA for the ground state of a molecule corresponds to the sum of correlated ring diagrams. One would think there would be some kind of obvious connection?

The above question has caused much consternation over the years, as it was felt that an identification of a consistent correlated ground state¹⁶⁻¹⁹ could be used to define an optimum method that would naturally build electron correlation into RPAs excited states, enabling it to provide much more accurate results than the normal RPA based on an assumption of HF ground state. The origin of this dilemma sheds some light on the different philosophy of propagators and wavefunctions. The polarization propagator focuses on the choice of *intermediate states*,^{20,21} through particle-hole (*ph*) excitations and de-excitations (*hp*), while trying to de-emphasize the explicit role of the correlated ground state.²² At the time, the hope seemed to be that the correlation problem for ground states was more difficult than that for excited states, so some easily obtained ground state approximation could then be used to complete the cycle to provide excitation energies. Once this

ground state is chosen to be the HF one, then the equations provide the usual RPA=TDHF excitation energies as the poles and the intensities as the residues at the poles, clearly without correlation. Another way of saying the same thing is that the exact answer (full CI) can be obtained from using all intermediate states, $\{ph, 2p2h, 3p3h, \}$ and their de-excitations $\{hp, 2h2p, 3h3p, \}$ minus the Fermi vacuum $|0\rangle$ as they constitute a complete space.²³ This is the choice of propagator theory. This is the contrary to the choice of CC theory and EOM-CC, which is how correlation will be added in this paper i.e. by including the vacuum (reference determinant) plus all single, double, triple, . . . excitations, eventually giving the full CI. A third way to think about the problem is that of Rowes equation-of-motion (EOM) approach to RPA,^{8,24} that shows the lack of correlation in RPA arises from the failure of the *killer* condition that an operator, O , composed of ph and hp terms, does not satisfy $O|\Psi_0\rangle = 0$. This is contrary to CIS, where O consists of just the excitation operators and thus $O|0\rangle = 0$, or for the CC wavefunction where also $O|\Psi_{CC}\rangle = 0$. In the latter case this *killer* condition is satisfied for any degree of excitation in O because there is no degree of freedom left in the CC wavefunction. A *consistent* ground state has to be correlated, but what level of correlation is optimum? And is there a sweet spot where the balance between the intermediate states, and the ground state correlation is ideal?

One initial attempt to introduce a correlated ground state was done by Shibuya and McKoy, leading to what is termed higher-RPA.²⁵⁻²⁷ By using such a first-order correlated reference wavefunction (MBPT(1)) as the correlated ground state in the RPA evaluation, the numerical excitation energies limited to ph and hp terms were shown to be improved. In principle, this approach could be generalized to higher-orders in MBPT, or even to CC theory. But even assessing the comparative importance of ground state correlation and more extensive intermediate states (such as $2p2h$, $2h2p$ and further) remains difficult. Another such approach was the second-order polarization propagator approximation (SOPPA) of Oddeshede, Sauer and co-workers.²⁸⁻³⁰ An independent route tried to identify on formal grounds the kind of wavefunction that would offer a consistent RPA ground state. This led to the introduction of the anti-symmetrized geminal power (AGP) wavefunction of Linderberg, Ohrn, Weiner and Goscinski, equivalent to a projected BCS solution.^{18,31,32} But as shown by Dalgaard an AGP is not the correct solution.³³ A new route could be suggested, too. Verma and Bartlett show that a one-particle correlation potential generated from RPAs ground state correlation can be rigorously defined to augment the usual Fock operator of standard RPA (=TDHF), which would turn RPA into a correlated method in a different way, more familiar in TDDFT circles.³⁴ But unlike others in TDDFT, this RPA-OEP potential is *ab-initio*. This can also

be done for CC approximations in the same way. Such methods will be considered in future work.

In context of this work, we are interested in the ramifications of the equivalence of (direct)RPA with (direct)ring-CCD,^{13,14,35} and the subsequent equivalence for excitation energies predicted by RPA and equation-of-motion approach based on (ring) coupled cluster doubles (rCCD) ground state wavefunction as presented recently by Berkelbach³⁶. This identity has a potential to enrich both the RPA and EOM-CC family of methods. In particular, we could benefit from the past two decades of work introducing and establishing EOM-CC methods as the an accurate benchmark for excited and ionized states of molecular systems.

Equation of motion approach based on a coupled cluster^{37,38} ground state reference (EOM-CC)³⁹⁻⁴² has been shown to accurately calculate the excitation energies for molecular systems⁴³⁻⁴⁶ and, more recently, for condensed matter systems^{47,48}. EOM-CCSD method (N^6 scaling) offers an accuracy of 0.2-0.3 eV for states with dominant single excitation character^{49,50} and has recently been applied to large molecular systems based on local coupled cluster⁵¹. Complete inclusion of triples leads to EOM-CCSDT method⁵²⁻⁵⁴ whose error estimate has been shown to be 0.05-0.1 eV off the full configuration interaction(FCI) results for singly and doubly excited states. Several approaches with approximate treatment of triples exist (EOM-CCSDT-3⁵⁵, EOM-CCSD(T)^{49,56}, EOM-CCSDR3,⁵⁷ EOM-CCSDT-1a*⁵⁸ and CC3⁵⁹) and offer a balance between accuracy and computational cost^{49,55,56,60}. But even EOM-CCSD is computationally expensive for moderately large systems^{46,61} and hence, approximations (EOM MBPT(2)/EOM CCSD(2), partitioned EOM MBPT(2), CIS(D) and CIS(D_∞), potentially scaling lower than N^6 , have been developed^{51,62-73}. In the context of this work, we are interested in the potential for the development of a low-scaling EOM-CC method inspired by its RPA connection.

As the excitation energies estimate from RPA show large deviation from highly accurate EOM-CCSD result, an effort in direction of improving it by the inclusion of double excitation effects, RPA(D), was made by Sauer et al.^{30,74} This is done in similar spirit to the non-iterative (D) correction to CIS method as put forth by Head-Gordon et al.⁶³ In the realm of polarization propagator approaches, RPA is seen to incorporate first-order effects and consequently, second-order approaches (SOPPA) have been proposed as well^{28,75}. In a recent work using RPA based on KS states, a TDDFT formulation was applied to treat molecular excited states⁷⁶. In a different direction, exploratory papers by Pernal et al., DePrince et al., and Ayers et al. studied the performance of extended RPA (RPA) approach, using geminal wavefunction as a reference, in a formalism employing reduced density matrices(RDMs).⁷⁷⁻⁸¹ A formulation of particle-particle RPA, analo-

gous to the more explored particle-hole RPA, has also been used to calculate excited state energies (double excitations) and other properties.^{82–84}

A recent upsurge of interest in RPA has been due to its use in density functional theory (DFT) to develop more accurate exchange-correlation functionals.^{35,85,86} Adiabatic connection fluctuation dissipation theorem (ACFDT)^{11,87,88} gives expression for exchange-correlation energy in terms of (density) response functions⁸⁵. Evaluating this expression by transition density matrices from Kohn-Sham based RPA (KS-RPA), one obtains post KS-DFT corrections. Authors have argued that these functionals produce results close to *ab-initio* quality in benchmark studies and are generally classified as 'fifth rung of the Jacob's ladder' of DFT functionals^{89,90} which in addition to density and its gradient, requires full set of occupied orbitals and virtual orbitals, and where then RPA correlation is added on top of exact HF exchange included in KS-DFT. RPA has also been used to propose functionals in the double hybrid category by Kallay, Ruzinszky, Toulouse and others.^{91–93} Scuseria and co-workers proposed the use of direct RPA and later, dRPA+SOSEX (Second-order screened exchange) as the long-range component of the DFT correlation energy with the incorporation of short range correlation through local spin density approximation (LSDA).^{94–96} This is based on RPA including a significant portion of the long-range component of the correlation energy, and hence used for improving the dispersion description for large molecular systems.^{97,98} Other developments include hybrid and double hybrid functional (dRPA75 - dRPA correlation + 75 percent exact exchange + semilocal exchange) and application to transition metals and probe of dependence on choice of reference determinant.

Recent developments enriching the RPA toolbox also include devising of F12 corrections by Klopper et al.,^{99–101} a multi-reference formulation,^{102,103} addition of the effect of single excitations (or orbital relaxation),¹⁰⁴ analytical gradients,^{105–107} and devising of exchange corrections to direct RPA. RPA is non-perturbative and hence, more robust when dealing with state degeneracies.¹⁰⁸ As dRPA suffers from self-interaction error (it violates Pauli's exclusion principle), a lot of effort have been put to propose approximations that eliminate parts of it (one-electron self-interaction error) and reduce the many-body self-interaction error as well.¹⁰⁹ The acronyms SOX, SOSEX¹¹⁰, RPA+, IOSEX¹¹¹ and more recently gRPA+¹¹² all refer to such approximations. Another way to overcome Pauli principle violation was reported by Kosov¹¹³ who proposed an a posteriori correction to single particle density matrix obtained after HF based dRPA calculation. Unresolved connections exist between the treatment of static correlation and the presence of self-interaction error.¹¹⁴ (d)rCCD methods have also been studied and extended through the paradigm of coupled

cluster perturbation theory where (d)rCCD is considered to be the zeroth-order problem.¹¹⁵

Another stream of work has focused on reducing the computational cost associated with RPA methods.^{85,116} Formally RPA scales as N^6 , but many recent work employing density-fitted (DF) basis have reported cubic scaling (N^3) implementations thus leading to massive reduction in cost.^{117–121} Employing localized orbitals has led to linear scaling implementation for dRPA¹²² and has resulted in lower scaling for models including exchange corrections.¹²³ Most of work employing RPA have insisted on the use of KS reference determinant rather than a HF reference. It is justified on the basis of relatively good numerical results but awaits rigorous explanation.

The intent of this paper is to explore the systematic inclusion of electron correlation via coupled-cluster theory to try to obtain improved approximations to RPA. Compared to propagator methods where the correlated reference state is considered secondary (a different view could be seen in the work of Ortiz, Sauer and Dreuw and co-workers),^{75,124–126} using the CC wavefunction as the reference state can have some major consequences. For example, in the electron propagator (EP) once $|\Psi_{CC}\rangle = e^T |\Psi_0\rangle$ is inserted into it, several benefits occur.^{127–129} First, the frequency dependence of the self-energy is rigorously removed. Second, the EP divides naturally into an ionization problem, IP-EOM-CC and an independent electron affinity problem, EA-EOM-CC, eliminating the unphysical coupling that exists in the EP.¹³⁰ Third, the dominate IPs and EAs are the first solutions obtained from diagonalizing the similarity transformed Hamiltonian (\bar{H} in CC theory) in the IP/EA-EOM-CC equations, instead of being hidden among the full set of all possible solutions of the EP like those due to shake-ups. Somewhat analogously, this paper wants to address the insertion of the CC wavefunction as the correlated reference into the RPA excited state problem in general, or the polarization propagator in particular; and observe the consequences. All such approaches begin with the electronic excitation energy variant (EE)-EOM-CC,^{39,41,42} that has two places where electron correlation appears: (1) The similarity transformed Hamiltonian, $\bar{H} = e^{-T} H e^T$ that has the ground state correlation in it, and (2) its projection onto an excitation only Hilbert space that defines the correlated excited states, $\{R_k\}$ and their left-hand complements, $\{L_k\}$ and thus the $\bar{H}R_k = \omega_k R_k$, that provides the $\{\omega_k\}$ with their bi-orthogonal norm, $\langle L_k | R_k \rangle = \delta_{kl}$ and their associated transition moments. The full CI requires that the Hilbert space generated by T and used in \bar{H} include the Fermi vacuum and all possible excitations from it. This is a formally important boundary condition, but would seem to be redundant if the goal is to find a mutually beneficial level of ground state correlation coupled to a representation of the excited states that would maximize results while offering a reasonable level of computation. But

for that model to be completely satisfactory, one still needs to be able to recover the FCI at some representative level. One important distinction between EOM-CC and RPA or the polarization propagator as mentioned above, is that EOM-CC exclusively uses excitation operators, with no de-excitations included in the projection of \bar{H} . Their inclusion greatly complicates the EOM-CC theory, because the excitation operator, T , does not commute with de-excitation operators, but could possibly be done. Another distinction is that EOM-CC is non-Hermitian, as is the most natural matrix form of the RPA equations, but unlike the former, the RPA equations can be put into a purely Hermitian form. So with this overview, we embark on this RPA to EOM-CC study.

(direct) ring CCD equations:
 $\langle \phi_{ij}^{ab} | (e^{-T_2} H_N e^{-T_2}) | \psi_{HF} \rangle = 0 \quad \forall \{i, j, a, b\}$

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} X \\ Y \end{pmatrix}$$

↔

$$\bar{H}R_1 = \omega R_1$$

$$\begin{pmatrix} H_{SS} & H_{DO} \\ -H_{DO} & -H_{SS} \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} X \\ Y \end{pmatrix}$$

↔

$$((H + HT_2)R_1)_c = \omega R_1$$

$$A = \langle \phi_i^a | H | \phi_j^b \rangle = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + \langle ib || aj \rangle$$

$$B = \langle \phi_{ij}^{ab} | H | \psi_{HF} \rangle = \langle ab || ij \rangle$$

FIG. 1: Relationship between random phase approximation for excited states and the equation of motion coupled cluster based on (direct) ring CCD

We develop approximations based on EOM-CC approach, starting from those numerically equivalent to (d)RPA, and assess the suitability of various iterative and perturbative corrections to these parent models by a numerical analysis of the results for small molecular systems. In the next section (II), we develop the theoretical background behind the RPA methods and how it links with general equation of motion (EOM) approach. We then probe how a connection of RPA with coupled cluster approximation for ground state leads to a relationship between RPA excited states and EOM based on CC ground state and consequently, how different corrections to RPA excitation energy could potentially improve it. We analyze the results of these approximations in the

subsequent section (III).

II. THEORY

A. An equation of motion approach to excited states in random phase approximation

We shall briefly lay down the theory of random phase approximation and its connection to the other established methodologies in quantum chemistry. To begin, let's denote ground state Hartree-Fock (HF) wavefunction as $|\Psi_{HF}\rangle$. We define the RPA creation operator to be composed of excitation (particle-hole creation) and de-excitation (particle-hole annihilation) operators.

$$O^\dagger = X_{ai}\{a_a^\dagger a_i\} - Y_{ia}\{a_i^\dagger a_a\} \quad (1)$$

The application of O^\dagger to the RPA ground state, $|\Psi_{ground}\rangle$, leads to the creation of excited states

$$O^\dagger |\Psi_{ground}\rangle = |\Psi_{excited}^{RPA}\rangle \quad (2)$$

The corresponding annihilation operator (O) should satisfy the *killer condition* :

$$O |\Psi_{ground}\rangle = 0 \quad (3)$$

Writing the Schrödinger equation for the ground and the excited state,

$$H |\Psi_{ground}\rangle = E_g |\Psi_{ground}\rangle \quad (4)$$

and

$$H |\Psi_{excited}\rangle = E_{ex} |\Psi_{excited}\rangle \quad (5)$$

Using the relation II A and subtracting the two equations, we obtain,

$$HO^\dagger |\Psi_{ground}\rangle - O^\dagger H |\Psi_{ground}\rangle = (E_{ex} - E_g)O^\dagger |\Psi_{ground}\rangle \quad (6)$$

which leads to the equation,

$$[H, O^\dagger] |\Psi_{ground}\rangle = (E_{ex} - E_g)O^\dagger |\Psi_{ground}\rangle \quad (7)$$

and we can define the quantity $\omega = (E_{ex} - E_g)$ as the excitation energy. Considering variations of O , δO such that $\delta O |\Psi_{ground}\rangle = 0$, we arrive at

$$\delta O[H, O^\dagger] |\Psi_{ground}\rangle = (E_{ex} - E_g) \delta O O^\dagger |\Psi_{ground}\rangle \quad (8)$$

which furthermore leads to the double commutator relation,

$$[\delta O, [H, O^\dagger]] |\Psi_{ground}\rangle = (E_{ex} - E_g) [\delta O, O^\dagger] |\Psi_{ground}\rangle \quad (9)$$

If we try evaluating above expression by considering variations of O based on its definition (1), δO which are $X_{ai}\{a_a^\dagger a_i\}$ and $Y_{ia}\{a_i^\dagger a_a\}$ respectively, we get the following commutator terms on the right hand side,

$$\langle \Psi_{ground} | [a_a^\dagger a_i, a_j^\dagger a_b] | \Psi_{ground} \rangle \quad (10)$$

It is unclear what an appropriate ground state wavefunction, $|\Psi_{ground}\rangle$, is for random-phase approximation (RPA) and has been the subject of intense debate over last few decades. To evaluate the above expression, we need to invoke the assumption that HF wavefunction is the ground state for RPA i.e. $|\Psi_{ground}\rangle = |\Psi_{HF}\rangle = |\Psi_0\rangle$. And the second related assumption is the so-called *quasi-boson approximation* which allows the replacement of the expectation value of the commutator with $|\Psi_{ground}\rangle$ by the the expectation value of the commutator with $|\Psi_{HF}\rangle$ wavefunction and thus results in boson-like commutator relations which is to say

$$\langle \Psi_{HF} | [a_a^\dagger a_i, a_j^\dagger a_b] | \Psi_{HF} \rangle = \delta_{ij} \delta_{ab} \quad (11)$$

Evaluating the matrix elements using the above assumptions and breaking the double-commutator relation into parts, we obtain

$$((\varepsilon_e - \varepsilon_m) \delta_{ae} \delta_{im} + \langle ma || ei \rangle) X_{em}^k - \langle ea || mi \rangle Y_{em}^k = \omega_k X_{ai}^k \quad (12)$$

$$-((\varepsilon_e - \varepsilon_m) \delta_{ae} \delta_{im} + \langle ei || ma \rangle) Y_{em}^k - \langle mi || ea \rangle X_{em}^k = \omega_k Y_{ai}^k \quad (13)$$

These two equations (12) and (13) can be written in a compact matrix form as

$$\begin{pmatrix} A & B \\ -B^\dagger & -A^\dagger \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} X \\ Y \end{pmatrix} \quad (14)$$

where elements of A and B blocks are defined as

$$A_{ai,em} = (\varepsilon_e - \varepsilon_m) \delta_{ae} \delta_{im} + \langle ma || ei \rangle \quad (15)$$

and

$$B_{ai,em} = -\langle ea||mi\rangle \quad (16)$$

and ω is a set of eigenvalues consisting of two identical blocks of positive and negative eigenvalues.

B. Coupled cluster connection to the correlated ground state for RPA

There has been an unending debate on the true nature of RPA ground state^{18,131}. The fact that RPA allows for ground state correlation through the de-excitation operators suggests that the corresponding wave function would not be a single Slater determinant. This has led to a series of studies exploring self-consistent ground state for RPA (SC-RPA). Associated with this concern is the fulfillment of the killer condition i.e. the application of RPA annihilation operator should destroy the ground state

$$O|\Psi_{RPA}\rangle = 0 \quad (17)$$

If the ground state is a HF wavefunction (HF-RPA), the killer condition is not satisfied.

$$O|\Psi_{HF}\rangle \neq 0 \quad (18)$$

A correlated ground state may satisfy this condition.^{18,131}

Recently, the work of Scuseria et al. showed analytical equivalence between a subset of CCD (named direct ring-CCD or dr-CCD) residual equations and direct random phase approximation (dRPA) equations.¹⁴ This potentially provides a consistent ground state for RPA approximation but the wavefunction form still appears to be unclear as there is no clear exponential form deducible from the truncated subset of drCCD residual equations (which is shown equivalent to dRPA equations and the double excitation amplitude, $T_2^{drCCD} = YX^{-1}$).

Considering the normal-ordered Hamiltonian as

$$\hat{H} = \hat{f}_{pq}\{a_p^\dagger a_q\} + \frac{1}{4}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\} \quad (19)$$

where p, q, \dots are spin-orbitals that are obtained after convergence of HF equations: $\hat{f}|p\rangle = \epsilon_p|p\rangle$. Also, the antisymmetrized integrals are defined as $\langle pq||rs\rangle = \langle pq|rs\rangle - \langle pq|sr\rangle$, and $\langle p|q\rangle = \delta_{pq}$. Einstein summation is assumed wherever required throughout the manuscript.

If we begin with the coupled cluster doubles parameterization of the wavefunction,

$$|\Psi_{CCD}\rangle = e^{T_2}|\Psi_{HF}\rangle \quad (20)$$

The double excitation operator, $T_2 = \frac{1}{4}t_{ij}^{ab}\{a_a^\dagger a_b^\dagger a_j a_i\}$ is defined as such and the associated amplitudes t_{ij}^{ab} could be calculated from the doubles residual equation

$$R_{ij}^{ab} = \langle D | \bar{H} | \Psi_{HF} \rangle = 0 \quad (21)$$

where $\bar{H} = e^{-T} H e^T$ is the similarity transformed Hamiltonian and the projection from left is through doubly excited determinants ($\langle D |$). Without delving into the complete derivation of coupled cluster doubles (CCD) equations^{37,38,132,133}, we would like to draw connections to the terms that are present in the ring CCD and direct-ring CCD approximation,

To revisit the (d)ring-CCD equations for ground state, we have

$$R_{ij}^{ab} = \langle ab || ij \rangle + (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)t_{ij}^{ab} + P(ij)P(ab)t_{im}^{ae}W_{ej}^{mb} \quad (22)$$

Only the coulomb integrals are used in case of direct ring-CCD equations and the consequent t_{ij}^{ab} amplitudes are not antisymmetric with the permutation of indices (i with j and a with b). We also restrict the permutation operator ($P(ij)P(ab)$), that antisymmetrizes the third term in the residual, to keep only the contributions that are totally symmetric to simultaneous exchange of i with j and a with b . That is $P(ij)P(ab) = 1 + P(ij)P(ab)$ and henceforth simply designated as $P_-(ij)P_-ab$. This leads to a form of r-CCD equation given as,

$$R_{ij}^{ab} = \langle ab || ij \rangle + (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)t_{ij}^{ab} + (t_{im}^{ae}\langle mb || ej \rangle + t_{jm}^{be}\langle ma || ei \rangle) + t_{im}^{ae}\langle mn || ef \rangle t_{nj}^{bf} \quad (23)$$

The amplitudes obtained are no longer antisymmetric in (d)rCCD. Restated, this is the Pauli principle violation that is in general not in CC methods or in the multitude of CCD/CCSD like approximations¹³⁴ with two exceptions: distinguished cluster(DCD, DCSD and DCSDT)¹³⁵⁻¹³⁹ and approximate coupled pair (ACP) variant (ACP-D14)^{140,141}. The consequences of this violation, which is a form of many-body self-interaction, is unclear. A link between self-interaction error present in RPA as used in density functional theory (DFT) and the ability to capture static correlation has been mentioned by Henderson et al.¹¹⁴.

It is important to once again point out that as opposed to the CCD wave function which is an exponential, neither of the r-CCD or dr-CCD wave functions can be written in terms of an exponential parametrization. It might be fair to say that these models do not have compact analytic

form of the wavefunction. The equations for the amplitudes (and for the corresponding energy) come out to be a subset of CCD equations but cannot be traced back to an exponential wavefunction ansatz themselves. This distinction to CCD is extensively used in subsequent development in this work. The forms of the energy expressions are discussed below after we show the identities of r-CCD and dr-CCD to RPA and d-RPA respectively.

Following Scuseria et al.,¹⁴ we introduce the terms A and B defined as $B_{ia,bj} = \langle ab||ij \rangle$ and $A_{ia,bj} = (\epsilon_a - \epsilon_i)\delta_{ab}\delta_{ij} + \langle ia||bj \rangle$ in the equation (II B) and with some manipulations, we obtain

$$R_{ij}^{ab} = \langle ab||ij \rangle + t_{im}^{ae} \langle mb||ej \rangle + (\epsilon_e - \epsilon_m)\delta_{eb}\delta_{mj}t_{im}^{ae} + t_{jm}^{be} \langle ma||ei \rangle + (\epsilon_e - \epsilon_m)\delta_{ea}\delta_{mi}t_{jm}^{be} + t_{im}^{ae} \langle mn||ef \rangle t_{nj}^{bf} \quad (24)$$

Defining $T_{ai,bj} = t_{ij}^{ab}$ and rewriting the equation, we obtain

$$B + TA + AT + TBT = 0 \quad (25)$$

We will now see that equation 25 is identical to the expression obtained from the RPA eigenvalue equation (14). As shown before, RPA is generally cast as an eigenvalue problem

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \begin{pmatrix} X \\ Y \end{pmatrix} \omega \quad (26)$$

where A and B are defined as

$$A = \langle \Phi_i^a | H | \Phi_j^b \rangle \quad (27)$$

$$B = \langle \Phi_{ij}^{ab} | H | \Psi_{HF} \rangle \quad (28)$$

and ω is the diagonal matrix containing the single excitation and de-excitation energies. We obtain an identical set of excitation energies and de-excitation energies.

Post-multiplying with X^{-1} on both sides and using $T = YX^{-1}$, we obtain

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{pmatrix} 1 \\ T \end{pmatrix} = \begin{pmatrix} 1 \\ T \end{pmatrix} X \omega X^{-1} \quad (29)$$

If we put substitute R for $X \omega X^{-1}$, we have

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{pmatrix} 1 \\ T \end{pmatrix} = \begin{pmatrix} 1 \\ T \end{pmatrix} R \quad (30)$$

which can be expanded to obtain two equations

$$A + BT = R \quad (31)$$

and

$$-B + AT = RT \quad (32)$$

Substituting equation 31 in 32, we get

$$B + TA + AT + TBT = 0 \quad (33)$$

which is the same equation obtained from ring CCD expression in equation (25). Depending on whether the above matrix is positive semi-definite, the eigenvalues may or may not be real. For the case of direct RPA, it is always positive definite and eigenvalues are real. This is not guaranteed for RPA (which includes exchange terms). The diagonalization of the matrix yields excitation energies (ω) for singly excited states and the eigenvectors which are the coefficients in terms of single excitations and de-excitations.

Recent work³⁶ by Berkelbach shows the numerical equivalence of the RPA excitation energies with those obtained from diagonalization, in the space of single excitation determinants, of similarity transformed Hamiltonian (\tilde{H}_{SS}) constructed for equation-of-motion approach based on ring CCD (or EOM r-CCD),

$$\tilde{H}_{SS} = \left[\langle S | \tilde{H} | S \rangle \right]$$

The rCCD and drCCD models are approximate ground state CC methods. From that viewpoint, we should be able to follow EOM-CC developments to formulate corresponding excited state analogs. We stated earlier that the r-CCD and dr-CCD only have defining equations for the amplitudes and for the corresponding energy, and unlike CCD that they do not conform to an exponential parameterization. Nevertheless, all the density matrices, and therefore the energy and all the other molecular properties can be obtained since having a compact analytic expression for the wave function is not a prerequisite to formulate the density matrices. We will discuss the caveats associated with these equivalences: dRPA to EOM-drCCD and RPA to EOM-rCCD. But first let us discuss the ground state correlation energy expression for various rCCD models and their equivalence with the RPA ground state correlation energy expressions.

C. Correlation energy expressions from CC and general RPA route

The lack of antisymmetry of double excitation amplitudes (T_2 ; $t_{ij}^{ab} \neq -t_{ji}^{ab}$ and $t_{ij}^{ab} \neq -t_{ij}^{ba}$) in r-CCD has several implications. As in CCD, the spin-orbital form of the r-CCD equations has three unique sets of amplitudes, t_{IJ}^{AB} , t_{ij}^{ab} and t_{Ij}^{Ab} where upper case and lower case letters designate α and β spin-orbitals respectively. In open-shell implementations (UHF or ROHF) we solve for three sets of residual equations corresponding to those three unique set of amplitudes. While for spin-adapted RHF, there are two set of amplitudes: the triplet spin-adapted amplitudes and the singlet spin-adapted amplitudes, and the two corresponding amplitude equations. In contrast, when the amplitudes are antisymmetric, there is only one set of spin-adapted RHF amplitudes (and one corresponding amplitude equation), and the UHF and the spin-adapted RHF implementations give identical energies for closed shell systems (assuming that the reference RHF and UHF states too are identical). This is due to $t_{IJ}^{AB} = t_{Ij}^{Ab} - t_{iJ}^{bA}$ (note $t_{Ij}^{Ab} = t_{bA}^{iJ}$ is the only unique amplitude) which no longer holds when the amplitudes are not antisymmetric. These points are easily seen by comparing the algebraic expressions for the CCD and r-CCD energies. First let us write the expressions for the CCD energies. We consider both the RHF and UHF references. The spin-orbital expressions,

$$E_{CCD} = \frac{1}{4} Tr(\bar{B}\bar{T}) = \frac{1}{2} Tr(B\bar{T}) \quad (34)$$

leads to the spin-integrated UHF CCD energy given as,

$$E_{UCCD} = \frac{1}{4} \bar{t}_{IJ}^{AB} \langle IJ || AB \rangle + \frac{1}{4} \bar{t}_{ij}^{ab} \langle ij || ab \rangle + t_{Ij}^{Ab} \langle Ij || Ab \rangle \quad (35)$$

while the RHF CCD energy is,

$$E_{RCCD} = \frac{1}{2} \bar{t}_{IJ}^{AB} \langle IJ || AB \rangle + t_{Ij}^{Ab} \langle Ij || Ab \rangle \quad (36)$$

(since $\langle IJ || AB \rangle = \langle ij || ab \rangle$ and $t_{IJ}^{AB} = t_{ij}^{ab}$) or the spin-adapted form,

$$E_{RCCD} = t_{Ij}^{Ab} (2 \langle Ij || Ab \rangle - \langle Ij || bA \rangle) \quad (37)$$

The overbar explicitly identifies the antisymmetric quantities. We can immediately see that for the closed shell molecules UHF and RHF CCD correlation energies are identical when the two reference states are also identical. The situation with r-CCD is different. Unlike the CCD energy, the spin-orbital energy,

$$E_{r-CCD} = \frac{1}{4} Tr(\bar{B}T) \quad (38)$$

can only be expressed in terms of the antisymmetrized integrals \bar{B} (since T is not antisymmetric). There are two possible UHF and the corresponding spin-adapted RHF formulations. One of them neglect the spin-flip excitations⁹⁹ and the corresponding UHF/ROHF energy in spin-integrated form is

$$E_{Ur-CCD} = \frac{1}{4}\bar{t}_{IJ}^{AB}\langle IJ||AB\rangle + \frac{1}{4}\bar{t}_{ij}^{ab}\langle ij||ab\rangle + \frac{1}{2}t_{Ij}^{Ab}\langle Ij||Ab\rangle \quad (39)$$

while the corresponding RHF spin-adapted energy is,

$$E_{Rr-CCD} = \frac{1}{4}({}^3B^3T + {}^1B^1T) \quad (40)$$

where singlet and triplet spin-adapted integrals, 1B and 3B are given by ${}^1B = 2\langle Ij||Ab\rangle - \langle Ij||bA\rangle$ and ${}^3B = -\langle Ij||bA\rangle$ respectively. Similarly, the singlet and triplet spin-adapted r-CCD amplitudes, 1T and 3T are given by $t_{Ij}^{AB} + t_{Ij}^{Ab}$ and $t_{Ij}^{AB} - t_{Ij}^{Ab}$ respectively. Let us postpone the discussion of spin-flip r-CCD until we present ground state correlation energy expressions for RPA. That approach is more transparent since it is very easy to see the origin of the spin-flip excitation in the context of RPA and then import those ideas to r-CCD. In the case of dr-CCD all the two electron integrals are Coulomb only and symmetric. Therefore the spin-orbital expression for the energy is,

$$E_{dr-CCD} = \frac{1}{2}Tr(BT) \quad (41)$$

(here the factor is $\frac{1}{2}$ instead of $\frac{1}{4}$ because B is symmetric). The spin-integrated UHF/ROHF energy is,

$$E_{Udr-CCD} = \frac{1}{2}t_{IJ}^{AB}\langle IJ||AB\rangle + \frac{1}{2}t_{ij}^{ab}\langle ij||ab\rangle + t_{Ij}^{Ab}\langle Ij||Ab\rangle \quad (42)$$

The corresponding spin-adapted RHF energy is

$$E_{Udr-CCD} = 2t_{Ij}^{Ab}\langle Ij||Ab\rangle \quad (43)$$

All the above expressions are derived from the rCCD/drCCD viewpoint. Now let us turn our attention to the RPA approach (without appealing to the identity to rCCD). A concept of a ground state energy for RPA (which is primarily an excited states theory) can be developed by conceptualizing that the RPA excitations are bosonic oscillators and the excitation energies are the corresponding oscillatory frequencies. From that view point and analogous to the zero point energy of molecular vibrations, the RPA ground state correlation energy for dr-CCD is,

$$E_{dr-CCD} = E_{d-RPA} = \frac{1}{2}\sum_i(\omega_i - Tr(A)) \quad (44)$$

while for the r-CCD the energy is,

$$E_{r-CCD} = E_{RPA} = \frac{1}{4} \sum_i (\omega_i - Tr(A)) \quad (45)$$

In terms of r-CCD/dr-CCD, we know that $T = YX^{-1}$, $A + BT = R$ and $R = X\omega X^{-1}$. This leads to,

$$Tr(BT) = Tr(R) - Tr(A) \quad (46)$$

$$Tr(BT) = Tr(X\omega X^{-1}) - Tr(A) \quad (47)$$

$$Tr(BT) = \sum_i (\omega_i - \sigma_i) \quad (48)$$

where $\sigma_i = Tr(A)$ are configuration interaction singles (CIS) excitation energies. Notwithstanding the debate that RPA is a correlated method, the above equation can be interpreted as an expression for the energy difference between a correlated and a reference uncorrelated method (CIS). Purely from the r/dr-CCD view point, we can unambiguously write the correlation energy as $\frac{1}{4}Tr(\bar{B}T)$ and $\frac{1}{2}Tr(BT)$ for r-CCD and dr-CCD respectively. However, physical attribution of the RPA states to bosonic vibrators leads to factor $\frac{1}{2}$ instead of $\frac{1}{4}$ for RPA correlation energy (as far as we know this ambiguity has not been fully resolved). The RPA or CIS solutions are singlet or triplet states. Both singlet and triplets states enter the correlation energy expression and can be factorized for direct-RPA as,

$$E_{d-RPA} = \frac{1}{2} \sum_i [(\omega_i - \sigma_i)^1 + (\omega_i - \sigma_i)^3] \quad (49)$$

In the case of RPA, we have two corresponding expressions. One with the spin-flip excitation included is given as,

$$E_{RPA}^{(w/flip)} = \frac{1}{4} \sum_i [(\omega_i - \sigma_i)^1 + 3(\omega_i - \sigma_i)^3] \quad (50)$$

and the other without the spin-flip excitations given as,

$$E_{RPA}^{(w.o./flip)} = \frac{1}{4} \sum_i [(\omega_i - \sigma_i)^1 + (\omega_i - \sigma_i)^3] \quad (51)$$

where superscripts 1 and 3 refer to singlets and triplets respectively. There are no spin-flip excitations in dr-RPA, since all the integrals in A and B matrices are Coulomb only. The spin-flip forms take into account the excitations (and de-excitations) like $a_\alpha^\dagger i_\beta$ and $i_\beta^\dagger a_\alpha$. For a closed shell ground state, these excitations increase \hat{s}_z by 1 (or decrease by 1 for deexcitations). The operators, $a_\alpha^\dagger i_\beta$, $i_\beta^\dagger a_\alpha$ and $\frac{1}{\sqrt{2}}(a_\alpha^\dagger i_\beta + i_\beta^\dagger a_\alpha)$ are the triplet occupied-virtual one electron replacement operators corresponding to the $\hat{s}_z = 1, -1$ and 0 components. When these excitations are included in

the RPA problem, the triplet states appear as triply degenerate (we only include the $\hat{s}_z = 0$ component of the triplet while considering RPA without the spin-flip excitation). Therefore, when the spin-flip excitations are included the RPA correlation energy expression carries a factor 3 for the triplet states reflecting the degeneracy of the state (see Eqn. II C). In order to account for the RPA spin-flip excitations, the r-CCD (no spin-flip excitations in dr-CCD) needs to be reformulated since the canonical r-CCD equations do not include spin-flip excitations as a consequence of the antisymmetry of the amplitudes^{99–101,142}. Let us show how this is done in detail since the literature is incomplete. The spin-orbital r-CC equations are given by

$$\langle ab||ij\rangle + t_{ij}^{ab}(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) + t_{im}^{ae}\langle mb||ej\rangle + t_{jm}^{be}\langle ma||ei\rangle + t_{im}^{ae}\langle mn||ef\rangle t_{nj}^{bf} = 0 \quad (52)$$

Opposed to the canonical r-CCD, where we need to consider only three unique spin-combinations for the UHF implementations, the spin-flip r-CCD has four unique spin combinations corresponding to the t_{ij}^{AB} , t_{ij}^{ab} , t_{ij}^{Ab} and t_{ij}^{aB} amplitudes. Equations for the first three combinations are identical to canonical r-CCD, and the amplitude equation for $t_{ij}^{aB} (= t_{i\alpha j\beta}^{a\beta b\alpha})$ is given by,

$$\langle aB||Ij\rangle + t_{Ij}^{aB}(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) + t_{Im}^{aE}\langle mB||Ej\rangle + t_{jM}^{Be}\langle Ma||eI\rangle = 0 \quad (53)$$

The spin-orbital energy with the spin-flip excitations is,

$$E_{(r-CCD)}^{w/flip} = \frac{1}{4}Tr(\bar{B}T) \quad (54)$$

spin-integrated into the expression for UHF,

$$E_{Ur-CCD} = \frac{1}{4}t_{IJ}^{AB}\langle IJ||AB\rangle + \frac{1}{4}t_{ij}^{ab}\langle ij||ab\rangle + \frac{1}{2}t_{Ij}^{Ab}\langle Ij||Ab\rangle - \frac{1}{2}t_{Ij}^{aB}\langle Ij||aB\rangle \quad (55)$$

or spin adapted RHF,

$$E_{Rr-CCD} = \frac{1}{4}(3({}^3B^3T) + {}^1B^1T) \quad (56)$$

with the singlet and triplet spin-adapted integrals and amplitude defined above (note that ${}^3T = t_{ij}^{aB}$). We believe that the approach we have taken - first to discuss the spin-flip excitation in the RPA context and then importing those ideas to r-CCD - is informative.

D. Towards excited states through the formulation of Λ equations and effective Hamiltonian (\bar{H}) for ring-CCD

CC(and CCD in particular) is a non-symmetric theory. Therefore the left and right hand wave functions are not identical and the left hand wave function must be determined independently. Both

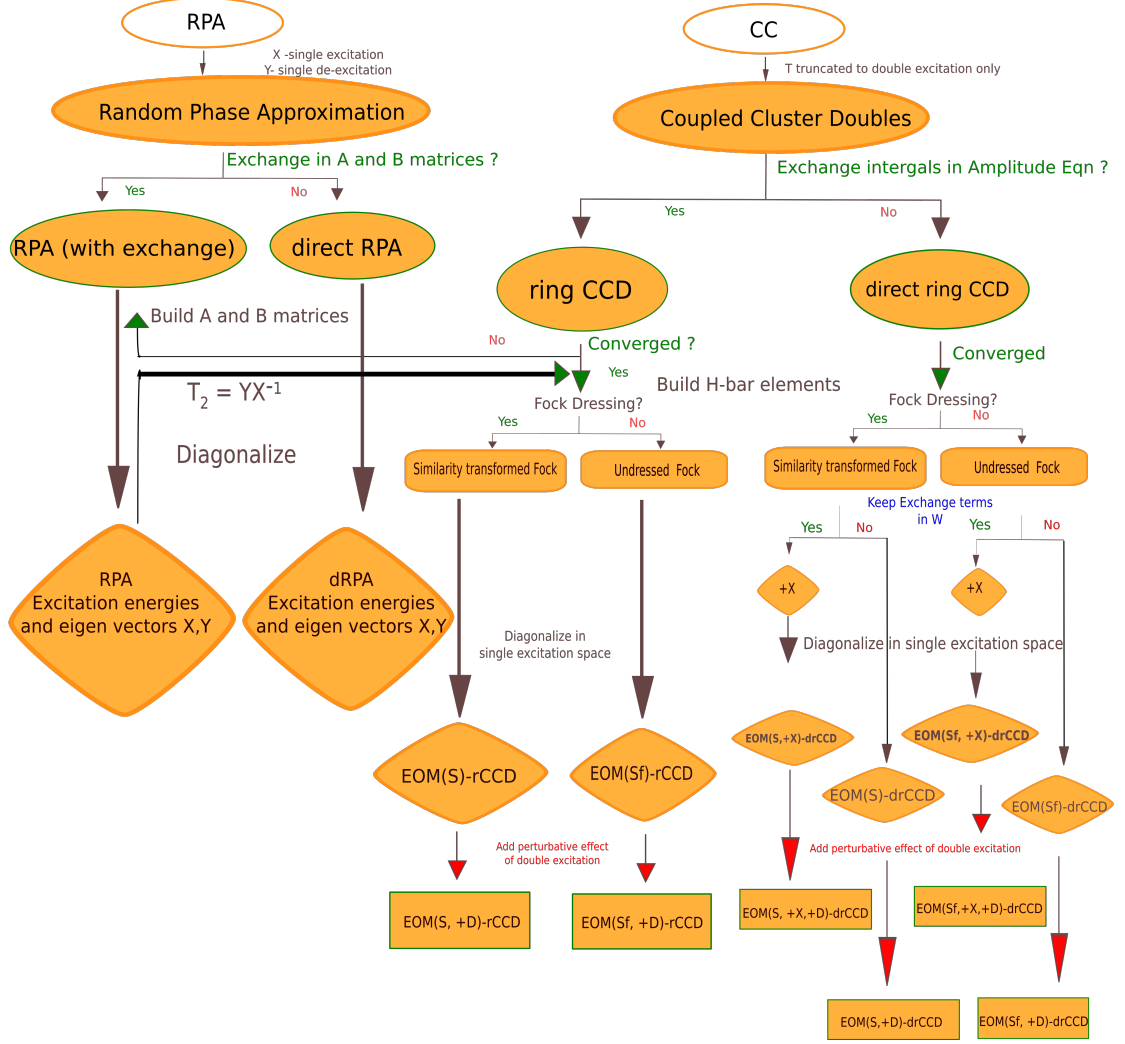


FIG. 2: A flowchart depicting various methods in CC and RPA family studied in this paper

the r-CCD and dr-CCD, which are approximations to CCD, share this property. As we have an equation that defines the amplitudes for the right hand side, the Lagrangian multiplier techniques can be used to define an equation for the left hand as,

$$L = \langle 0 | (HT_2)_c | 0 \rangle + \sum_{i,j,a,b} \lambda_{ab}^{ij} R_{ij}^{ab} \quad (57)$$

We can rewrite the r/dr-CCD Lagrangian simplifying the first-term (energy) and substituting for R_{ij}^{ab} to obtain,

$$L = \frac{1}{4} \langle ab || ij \rangle t_{ij}^{ab} + \lambda_{ab}^{ij} [\langle ab || ij \rangle + t_{ij}^{ab} (f_{ae} \delta_{ea} + f_{bf} \delta_{fb} - f_{mi} \delta_{im} - f_{nj} \delta_{jn}) + (1 + P(ij)P(ab)) t_{im}^{ae} W_{ej}^{mb}] \quad (58)$$

where T_2 satisfies the r-CCD or dr-CCD residual equation and $\Lambda_2 = \sum \lambda_{ab}^{ij} \{i^\dagger j^\dagger ba\}$ is a de-excitation operator corresponding to r-CCD or dr-CCD For comparison, the parent CCD model

can be written compactly as

$$L = \langle 0 | \bar{H} | 0 \rangle + \sum_{\mu} \mu \lambda_{\mu} \langle \mu | \bar{H} | 0 \rangle, \mu = i, j, a, b \quad (59)$$

In order to obtain an equation for Λ_2 , we apply the stationary condition to L with respect to variation of T_2 . (Diagrammatically, this is identical to opening the T_2 and H interacting lines in all possible ways of the closed L diagrams). This leads to,

$$\langle ab || ij \rangle + [(f_{ae} \delta_{ea} + f_{bf} \delta_{fb} - f_{mi} \delta_{im} - f_{nj} \delta_{jn}) \lambda_{ab}^{ij} + (1 + P(ij)P(ab))(W_{ej}^{mb} + \frac{1}{2} t_{nj}^{fb} + \langle mn || ef \rangle) \lambda_{ae}^{im}] = 0 \quad (60)$$

which is the lambda equation for r-CCD or dr-CCD. This can be rewritten as,

$$\bar{H}_{ab}^{ij} + \lambda_{eb}^{ij} (1 + P(ab)) \bar{H}_e^a + \lambda_{ab}^{im} (1 + P(ij)) \bar{H}_m^i + \lambda_{ae}^{im} (1 + P(ij)P(ab)) \bar{H}_{ej}^{mb} = 0 \quad (61)$$

where we have defined $\bar{H}_{ab}^{ij} = \langle ij || ab \rangle$, $\bar{H}_e^a = f_{ae}$, $\bar{H}_m^i = f_{mi}$ and $\bar{H}_{ej}^{mb} = W_{ej}^{mb} + \frac{1}{2} t_{fb}^{nj} \langle mn || ef \rangle$ analogous to the coupled cluster effective Hamiltonian \bar{H} defined above. The critical difference however is that the r-CCD and dr-CCD do not have an exponential form and $\bar{H}^{(d)r-CCD}$ does not correspond to the $\bar{H} = e^{-T} H e^T$ form. As we have shown above, one has to resort to the CC Lagrangian to formulate \bar{H} for r-CCD and dr-CCD. With this protocol, the \bar{H} is defined such that eigenvectors of the lowest (ground state) left solution is Λ_2 . Therefore, it follows that for r-CCD and dr-CCD,

$$\bar{H}_{ij}^{ab} = 0 \quad (62)$$

$$\langle 0 | \bar{H} | 0 \rangle = \Delta E \quad (63)$$

$$\langle 0 | (1 + \Lambda_2) \bar{H} | 0 \rangle = \Delta E \quad (64)$$

where ΔE is the r-CCD or dr-CCD correlation energy. This establishes the fact that we can define a CC like effective Hamiltonian for r-CCD and dr-CCD such that when acted upon from left by $\langle 0 | (1 + \Lambda_2)$ and from right by $|0\rangle$ produces the r-CCD (or dr-CCD) ground state energies. This \bar{H} matrix has the following structure,

$$\begin{pmatrix} \Delta E & \bar{H}_{0S} & \bar{H}_{0D} \\ \bar{H}_{S0} & \bar{H}_{SS} & \bar{H}_{SD} \\ \bar{H}_{D0} & \bar{H}_{DS} & \bar{H}_{DD} \end{pmatrix} \quad (65)$$

with \bar{H}_{SS} , \bar{H}_{SD} , \bar{H}_{DS} and \bar{H}_{DD} are single-single, single-double, double-single and double-double blocks of the matrix and the \bar{H}_{S0} and \bar{H}_{D0} blocks are zero as they constitute the single and double amplitude residual equation. This paves the way for us to consider EOM-CC like formulation for excited states of r-CCD and dr-CCD. Following the standard derivation of EOM-CC, the equation of motion of r-CCD and dr-CCD excited states can be written as,

$$[\bar{H}_{SS}, R_k] |0\rangle = \omega_k R_k |0\rangle \quad (66)$$

where R_k , $r_i^a \{a^\dagger i\}$ is a single excitation operator, \bar{H}_{SS} is the effective Hamiltonian for r-CCD or dr-CCD and ω_k is the excitation energy. The equation for the $(\bar{H}_{SS}R)$ is

$$[\bar{H}_{SS}R]_i^a = \bar{H}_e^a r_i^e - \bar{H}_m^i r_m^a + \bar{H}_{ei}^{ma} r_m^e \quad (67)$$

and the matrix element $[\bar{H}_{SS}R]_{(ai,bj)}$ given by,

$$[\bar{H}_{SS}R]_{ai,bj} = \bar{H}_e^b - \bar{H}_m^j + \bar{H}_{bj}^{ia} \quad (68)$$

Substituting for \bar{H} elements we get,

$$[\bar{H}_{SS}R]_{ai,bj} = (\epsilon_e - \epsilon_m) \delta_{ae} \delta_{im} + \langle ia || bj \rangle + t_{im}^{ae} \langle mj || eb \rangle \quad (69)$$

Since $A_{ai,bj} = (\epsilon_e - \epsilon_m) \delta_{ae} \delta_{im} + \langle ia || bj \rangle$ and $B_{bj,em} = \langle mj || eb \rangle$, we obtain

$$[\bar{H}_{SS}R]_{ai,bj} = A_{ai,bj} + B_{bj,em} t_{ai}^{em} = A + BT \quad (70)$$

We have already shown that the r/dr-CCD residual equation satisfies,

$$(T^{-1}) \begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{pmatrix} 1 \\ T \end{pmatrix} = T^{-1} \begin{pmatrix} 1 \\ T \end{pmatrix} R \quad (71)$$

where $R = A + BT$. Given the eigenvectors and the corresponding eigenvalues of R are X and ω respectively, we can write

$$R = X \omega X^{-1} \quad (72)$$

Comparison of Eqns. shows that the EOM-CC formulation of r/dr-CCD leads to the corresponding RPA formulation for the excited states. Unlike the canonical derivation of the RPA equations where the ground state is left arbitrary, this approach establishes unambiguously that the ground state for RPA (d-RPA) is r-CCD (dr-CCD). In the context of RPA, this is an important finding.

Berkelbach has explored the EOM-CC formulation of r/dr-CCD recently. The one particle effective Hamiltonian elements, if constructed assuming $\bar{H} = e^{-T} H e^T$ form for the r/dr-CCD approximations, would be

$$\bar{H}_m^i = f_{im} \delta_{im} + \frac{1}{2} t_{nm}^{fa} \langle ni || fa \rangle \quad (73)$$

$$\bar{H}_e^a = f_{ae} \delta_{ae} - \frac{1}{2} t_{mn}^{fa} \langle mn || fe \rangle \quad (74)$$

But as we have seen from our discussion, it is not precisely correct to assume that form for r/dr-CCD. Instead, the expressions for \bar{H} elements have to be obtained from the r/dr-CCD Lagrangian. When the \bar{H} elements are strictly r/dr-CCD, as we have shown that the EOM-CC formulation naturally leads to RPA with the r/dr-CCD being the proper ground state. This has also been discussed by Berkelbach who states that the equivalence between RPA and EOM CC approaches occur only if the *one-particle part of the Hamiltonian is **not** similarity transformed*. In general, \bar{H} for a regular CC calculation is

$$\begin{aligned} \bar{H} &= e^{-T} H e^T \\ &= e^{-T} (F + W) e^T \\ &= e^{-T} F e^T + e^{-T} W e^T \end{aligned} \quad (75)$$

$$\bar{H} = \bar{F} + \bar{W} \quad (76)$$

But as we intend not to transform the Fock operators (we use F instead of \bar{F}). This would mean

$$\begin{aligned} \bar{H}_{SS} &= \langle S | \bar{H} | S \rangle = \langle \Phi_i^a | \bar{H} | \Phi_j^b \rangle \\ &= f_{ij} \delta_{ij} - f_{ab} \delta_{ij} + \bar{W}_{iajb} \end{aligned} \quad (77)$$

where $\bar{W}_{iajb} = \langle ia || jb \rangle + \sum t_{jm}^{eb} \langle mi || eb \rangle$. We will denote such approximations as EOM(**Sf**); **f** underscoring the fact that the Fock matrix elements (f_{pq}) are not dressed and **S** highlighting the diagonalization space to be composed of only singly excited determinants. If instead, similarity transformed Fock operator (\bar{F}) is used, we refer to those approximations as EOM(**S**). The justification for use of either formulations might be on numerical grounds which we intend to assess in this study.

Following a notation used by Berkelbach,³⁶ our parent models in this study are EOM(**Sf**) r-CCD and EOM(**Sf**) dr-CCD where the one-particle \bar{H} elements limited to Fock-diagonals $\bar{H}_e^a = f_{ae}$ and

$\bar{H}_m^i = f_{mi}$. It has been shown that these EOM models are methodological equivalent of RPA and d-RPA respectively. As mentioned before, we augment these parent models by using dressed one-particle \bar{H} elements, and call the resulting approximations EOM(S) r-CCD and EOM (S) dr-CCD.

E. Doubles correction to EOM-(S)-(d)r-CCD and EOM-(SF)-(d)r-CCD models

The EOM ansatz, $R_k = r_0 + r_i^a \{a^\dagger i\}$, limited to a single excitation operator and the (d)r-CCD ground state leads to the EOM models presented above, and it is obvious that they are *single excitation models*. In contrast, the configuration interaction singles (CIS) is a single excitation model of the HF ground state. There are numerous studies documenting the deficiencies of single excitation models like CIS and RPA (which is of course EOM(Sf)r-CCD) predicting excitation spectra. The improvements have been formulated by considering the perturbative inclusion of double excitation effects as in CIS(D) of Head-Gordon and co-workers⁶³ and RPA(D) of Sauer and co-workers.⁷⁴ Drawing from our experience in formulating the perturbative triples correction to EOM-CCSD (EOM-CCSD(T))^{49,56}, we present a formulation of perturbative doubles correction to the EOM (d)r-CCD models.

Let us define the projections $|P\rangle = |0\rangle + |S\rangle$ and $|Q\rangle = |D\rangle + |T\rangle + \dots$ where $|S\rangle$, $|D\rangle$, $|T\rangle$ are single, doubly and triply excited configurations. We also note that $\langle Q|P\rangle = 0$. The EOM (d)r-CCD equations can be approximately written in terms of the projection operators as,

$$\begin{pmatrix} \bar{H}_{PP} & \bar{H}_{PQ} \\ \bar{H}_{QP} & \bar{H}_{QQ} \end{pmatrix} \begin{pmatrix} R_{kP} \\ R_{kQ} \end{pmatrix} = \omega \begin{pmatrix} R_{kP} \\ R_{kQ} \end{pmatrix} \quad (78)$$

Before continuing we note that except for the \bar{H}_{PP} block, all the other blocks are approximations for the same reason as discussed above. As a result, to a good approximation the \bar{H} elements in these blocks are limited to the corresponding bare integrals (those are the lead terms in expressions for \bar{H}). Using Lwdin partitioning technique, this can be rewritten as

$$\bar{H}_{PP}R_{kP} + \frac{\bar{H}_{PQ}\bar{H}_{QP}}{(\omega_k - \bar{H}_{QQ})}R_{kP} = \omega_k R_{kP} \quad (79)$$

where $R_{kP} = \langle P|R_k\rangle$. It is clear from the above expression the correction to ω_k come from $\bar{H}_{PQ}(\omega_k - \bar{H}_{QQ})^{(-1)}\bar{H}_{QP}$. Following the steps outlined previously, it can be shown that the lowest order correction terms due to double excitation effects arise from the expansion,

$$\Delta\omega = \frac{\bar{H}_{PD}\bar{H}_{DP}}{(\omega_k - \bar{H}_{DD})} \quad (80)$$

with $\Delta\omega$ designating the correction due to the double excitations. This can be rewritten in more convenient form for computations as,

$$\Delta\omega = \frac{\langle 0|L_k\bar{H}|D\rangle\langle D|\bar{H}R_k|0\rangle}{(\omega_k - \langle D|\bar{H}|D\rangle)} \quad (81)$$

where L_k is the left state corresponding to the right state R_k . The algebraic expression for $L_{ij,ab} = \langle 0|L_k\bar{H}|D\rangle$ is given by,

$$L_{ij,ab} = P_-(ij)l_{ie}\langle ej||ab\rangle - P_-(ab)l_{ma}\langle ij||mb\rangle \quad (82)$$

and similarly for $R_{ab,ij} = \langle D|\bar{H}R_k|0\rangle$,

$$R_{ab,ij} = P_-(ij)r_{ei}\langle ab||ej\rangle - P_-(ab)r_{am}\langle mb||ij\rangle \quad (83)$$

Therefore, the doubles correction,

$$\Delta\omega = \frac{L_{ij,ab}R_{ab,ij}}{4D_{ijab}} \quad (84)$$

where $(\omega_k - \langle D|\bar{H}|D\rangle)$ is $D_{ijab} = (\omega_k - (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j))$. We assign the labels EOM(Sf, +D) r-CCD, EOM(Sf,+D) dr-CCD, EOM(S,+D) dr-CCD and EOM(S,+D) dr-CCD to indicate that the perturbative effects due to double excitation are included. This correction term appears similar to the lead correction term in CIS(D). It appears that the only difference is that in CIS L_k is identical to R_k (CIS being a symmetric theory). The second term in the CIS(D) correction arises from a contribution,

$$c_m^e \bar{H}_{ej}^{mb} c_j^b \quad (85)$$

where $\bar{H}_{ej}^{mb} = \frac{1}{2}t_{jn}^{fb}\langle mn||ef\rangle$ and c_i^a are CIS coefficients. In RPA, this contribution is included to infinite order (i.e. in the RPA matrix) as a term arising from the B matrix. Therefore, in RPA or in EOM(Sf) (d)r-CCD, the only perturbative double correction is $\Delta\omega$ given above.

F. Exchange corrections to EOM CC based on direct ring-CCD ground state

For a direct-ring CCD based excited state calculation, we remove the exchange piece in $\bar{W}_{ia,jb}$ and we christen the method EOM(S) dr-CCD and when we keep the exchange piece, we shall call it EOM(S,+X) dr-CCD. Finally, a third option (not studied in this work) could be to add the exchange piece as a non-iterative correction at the end in the spirit of second order exchange(SOX) and second order screened exchange (SOSEX) correction to the ground state drCCD energy. Such a

problem does not arise for ring CCD based EOM calculation (EOM(S) rCCD) where we naturally have the complete \bar{W}_{iajb} with exchange piece intact. We could make the choice to eliminate it completely (EOM(S) rCCD-X) or eliminate it before diagonalization and put it back as a non iterative correction (EOM(S) rCCD(X)) but we have not assessed these corrections for rCCD based EOM model here.

Our aim in this work is to study all these different approximations and compare them with EOM CCSD results. We intend to find out if any one of these methods have advantages associated with dr-CCD(dRPA) or dr-CCD+SOSEX methods. We would be particularly interested in finding a variant of EOM dr-CCD that builds on good results seen for drCCD(dRPA) for strong correlation problems, for excited states as a function of bond distance and furthermore, explore its performance for excited states with substantial double excitation character. Our aim will also be to explore how to better the performance of EOM based on the r-CCD model though there are significant issues with the convergence of r-CCD ground state calculations. We have found that RPA or the ring-CCD equations are prone to instability and fail to converge in many cases. An instability of the reference determinant in any one of the irreducible representations in the point group symmetry is diagnosed to be the cause of non-convergence. In contrast, the solution to dRPA or direct ring-CCD equations converge in general. As a *workaround*, whenever ring-CCD equations do not converge, we solve the RPA eigenvalue equation to solve for single excitation and de-excitation operators (X, Y) which are then used to construct the T_2 amplitudes and \bar{H} for the EOM-CC problem. Thus, an alternate route to getting to excitation energies is constructed which ends up giving the same excitation energies as RPA. This and other considerations in the design of the methods studied in this paper are illustrated through a flowchart in figure 2. In the next section, we focus our attention on numerical performance of these EOM (d)rCCD approximations.

III. IMPLEMENTATION AND RESULTS

All the methods mentioned are implemented in the development version of software packages *ACES II*^{143,144} and *Massively Parallel Quantum Chemistry (MPQC)*^{145,146}. To test these methods, we did a simple study of singlet excited states of small closed-shell molecules such as water, N₂, Ne, CH₂ and BH in modified cc-pVDZ basis augmented with diffuse basis functions which were used in an earlier study by Christiansen, Sauer and co-workers^{57,74}.

A. Effect of similarity transformation or dressing of Fock matrix elements on RPA excitation energies

TABLE I: Effect of dressing of Fock matrix elements, $\Delta_{FockDressing}$, on the excitation energies of various small molecules in aug-cc-pVDZ* basis.

Molecule	State	FCI	EOM CCSD	EOM(Sf) r-CCD (RPA)	EOM(S) r-CCD	$\Delta_{FockDressing}^{EOMr-CCD}$	EOM(Sf) dr-CCD (dRPA)	EOM(S) dr-CCD	$\Delta_{FockDressing}^{EOMdr-CCD}$
H ₂ O	1^1B_1	7.45	7.38	8.63	10.33	1.70	14.93	15.48	0.56
	1^1A_2	9.21	9.12	10.32	12.05	1.74	15.47	16.03	0.55
	2^1A_1	9.87	9.81	10.95	12.62	1.67	17.01	17.58	0.57
	1^1B_2	11.61	11.52	12.61	14.29	1.69	17.54	18.11	0.57
N ₂	$1^1\Pi_g$	9.58	9.66	9.82	12.74	2.92	23.43	24.38	0.95
	$1^1\Sigma_u$	10.33	10.47	8.09	12.01	3.92	21.42	23.89	2.47
	$1^1\Delta_u$	10.72	10.90	8.96	10.02	1.06	22.74	23.89	1.15
Ne	1^1P	16.40	16.16	18.09	19.18	1.09	25.51	26.08	0.57
	1^1D	18.21	17.96	19.94	21.03	1.09	24.99	25.55	0.56
	1^1S	18.26	18.01	19.98	21.06	1.08	25.03	25.59	0.56
CH ₂	1^1B_2	1.79	1.78	1.64	2.37	0.73	13.74	14.26	0.52
	1^1A_2	5.85	5.86	6.03	6.88	0.85	17.75	18.29	0.54
	3^1A_1	6.51	6.51	6.94	7.68	0.74	11.51	11.92	0.41
	1^1B_1	7.70	7.71	8.10	8.83	0.73	12.37	12.78	0.41
	4^1A_1	8.48	8.46	8.84	9.55	0.71	12.83	13.25	0.41
BH	$A^1\Pi^+$	2.94	2.96	2.85	3.20	0.35	9.77	10.12	0.35
	$B^1\Sigma^+$	6.38	6.42	6.37	6.72	0.35	9.67	10.01	0.35
	$D^1\Pi$	7.47	7.50	7.36	7.70	0.34	10.80	11.16	0.36
	$E^1\Sigma^+$	7.56	7.39	7.38	7.72	0.34	9.80	10.15	0.35
	$G^1\Pi$	8.24	8.28	8.11	8.44	0.33	11.68	12.03	0.35

Previous studies have documented the accuracy of excitation energies from RPA method and found it to be slightly better than configuration interaction singles (CIS) method which are in error of 1 to 1.5 eV for singly excited states. Our test results for small molecules (See results for water in Table I) reiterate the previous findings. As RPA excitation energies are equivalent to those of EOM(Sf)-rCCD methods which uses bare Fock matrix elements, our aim is to quantify the effect of *similarity transformation of Fock operators* or *dressing of Fock matrix elements* on the excitation energies. The results below indicate the magnitude of $\Delta_{FockDressing}^{EOMrCCD}$, to be significantly large (≈ 1.70 eV) and is indicated to worsen the estimate of excitation energy further. This result might be in agreement with recent work by Lange and Berkelbach who investigated the effect of class of diagrams present in EOM-CCSD but absent in RPA and concluded that 'high-quality vertex

corrections (from EOM-CCSD) to the polarizability do not improve the ionization potentials of small molecules within the GW approximation^{147,148}.

Another observation is about the direct RPA (dRPA) excitation energies which are not adequately reported in literature. EOM(SF) dr-CCD (= dRPA) estimates are $\approx 5 - 6$ eV worse than EOM(SF) rCCD. Interestingly, the effect of dressing of Fock matrix elements through similarity transformation is considerably less, $\Delta_{FockDressing}^{EOMdr-CCD} \approx 0.6$ eV, in this case. In the next subsection, we seek improvement in dRPA/EOM(SF) dr-CCD method by adding exchange corrections to \bar{H} elements for dr-CCD.

B. Addition of exchange corrections to EOM based on direct ring CCD ground state calculations

TABLE II: Effect of adding exchange corrections to EOM models based on direct ring CCD ground state calculation

Molecule	State	EOM CCSD	CIS	EOM(Sf) dr-CCD (dRPA)	EOM(Sf,+X) dr-CCD	$\Delta_{Exchange}^{SF}$	EOM(S) dr-CCD	EOM(S,+X) dr-CCD	$\Delta_{Exchange}^S$
H ₂ O	¹ B ₁	7.38	8.67	14.93	8.66	6.26	15.48	9.29	6.19
	¹ A ₂	9.12	10.36	15.47	10.36	5.11	16.03	11.00	5.03
	² A ₁	9.81	10.98	17.01	10.98	6.03	17.58	11.61	5.97
	¹ B ₂	11.52	12.64	17.54	12.64	4.90	18.11	13.27	4.83
N ₂	¹ Π _g	9.66	10.07	23.43	10.04	13.39	24.38	11.06	13.32
	¹ Σ _u	10.47	8.65	21.42	8.65	12.77	23.89	9.86	14.03
	¹ Δ _u	10.9	9.23	22.74	9.27	13.46	23.89	10.48	13.40
Ne	¹ P	16.16	18.09	25.51	18.09	7.43	26.08	18.66	7.42
	¹ D	17.96	19.94	24.99	19.95	5.04	25.55	20.51	5.04
	¹ S	18.01	19.98	25.03	19.98	5.05	25.59	20.55	5.04
CH ₂	¹ B ₂	1.78	1.64	13.74	1.60	12.15	14.26	2.13	12.13
	¹ A ₂	5.86	6.07	17.75	6.06	11.69	18.29	6.61	11.68
	³ A ₁	6.51	6.95	11.51	6.95	4.56	11.92	7.38	4.54
	¹ B ₁	7.71	8.11	12.37	8.12	4.25	12.78	8.55	4.23
	⁴ A ₁	8.46	8.86	12.83	8.86	3.97	13.25	9.28	3.97
BH	^A Π ⁺	2.96	2.84	9.77	2.80	6.97	10.12	2.19	7.93
	^B Σ ⁺	6.42	6.37	9.67	6.37	3.30	10.01	5.74	4.28
	^D Π	7.5	7.36	10.80	7.37	3.43	11.16	6.93	4.22
	^E Σ ⁺	7.39	7.39	9.80	7.39	2.41	10.15	6.93	3.21
	^G Π	8.28	8.12	11.68	8.11	3.57	12.03	7.71	4.32

In contrast to the ground state correlation energies for which dr-CCD seems to be provide qual-

itatively correct estimates, we find that its excited analog is poor. As there has been a lot of recent work on how to improve dr-CCD correlation energies by adding exchange corrections perturbatively, we try similar corrections to some \bar{H} matrix elements constructed by similarity transforming with the t -amplitudes (from dr-CCD ground state calculation). To be abundantly clear, we do not add these corrections to the ground-state amplitude equations or ground state energy, but add them post ground state calculations while constructing \bar{H} before the diagonalization step.

As we have observed before and see it in these results, we cannot remove exchange terms from \bar{W}_{iajb} without a significant loss in accuracy. Such exchange corrections ($\Delta_{Exchange}^{S/SF}$) improve the estimates by a large amount. In particular, we find that EOM(Sf,+X)-drCCD tends to be very close to EOM(Sf)-rCCD values. This is not expected as ground state amplitudes and energies obtained from drCCD and rCCD methods tend to be different. These differences in the T amplitudes would be more severe when away from equilibrium geometries or in static correlation dominated systems. It will be interesting to check the performance of EOM-drCCD models in such cases.

Another finding is the exchange correction are almost the same for EOM(Sf) and EOM(S) variants, $\Delta_{Exchange}^{SF} \approx \Delta_{Exchange}^S$. Unexplained is the performance of EOM(S,+X) dr-CCD method which still behaves worse than CIS. The next subsection deals with going beyond single excitation space (S) and analyzing how to add the contribution of double excitations (D) fully and perturbatively?

C. Perturbative effect of double excitations on the energies of singly excited states

A cheap way to consider the effect of double excitation space, without increasing the diagonalization space for the effective Hamiltonian \bar{H} , is to add a perturbative correction. A variation of a non-iterative doubles correction proposed by Head-Gordon et al. for the CIS method, termed the (D) correction, is considered here. We shall consider the various ways of adding this correction to EOM-(d)rCCD variants.

We find that the doubles correction $\Delta_{Doubles}^{S/SF,+X,dr-CCD}$ are very large (≈ -3.5 eV) and similar in magnitude for every state. This correction leads to EOM dr-CCD energies underestimating the FCI values by around $\approx 2 - 2.5$ eV. The (D) correction for $\Delta_{Doubles}^{S/SF,r-CCD}$, is of similar magnitude and the effect is similar. The most complete of these methods in theoretically, EOM(S, +D) r-CCD, has deviations $0.7 - 0.9$ eV.

TABLE III: Perturbative estimate of the effect of doubles excitations added to EOM models (with exchange correction) based on direct ring CCD ground state calculation

Molecule	State	EOM	CCSD	CIS	EOM(Sf,+X)		EOM(Sf,+X,+D)	$\Delta_{Doubles}^{Sf,+X,dr-CCD}$	EOM(S,+X)		EOM(S,+X,+D)	$\Delta_{Doubles}^{S,+X,dr-CCD}$
					dr-CCD	dr-CCD			dr-CCD	dr-CCD		
H ₂ O	¹ B ₁	7.38	8.67	8.66	5.19	-3.47	9.29	5.75	-3.54			
	¹ A ₂	9.12	10.36	10.36	6.88	-3.48	11.00	7.43	-3.57			
	² A ₁	9.81	10.98	10.98	7.62	-3.36	11.61	8.18	-3.43			
	¹ B ₂	11.52	12.64	12.64	9.25	-3.39	13.27	9.80	-3.47			
N ₂	¹ Π _g	9.66	10.07	10.04	6.85	-3.19	11.06	7.81	-3.25			
	¹ Σ _u	10.47	8.65	8.65	6.90	-1.74	9.86	8.10	-1.76			
	¹ Δ _u	10.9	9.23	9.27	7.42	-1.85	10.48	8.61	-1.87			
Ne	¹ P	16.16	18.09	18.09	14.00	-4.09	18.66	14.54	-4.12			
	¹ D	17.96	19.94	19.95	15.67	-4.27	20.51	16.21	-4.31			
	¹ S	18.01	19.98	19.98	15.72	-4.26	20.55	16.25	-4.29			
CH ₂	¹ B ₂	1.78	1.64	1.60	0.29	-1.30	2.13	0.82	-1.31			
	¹ A ₂	5.86	6.07	6.06	4.48	-1.58	6.61	5.02	-1.60			
	³ A ₁	6.51	6.95	6.95	5.29	-1.66	7.38	5.70	-1.68			
	¹ B ₁	7.71	8.11	8.12	6.47	-1.65	8.55	6.87	-1.67			
	⁴ A ₁	8.46	8.86	8.86	7.27	-1.59	9.28	7.67	-1.61			
BH	^A 1Π ⁺	2.96	2.84	2.80	1.76	-1.03	3.23	2.19	-1.04			
	^B 1Σ ⁺	6.42	6.37	6.37	5.39	-0.98	6.73	5.74	-0.99			
	^D 1Π	7.5	7.36	7.37	6.59	-0.78	7.72	6.93	-0.79			
	^E 1Σ ⁺	7.39	7.39	7.39	6.51	-0.88	7.72	6.93	-0.79			
	^G 1Π	8.28	8.12	8.11	7.37	-0.74	8.46	7.71	-0.75			

D. Analysis

In figure 3, we plot the errors in the EOM-CC approximations we have introduced in this paper compared to the full CI approaches. We find EOM(S, +D)-rCCD approach to be amongst the most accurate of the new approximations and an improvement over the CIS method, but significantly less accurate than the EOM-CCSD approach. The error spread of various methods is a mark of their consistency; EOM-CCSD shows the least spread followed by EOM(S,+D)-rCCD. The table III D affirms this and points to the the consistency that results by systematic corrections to the parent RPA (EOM(Sf)-rCCD) method.

TABLE IV: Perturbative estimate of the effect of doubles excitations added to EOM models (with exchange correction) based on ring CCD ground state calculation

Water	State	EOM CCSD	CIS	EOM(Sf) rCCD	EOM(Sf, +D) rCCD	$\Delta_{Doubles}^{SF,r-CCD}$	EOM(S) rCCD	EOM(S, +D) rCCD	$\Delta_{Doubles}^{S,r-CCD}$
H ₂ O	1^1B_1	7.38	8.67	8.63	5.17	-3.46	10.33	6.67	-3.65
	1^1A_2	9.12	10.36	10.32	6.86	-3.45	12.05	8.33	-3.72
	2^1A_1	9.81	10.98	10.95	7.60	-3.36	12.62	9.09	-3.53
	1^1B_2	11.52	12.64	12.61	9.23	-3.38	14.29	10.69	-3.60
N ₂	$1^1\Pi_g$	9.66	10.07	9.82	6.77	-3.05	12.74	9.53	-3.22
	$1^1\Sigma_u$	10.47	8.65	8.09	6.74	-1.35	12.01	10.84	-1.17
	$1^1\Delta_u$	10.90	9.23	8.96	7.22	-1.74	12.86	11.06	-1.80
Ne	1^1P	16.16	18.09	18.09	14.01	-4.08	19.18	15.04	-4.13
	1^1D	17.96	19.94	19.94	15.67	-4.27	21.03	16.69	-4.34
	1^1S	18.01	19.98	19.98	15.80	-4.18	21.06	16.85	-4.20
CH ₂	1^1B_2	1.78	1.64	1.64	0.38	-1.26	2.37	1.09	-1.28
	1^1A_2	5.86	6.07	6.03	4.49	-1.54	6.88	5.31	-1.57
	3^1A_1	6.51	6.95	6.94	5.30	-1.64	7.68	6.00	-1.68
	1^1B_1	7.71	8.11	8.10	6.48	-1.62	8.83	7.16	-1.67
	4^1A_1	8.46	8.86	8.84	7.27	-1.57	9.55	7.94	-1.61
BH	$A^1\Pi^+$	2.96	2.84	2.85	1.87	-0.98	3.20	2.21	-0.99
	$B^1\Sigma^+$	6.42	6.37	6.37	5.40	-0.97	6.72	5.75	-0.97
	$D^1\Pi$	7.50	7.36	7.36	6.65	-0.71	7.70	6.97	-0.73
	$E^1\Sigma^+$	7.39	7.39	7.38	6.51	-0.87	7.72	6.84	-0.88
	$G^1\Pi$	8.28	8.12	8.11	7.42	-0.69	8.44	7.74	-0.70

TABLE V: Statistical analysis for the studied benchmark set lists MAE(mean absolute error), MSE(mean signed error), MAX(maximum error) and STDEV (standard deviation) with respect to the FCI values.

	EOM CCSD	CIS	EOM(Sf) r-CCD	EOM(Sf, +D) rCCD	EOM(S) rCCD	EOM(S, +D) rCCD	EOM(Sf,+X,+D) dr-CCD	EOM(S,+X) dr-CCD	EOM(S,+X,+D) dr-CCD
MAE	0.09	0.77	0.79	1.89	1.63	0.72	1.88	1.05	1.31
MSE	-0.03	0.39	0.32	-1.89	1.63	-0.64	-1.88	0.98	-1.31
MAX	0.18	1.73	1.73	-0.82	3.16	0.51	-0.87	2.30	-0.53
STDEV	0.12	0.92	1.01	0.85	1.10	0.49	0.80	0.85	0.60

E. Dependence on reference: performance of EOM (d)-rCCD based on Kohn-Sham determinant

As RPA is often applied in conjunction with Kohn-Sham DFT (KS- DFT), it is worthwhile to check if the EOM models considered would yield better results when based on KS-DFT single

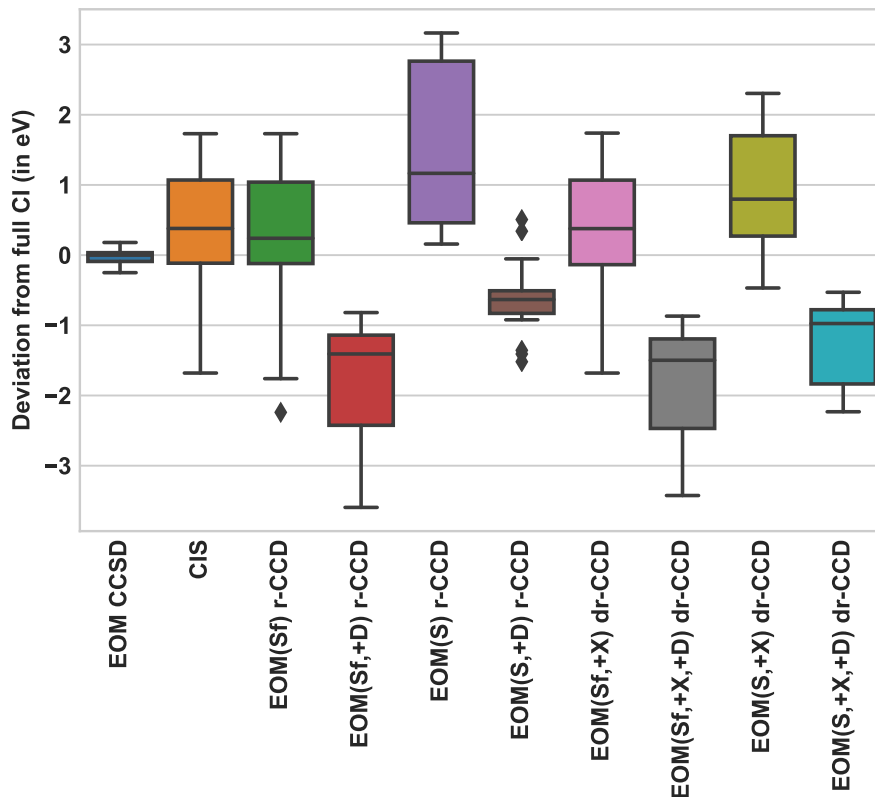


FIG. 3: Deviations from full CI (in eV) for EOM-CC approximations introduced in the paper

determinants rather than the HF determinant. With both PBE and B3LYP exchange-correlation functionals, we find similar change in EOM-CCSD and CIS making EOM-CCSD results closer to FCI while worsening the CIS estimates. None of the EOM dr-CCD or the EOM r-CCD models improve in accuracy in comparison to previous results. This is surprising and needs to be understood better. The results for water molecule are shown in Table VI and VII for EOM-CC based on KS-DFT reference using PBE and B3LYP functional and similar trend is seen for other molecules in the small set studied here.

TABLE VI: KS-DFT reference (PBE) for CIS and EOM-CC models for excited states of water molecule.

State	FCI	EOM CCSD	CIS	EOM(Sf,+X) dr-CCD	EOM(S,+X) dr-CCD	EOM(Sf) r-CCD	EOM(Sf,+D) r-CCD	EOM(S) r-CCD	EOM(S,+D) r-CCD
1^1B_1	7.45	7.41	8.76	8.75	9.42	11.85	8.88	10.27	6.40
1^1A_2	9.21	9.16	10.45	10.45	11.13	13.16	9.74	12.00	8.01
2^1A_1	9.87	9.84	11.11	11.10	11.78	11.07	7.53	12.61	9.86
1^1B_2	11.61	11.57	12.78	12.77	13.46	13.26	10.60	14.35	10.49

TABLE VII: KS-DFT reference (B3LYP) for CIS and EOM-CC models for excited states of water molecule.

State	FCI	EOM	CIS	EOM(Sf,+X)	EOM(S,+X)	EOM(Sf)	EOM(Sf, +D)	EOM(S)	EOM(S, +D)
		CCSD		dr-CCD	dr-CCD	r-CCD	r-CCD	r-CCD	r-CCD
1 1B_1	7.45	7.40	8.68	8.68	9.34	11.80	8.82	10.16	6.29
1 1A_2	9.21	9.15	10.37	10.38	11.05	13.08	9.63	11.88	7.90
2 1A_1	9.87	9.83	11.02	11.01	11.68	10.99	7.45	12.55	8.81
1 1B_2	11.61	11.56	12.69	12.69	13.36	13.20	10.55	14.22	10.37

IV. SUMMARY

In summary, we have presented an unified outlook of CC and random phase approximation highlighting their connections and differences. We have assessed the performance of random phase approximation(RPA) and associated methods for the excitation energies of singlet excited states. We have built on the connection of RPA with EOM-CCD to extend the theory to incorporate exchange corrections to direct RPA methods, perturbative effect of double excitations and reference determinant sensitivity. In particular, EOM(S,+D)-rCCD method improves considerably on RPA excitation energies. The current results lay down a baseline for introduction of more corrections as search for a low cost alternative to EOM-CCSD method continues. In future work, it might be worthwhile to limit the space of excitations to ph and hp excitations but have the ground state well correlated by CC methods such as CCSD and check the effect on excitation energies. Associated problem is the assessment of the importance of single excitations in RPA (or ring CCD) and how that might affect the excitation energy estimates. A more rigorous test on benchmark sets^{149–151} for the family of methods introduced would be done in future.

V. ACKNOWLEDGMENTS

VR thanks Prof. Ed Valeev, his postdoctoral advisor at Virginia Tech, for encouragement to pursue the project and support through U.S. National Science Foundation grants (Award Nos. 1550456 and 1800348).

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