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Assessment of low-scaling approximations to the equation of motion coupled-cluster singles and doubles equations

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Methods for fast and reliable computation of electronic excitation energies are in short supply, and little is known about their systematic performance. This work reports a comparison of several low-scaling approximations to the equation of motion coupled cluster singles and doubles (EOM–CCSD) and linear-response coupled cluster singles and doubles (LR–CCSD) equations with other single reference methods for computing the vertical electronic transition energies of 11 small organic molecules. The methods, including second order equation-of-motion many-body perturbation theory (EOM–MBPT2) and its partitioned variant, are compared to several valence and Rydberg singlet states. We find that the EOM–MBPT2 method was rarely more than a tenth of an eV from EOM–CCSD calculated energies, yet demonstrates a performance gain of nearly 30%. The partitioned equation-of-motion approach, P–EOM–MBPT2, which is an order of magnitude faster than EOM–CCSD, outperforms the CIS(D) and CC2 in the description of Rydberg states. CC2, on the other hand, excels at describing valence states where P–EOM–MBPT2 does not. The difference between the CC2 and P–EOM–MBPT2 can ultimately be traced back to how each method approximates EOM–CCSD and LR–CCSD. The results suggest that CC2 and P–EOM–MBPT2 are complementary: CC2 is best suited for the description of valence states while P–EOM–MBPT2 proves to be a superior $\mathcal{O}(N^5)$ method for the description of Rydberg states. © *2014 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4898709]

INTRODUCTION

Accurate and efficient methods for calculating excited state energies are few and far between. On the one hand, linear-response time-dependent Hartree-Fock (LR–TDHF, also known as RPA) and time-dependent density functional theory (LR–TDDFT)[1–3] are fast methods for calculating excited state energies, fast enough that they may be applied to large systems (>1000 basis functions) routinely, yet are plagued by many problems that affect their accuracy. LR–TDDFT, for example, often underestimates excitation energies of charge-transfer states,[2] fails to describe excitations containing multi-electron character, and generally fails to describe the effects of dispersion. Attempts have been made to correct these features of LR–TDDFT,[4–6] often with some success, but it is clear that a reliable black-box method for calculating excitation energies must look beyond the HF/DFT regime.

Methods based off the highly successful coupled cluster formalism (for two excellent reviews of coupled cluster theory, see the review by Crawford and Schaefer[7] and the book by Shavitt and Bartlett[8]), on the other hand, can provide extremely accurate excitation energies for even the most difficult systems. The first application of coupled cluster theory to electronic excited states was based off of the response formalism, and is known as linear response coupled cluster

(LR–CC).[9–13] This was followed by the equation of motion coupled cluster formalism (EOM–CC),[14] as well as symmetry adapted cluster configuration interaction (SAC-CI).[15] Despite their formal differences, LR–CC and EOM–CC when truncated at the same level of cluster operator will give the same value for excitation energies, although they differ with respect to transition properties.[13] In particular, the EOM–CC formalism[16,17] has led to extremely accurate and robust descriptions of excited states, yet may be prohibitively costly. The equation of motion coupled cluster singles and doubles (EOM–CCSD)[14,18] gives accurate qualitative and quantitative energies for most molecular systems, yet scales as $\mathcal{O}(N^6)$, making its application to large molecules difficult.

Methods that bridge the gap between the robust and highly accurate LR–CC and EOM–CC methods and the efficient but often-inaccurate LR–TDHF/LR–TDDFT are important for the quantitative study of electronic excitations in large systems. Methods that have been proposed to balance cost and accuracy are the iterative-hybrid CC2,[19] the CIS(D) family of perturbative corrections to the configuration interaction singles method,[20] and perturbative approximations to the EOM–CCSD,[21,22] known as second order equation-of-motion many-body perturbation theory (EOM–MBPT2). Most of these approximate methods can be formulated as $\mathcal{O}(N^5)$ methods, yet little is known about their systematic performance. Theoretically, CC2 and EOM–MBPT2 make very different assumptions regarding the relative importance of the coupled cluster operators. CC2, originally developed within

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the response theory formalism, was designed to retain maximal flexibility with respect to orbital rotations, which are known to be important when computing molecular properties. However, CC2 does so at the cost of neglecting much dynamic electron correlation, by removing many of the doubles cluster operators. EOM–MBPT2, in contrast, has no flexibility with respect to orbital rotation, but seeks to maximize inclusion of dynamic correlation through the use of the MP2 cluster operator. The contrast between these approximations has strong implications when selecting a method for studying electronic excited states.

Here, we investigate the implications of these approximations on a series of experimentally well-studied organic molecules. In particular, we find a striking difference between the methods in their ability to describe Rydberg and valence states. The results of our investigation provide critical information to aid in the choice of a cost-effective method for studying electronic excited states.

THEORY

In the present work, we adopt the notation that indices i, j, k, l refer to occupied orbitals, a, b, c, d refer to virtual orbitals, and p, q, r, s refer to any orbital. We also adopt Einstein summation, where the summation over common indices is implied.

In coupled cluster theory, the Schrödinger equation is parametrized by the exponential form of excitation operators $\hat{T}$, such that

$$\hat{H} e^{\hat{T}} |\Phi_0\rangle = E e^{\hat{T}} |\Phi_0\rangle. \qquad (1)$$

The operator $\hat{T}$ is an excitation operator that has the effect of generating excited determinants from the reference state $|\Phi_0\rangle$. It takes the form

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots = t_i^a a_a^\dagger a_i + t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \cdots. \qquad (2)$$

It is convenient to use the normal-ordered (relative to the Fermi vacuum) Hamiltonian $\hat{H}_N$, which is the Hamiltonian operator minus its reference expectation value

$$\hat{H}_N = f_{pq}\{a_p^\dagger a_q\} + \frac{1}{4}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\} \qquad (3)$$

or simply

$$\hat{H}_N = \hat{F}_N + \hat{V}_N. \qquad (4)$$

For the EOM–CCSD working equations, one must solve for the eigenvalues and eigenvectors of the following Hamiltonian matrix:

$$\begin{bmatrix} \langle\Phi_i^a|\bar{H}_N|\Phi_k^c\rangle & \langle\Phi_i^a|\bar{H}_N|\Phi_{kl}^{cd}\rangle \\ \langle\Phi_{ij}^{ab}|\bar{H}_N|\Phi_k^c\rangle & \langle\Phi_{ij}^{ab}|\bar{H}_N|\Phi_{kl}^{cd}\rangle \end{bmatrix}, \qquad (5)$$

where $\bar{H}_N = e^{(-\hat{T}_1-\hat{T}_2)}\hat{H}_N e^{(\hat{T}_1+\hat{T}_2)}$, and $|\Phi_k^c\rangle$, $|\Phi_{kl}^{cd}\rangle$ are singly and doubly excited determinants, respectively. The eigenvalues of the Hamiltonian correspond to excitation energies out of the coupled cluster ground state. Because of the similarity transformation, the matrix problem is non-Hermitian. The excited kets are generated by the linear operator $\hat{R}$, and the excited bras are generated by the linear operator $\hat{L}$

$$\hat{R} = \hat{R}_1 + \hat{R}_2 + \cdots = r_i^a a_a^\dagger a_i + r_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \cdots, \qquad (6)$$

$$\hat{L} = \hat{L}_1 + \hat{L}_2 + \cdots = l_a^i a_i^\dagger a_a + l_{ab}^{ij} a_i^\dagger a_j^\dagger a_b a_a + \cdots. \qquad (7)$$

Thus, the EOM–CCSD Hamiltonian looks,[14] with respect to a suitable reference state $|\Phi_0\rangle$ and truncated to $\hat{R}_1$ and $\hat{R}_2$ (and likewise for $\hat{L}$)

$$\begin{bmatrix} \langle\Phi_0|\hat{L}_1\bar{H}_N\hat{R}_1|\Phi_0\rangle & \langle\Phi_0|\hat{L}_1\bar{H}_N\hat{R}_2|\Phi_0\rangle \\ \langle\Phi_0|\hat{L}_2\bar{H}_N\hat{R}_1|\Phi_0\rangle & \langle\Phi_0|\hat{L}_2\bar{H}_N\hat{R}_2|\Phi_0\rangle \end{bmatrix}. \qquad (8)$$

In general, $\hat{R}^\dagger \neq \hat{L}$ and vice versa, and a full solution to the EOM–CCSD equations requires solutions to both the $\hat{R}$ and $\hat{L}$ amplitudes. However, if only excitation energies are desired, one may solve for only $\hat{R}$ or $\hat{L}$ amplitudes. In the case of this work, we only concern ourselves with excitation energies, and solve for the $\hat{R}$ amplitudes only, which is to say we solve the connected right-hand side

$$(\bar{H}_N\hat{R})_c|\Phi_0\rangle = \omega\hat{R}|\Phi_0\rangle, \qquad (9)$$

where ω are the excitation energies. Therefore, the matrix equations we wish to solve are

$$\begin{bmatrix} \bar{H}_{SS} & \bar{H}_{SD} \\ \bar{H}_{DS} & \bar{H}_{DD} \end{bmatrix} \begin{bmatrix} R_1 \\ R_2 \end{bmatrix} = \omega \begin{bmatrix} R_1 \\ R_2 \end{bmatrix}, \qquad (10)$$

where $\bar{H}_{SS} = \langle\psi_i^a|\bar{H}_N|\psi_k^c\rangle$, that is to say, the singles-singles block of the Hamiltonian matrix, and so on. The working equations may then be solved using non-Hermitian variants of the Davidson algorithm.[23–26]

When excitation energies are the subject of interest, the EOM–CC equation is equivalent to the Jacobian in the LR–CC formalism[12] for excitation energy calculations. The mathematical difference between LR and EOM formalisms arises when they are used to compute excitation properties, such as transition dipole and oscillator strengths. Jørgensen and coworkers have shown that the transition moment in LR–CC is size-intensive whereas EOM formalism is not,[13] although the difference in intensity between LR and EOM is very small for most computationally tractable systems.[27] In this work, we focus only on analyzing the performance of low-scaling alternatives to EOM–CCSD and LR–CCSD on excitation energies where these two formalisms are equivalent.

EOM–MBPT2

One of the first approximations that can be made to the EOM–CCSD Hamiltonian is to utilize the perturbation expansion technique, and keep only the terms through second order (see the Appendix for derivations). As a result, $\hat{T}_1$ vanishes and only the first order $\hat{T}_2^{(1)}$ remains in the EOM equations,

$$\hat{T}_1 \to t_i^a = 0; \quad \hat{T}_2^{(1)} \to t_{ij}^{ab(1)} = \frac{\langle ij||ab\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \qquad (11)$$

This second order perturbation approximation gives rise to the EOM–MBPT2 equation,

$$\begin{bmatrix} \bar{H}_{SS}^{(2)} & \bar{H}_{SD}^{(2)} \\ \bar{H}_{DS}^{(2)} & \bar{H}_{DD}^{(2)} \end{bmatrix} \begin{bmatrix} R_1 \\ R_2 \end{bmatrix} = \omega \begin{bmatrix} R_1 \\ R_2 \end{bmatrix}, \tag{12}$$

where $\bar{H}_{SS}^{(2)}$ is the singles singles block of the Hamiltonian through second order, and so on. A full derivation and the working equations are given in the Appendix. This approach was first derived by Stanton and Gauss,[21] and termed EOM–CCSD(2). Further work, and the development of the partitioned approach (detailed later) was derived by Gwaltney, Nooijen, and Bartlett[22, 28] and termed EOM–MBPT2. Both methods are equivalent. Because the EOM–MBPT2 Hamiltonian neglects contributions from the single excitation cluster operators, as well as uses the MP2 double excitation amplitudes, it can be understood as an excited state calculation of roughly MP2 quality. The neglect of the $\hat{T}_1$ operators neglects orbital relaxation in response to the addition of electron correlation through the $\hat{T}_2$ operator. The EOM–MBPT2 Hamiltonian still contains terms that scale computationally as $\mathcal{O}(N^6)$, and there is no obvious benefit from the asymptotic scaling compared to a full EOM–CCSD calculation, however, the neglect of the numerous $\hat{T}_1$ terms greatly reduces the prefactor of the calculation. Furthermore, the $\hat{T}_2^{(1)}$ amplitudes are completely determined prior to the excited state calculation. In other words, no iterative ground state calculation must be performed prior to solving the EOM equations, unlike the case for EOM–CCSD, where the CCSD ground state wavefunction must be iteratively determined.

P–EOM–MBPT2

The problem with the second order perturbative approach outlined above is primarily computational. Despite the advantage of not needing to perform a ground state coupled cluster calculation and reduction in terms computed, the leading order of scaling between EOM–CCSD and EOM–MBPT2 is identical with the latter having a smaller prefactor. Bartlett and co-workers[22, 28] offered a solution around the scaling problem by using the so-called Löwdin partitioning approach.[29] The idea is to determine a perturbative series in $\hat{R}$ (or equivalently $\hat{L}$), in addition to the Rayleigh-Schrödinger perturbative approach to $\hat{T}$ above. The central idea is to partition the effective EOM–MBPT2 Hamiltonian into a principal space spanned by the single excitations ($\hat{R}_1$) and an orthogonal complement spanned by the double excitations ($\hat{R}_2$). A perturbative series is generated for the orthogonal complement. Truncation of this series, along with utilization of canonical orbitals, replaces the $\bar{H}_{DD}$ block with the diagonal

$$\bar{H}_{DD} \approx \bar{H}_{DD}^{(0)} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j, \tag{13}$$

where ϵ_a is the orbital energy for the ath orbital and so on. This is the zeroth order effective Hamiltonian for the doubles-doubles block. The block matrix structure of the P–EOM–MBPT2 equations now has the form

$$\begin{bmatrix} \bar{H}_{SS}^{(2)} & \bar{H}_{SD}^{(2)} \\ \bar{H}_{DS}^{(2)} & \bar{H}_{DD}^{(0)} \end{bmatrix} \begin{bmatrix} R_1 \\ R_2 \end{bmatrix} = \omega \begin{bmatrix} R_1 \\ R_2 \end{bmatrix}. \tag{14}$$

It turns out that all the iterative $\mathcal{O}(N^6)$ terms are contained in the doubles-doubles block for EOM–MBPT2, thus by replacing $\bar{H}_{DD}$ by its partitioned counterpart, P–EOM–MBPT2 becomes an iterative $\mathcal{O}(N^5)$ method. (The P–EOM–MBPT2 method does require the formation of some $\mathcal{O}(N^6)$ intermediates, but these must be formed once and is dwarfed by the later $\mathcal{O}(N^5)$ iterations.)

CIS(D)

The CIS(D) method can be seen as an approximation to P–EOM–MBPT2.[30] As pointed out by Head-Gordon,[31] the CIS(D) excited state energy correction can be justified through a perturbation expansion of the excited state CCSD equations, or what we refer to as the EOM–MBPT2 equations. This can be seen from considering the effective Hamiltonian

$$\begin{bmatrix} \bar{H}_{SS}^{(2)} & \bar{H}_{SD}^{(1)} \\ \bar{H}_{DS}^{(1)} & \bar{H}_{DD}^{(0)} \end{bmatrix} \begin{bmatrix} R_1 \\ R_2 \end{bmatrix} = \omega \begin{bmatrix} R_1 \\ R_2 \end{bmatrix}. \tag{15}$$

Note that the off-diagonal blocks are approximated through first order. However, instead of solving the resulting matrix eigenvalue/eigenvector problem, the CIS(D) equations are formulated noniteratively by equating the R_1 amplitudes with the CIS amplitudes and then eliminating R_2. To see this, note that the effective Hamiltonian can be rewritten as two coupled equations

$$\bar{H}_{SS}^{(2)} R_1 + \bar{H}_{DS}^{(1)} R_2 = \omega R_1, \tag{16}$$

$$\bar{H}_{DS}^{(1)} R_1 + \bar{H}_{DD}^{(0)} R_2 = \omega R_2. \tag{17}$$

Rearranging the second equation to solve for R_2 ($\bar{H}_{DD}^{(0)}$ is diagonal, therefore invertible), and substituting this result into the first equation gives the CIS(D) electronic transition energy

$$\omega_{CIS(D)} = \langle \psi_{CIS} | \bar{H}_N^{(2)} | \psi_{CIS} \rangle$$
$$+ \frac{\langle \psi_{CIS} | \bar{H}_N^{(1)} | \psi_{ij}^{ab} \rangle \langle \psi_{ij}^{ab} | \bar{H}_N^{(1)} | \psi_{CIS} \rangle}{\omega_{CIS} - (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)}. \tag{18}$$

Thus, CIS(D) can be thought of as a non-iterative $\mathcal{O}(N^5)$ approximation to P–EOM–MBPT2. CIS(D) retains the CIS exited state wavefunction, and can only correct for energy. Any transition properties, such as oscillator strength, will be identical to the CIS description.

CC2

The CC2 method for excited states, known as linear response CC2 (LR–CC2),[19] is not based off of the perturbative approaches in the other methods. CC2 was originally derived from standard response theory as a way of computing accurate molecular properties. To do so, it was noted that under an external perturbation the effective orbital rotation operators, $\hat{T}_1$, appear to zeroth order in the fluctuation potential and first order in the external perturbation.[32] Since $\hat{T}_2$ appears to second order in the energy and first order in the wavefunction, the singles, it was reasoned, must be more important for molecular properties. Thus, no approximation to $\hat{T}_1$ is made in CC2.

Practically, CC2 is derived from the CC2 ground state reference, which is a second order approximation to CCSD in that the $\hat{T}_2$ operator is restricted to only connect to $\hat{F}$ when acted on by doubly excited bras. In other words, the CCSD equation to determine the $\hat{T}_2$ amplitudes changes from $\langle \psi_{ij}^{ab} | e^{-\hat{T}_1 - \hat{T}_2} \hat{H}_N e^{\hat{T}_1 + \hat{T}_2} | \psi_0 \rangle = 0$ to $\langle \psi_{ij}^{ab} | e^{-\hat{T}_1} \hat{H}_N e^{\hat{T}_1} + e^{-\hat{T}_2} F e^{\hat{T}_2} | \psi_0 \rangle = 0$. Extending this idea to the linear response formalism leads to the effective Jacobian block matrix for evaluating the excitation energies

$$\begin{bmatrix} \langle \psi_i^a | e^{-\hat{T}_1 - \hat{T}_2} \hat{H}_N e^{\hat{T}_1 + \hat{T}_2} | \psi_k^c \rangle & \langle \psi_i^a | e^{-\hat{T}_1 - \hat{T}_2} \hat{H}_N e^{\hat{T}_1 + \hat{T}_2} | \psi_{kl}^{cd} \rangle \\ \langle \psi_{ij}^{ab} | e^{-\hat{T}_1} \hat{H}_N e^{\hat{T}_1} | \psi_k^c \rangle & \langle \psi_{ij}^{ab} | e^{-\hat{T}_2} \hat{F}_N e^{\hat{T}_2} | \psi_{kl}^{cd} \rangle \end{bmatrix}$$
$$\times \begin{bmatrix} R_1 \\ R_2 \end{bmatrix} = \omega \begin{bmatrix} R_1 \\ R_2 \end{bmatrix}. \tag{19}$$

The solution scheme for the CC2 equations is similar to EOM–CCSD: a ground state calculation is performed first to obtain optimized values for $\hat{T}_1$ and $\hat{T}_2$ amplitudes, followed by the iterative solution of the above effective Hamiltonian to solve for R (if only energies are desired). This is unlike the perturbative approaches, in which the $\hat{T}$ amplitudes are directly determined (and thus no ground state calculation is required). As an approximation to LR–CCSD, CC2 eliminates all of the highest order scaling terms, thus making CC2 an $\mathcal{O}(N^5)$ method.

RESULTS AND DISCUSSION

Both P–EOM–MBPT2 and CC2 are $\mathcal{O}(N^5)$ scaling wave function based methods, although this computational scaling is obtained in a very different manner. Their parameter-free nature holds the potential for computing many-electron excited states with a well-balanced predictability. We test the quality of these low-scaling excited state methods across a wide-range of excitations (e.g., from valence to Rydberg excitations). After comparing each methods' performance against experimental data, we rationalize our observations in light of the formal characteristics of each method. We hope this work will provide confidence and guidance to the utility of low-scaling approximations to LR–CCSD and EOM–CCSD methods.

As low-scaling wave function based methods, P–EOM–MBPT2 and CC2 can be considered complementary excited state methods to each other. Both methods have the same expression for the doubles-doubles block, but the rest of the blocks differ in their approximations. In particular, CC2 eliminates many of the connected $\hat{T}_2$ terms so that a majority of the terms depend on $\hat{T}_1$. In contrast, the P–EOM–MBPT2 methods eliminate all terms that have a contraction with $\hat{T}_1$, because $\hat{T}_1$ is zero, so that the majority of the terms are $\hat{T}_2$ dependent. In other words, one way to view the difference between CC2 and P–EOM–MBPT2 is that the former favors $\hat{T}_1$ (or is "$\hat{T}_1$ heavy") and the latter favors $\hat{T}_2$ ("$\hat{T}_2$ heavy"). The $\hat{T}_1$ operator has long been understood as accounting for orbital response to electron correlation and the $\hat{T}_2$ operators are understood as accounting for the dynamic (pairwise) electron correlation. Which contribution matters most to electronic ex-
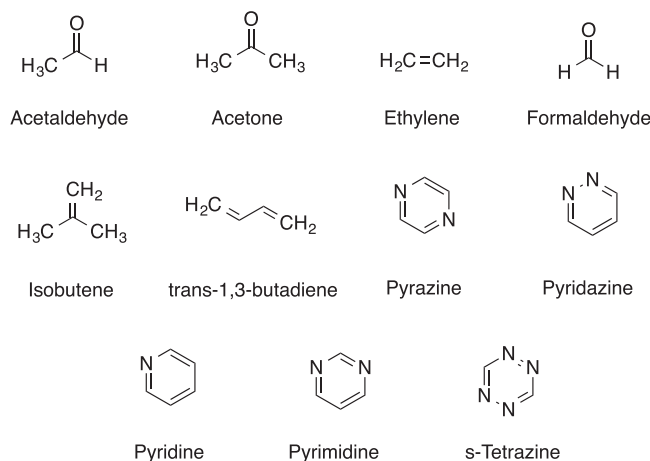

FIG. 1. Molecules used to test the accuracy of excited state methods. All molecules were optimized at the MP2/6-311+G** level of theory.

citation energies is an open question, and a comparison of CC2 with P–EOM–MBPT2 provides an excellent case study of the importance of each excitation operator. It should be noted that CC2 still retains some $\hat{T}_2$ contributions, as $\hat{T}_1$ depends on $\hat{T}_2$ (if $\hat{T}_2$ were zero, then $\hat{T}_1$ would necessarily be zero due to Brillouin theorem). However, CC2 eliminates all of the $\hat{T}_2$ terms in the doubly excited bra space, and the effect of dynamic correlation in this space can only be incorporated indirectly through $\hat{T}_1$.

The EOM–MBPT2 and P–EOM–MBPT2 methods, along with CC2, have been implemented and tested in the development version of the Gaussian electronic structure theory suite.[33] The accuracy of these methods is tested against EOM–CCSD, LR–TDDFT/B3LYP, CIS(D), RPA, and CIS methods. The methods were tested using the Pople split-valence basis set 6-311(3+,3+)G**, where all atoms were augmented with three diffuse functions. This type of basis has been shown satisfactory for calculating excitation energies.[34–36] The molecules chosen for testing, given in Fig. 1, have been extensively studied in the gas phase, and reliable experimental data are available in the literature. Sixty-nine excited states in all were calculated and compared to experiment, and of the 69 states, 30 were considered valence states, and 39 were considered Rydberg states. In addition to experimental comparisons, direct comparisons between the low scaling methods and EOM–CCSD were performed. Because each method can be seen as an approximation to EOM–CCSD, the CCSD excitation energies are a critical reference.

Due to the unreliability of experimental excited state energies for triplets,[35] only comparisons to singlet excitations were studied. All excitation energies obtained are compared to experimental values, using the metric of mean absolute error to experiment (Mean AE), maximum absolute error to experiment (Maximum AE), and root mean square (RMS) error to experiment. Geometries, which were optimized at the ground state MP2/6-311+G** level of theory, were taken from the test set by Caricato *et al.*[34] The values for LR–TDDFT/B3LYP, experimental values, and CIS/CIS(D)/RPA values are taken from those reported previously.[35]

TABLE I. Mean absolute error (Mean AE), error root mean square (RMS), maximum absolute error (Max AE), and mean signed error (MSE) compared to EOM–CCSD for the first state and all the states of all the molecules (eV), 69 states total.

| | All molecules, compared to EOM–CCSD | | | | | | | |
| | First state | | | | All states | | | |
	Mean AE	RMS	Max AE	MSE	Mean AE	RMS	Max AE	MSE
EOM–MBPT2	0.14	0.16	0.33	0.04	0.13	0.20	1.19	−0.01
P–EOM–MBPT2	0.39	0.43	0.66	0.39	0.25	0.35	0.78	0.21
CC2	0.16	0.17	0.25	−0.12	0.40	0.52	1.69	−0.39
CIS(D)	0.08	0.09	0.14	0.00	0.34	0.45	1.16	−0.24
B3LYP	0.44	0.51	0.85	−0.44	0.78	0.87	1.59	−0.76
RPA	0.52	0.57	1.04	0.39	0.92	1.11	2.61	0.69
CIS	0.62	0.70	1.19	0.55	0.96	1.16	2.65	0.80

While the assignment of excited states for the selected molecules has been detailed elsewhere,[35] and indeed the present work can be seen as an extension of Caricato *et al.*, we briefly explain our methodology here. Valence states may be identified by examining the dominant orbital contributions to the excitation. Rydberg states, which are more difficult to assign, were separated by irreducible representation, energy ordered, and then matched with experimental data. The results and assignments for each excitation are given in the supplementary material.[37] This methodology has also been applied successfully to the same molecules in the work by Wiberg *et al.*[36] Vibronic effects are not necessarily negligible, especially for the azabenzenes (in particular the symmetry forbidden $n \rightarrow \pi^*$). These transitions are broad and have low intensity, thus the experimental uncertainty is larger for these transitions. In spite of this, vibronic corrections are beyond the scope of this paper and were not included. This will be the focus of a later work.

Comparing first directly to EOM–CCSD in Table I, we find that the EOM–MBPT2 approximation performs closely to EOM–CCSD with a mean absolute error of only 0.13 eV. However, because it has the same polynomial scaling cost, there is little practical advantage to its use. On the other hand, the $\mathcal{O}(N^5)$ P–EOM–MBPT2 gives EOM–CCSD quality results within 0.25 eV, followed by CIS(D) and CC2. In general, P–EOM–MBPT2 overestimates excitation energies relative to EOM–CCSD, whereas CC2 and CIS(D) underestimate excitation energies.

Of all the molecules tested in Fig. 1, EOM–CCSD provides excitation energies closest to those of experiment for all states considered in Table II. It has a root-mean-square error of 0.36 eV. EOM–MBPT2 generally has similar performance to EOM–CCSD, which suggests the relative importance of including the double excitation subspace when calculating excited state energies. Methods that do not include a double excitation subspace, namely, CIS and RPA, have a much poorer description of experimental excitations, with a RMS around 1.25 eV. The partitioned approach, P–EOM–MBPT2 contains much double excitation character, though much less than EOM–CCSD or EOM–MBPT2, on account of the severe restrictions on the doubles-doubles block. LR–TDDFT/B3LYP performs modestly, with a RMS of 0.84 eV, which is far better than simple wave function based methods like RPA and CIS. CIS(D) has performance similar to P–EOM–MBPT2 in general. CC2 performs quite well for all states, with an accuracy lying between the EOM–MBPT2 and P–EOM–MBPT2 methods.

It is perhaps more revealing, however, to note the differences in the estimation of valence states versus Rydberg states. It should be noted that all states considered are well under the CCSD ionization potential and therefore may be classified as valence or Rydberg. In the direct comparisons to

TABLE II. Mean absolute error (Mean AE), error root mean square (RMS), maximum absolute error (Max AE), and mean signed error (MSE) compared to experiment for the first state and all the states of all the molecules (eV), 69 states total.

| | All molecules, compared to experiment | | | | | | | |
| | First state | | | | All states | | | |
	Mean AE	RMS	Max AE	MSE	Mean AE	RMS	Max AE	MSE
EOM–CCSD	0.35	0.44	0.82	0.35	0.27	0.36	1.02	0.20
EOM–MBPT2	0.43	0.54	0.96	0.39	0.30	0.43	1.12	0.20
P–EOM–MBPT2	0.74	0.83	1.32	0.74	0.47	0.65	1.40	0.41
CC2	0.23	0.29	0.60	0.23	0.44	0.53	1.26	−0.19
CIS(D)	0.35	0.45	0.78	0.35	0.49	0.61	1.83	−0.04
B3LYP	0.22	0.29	0.55	−0.09	0.67	0.84	1.82	−0.56
RPA	0.75	0.93	1.86	0.74	1.01	1.26	3.63	0.90
CIS	0.90	1.08	2.01	0.90	1.07	1.34	3.67	1.01

TABLE III. Mean absolute error (Mean AE), error root mean square (RMS), maximum absolute error (Max AE), and mean signed error (MSE) compared to EOM–CCSD for all the valence states of all the molecules (eV), 30 states total.

All molecules, compared to EOM–CCSD, valence states only			
	Mean AE	RMS	Max AE	MSE
EOM–MBPT2	0.20	0.29	1.19	0.04
P–EOM–MBPT2	0.48	0.51	0.78	0.41
CC2	0.30	0.47	1.69	− 0.27
CIS(D)	0.18	0.29	1.16	0.02
B3LYP	0.47	0.51	0.85	− 0.41
RPA	0.89	1.02	2.61	0.61
CIS	0.96	1.10	2.65	0.82

TABLE V. Mean absolute error (Mean AE), error root mean square (RMS), maximum absolute error (Max AE), and mean signed error (MSE) compared to experiment for all the valence states of all the molecules (eV), 30 states total.

All molecules, compared to experiment, valence states only			
	Mean AE	RMS	Max AE	MSE
EOM–CCSD	0.47	0.52	1.02	0.47
EOM–MBPT2	0.56	0.63	1.12	0.51
P–EOM–MBPT2	0.89	0.96	1.40	0.88
CC2	0.36	0.42	1.00	0.20
CIS(D)	0.50	0.59	1.83	0.49
B3LYP	0.20	0.26	0.59	0.06
RPA	1.19	1.44	3.63	1.08
CIS	1.29	1.55	3.67	1.29

EOM–CCSD valence energies in Table III, we find that CC2 gives EOM–CCSD quality results to 0.3 eV, versus P–EOM–MBPT2, which has errors of nearly 0.5 eV. Of all the $\mathcal{O}(N^5)$ methods, CIS(D) reproduces CCSD-quality results the best. For Rydberg states, the performance of the methods compared to EOM–CCSD is more stark (see Table IV). Both the EOM–MBPT2 and P–EOM–MBPT2 reproduce EOM–CCSD quality results to 0.07 eV, compared to CC2 and CIS(D), which reproduce the CCSD excitation energies to almost 0.5 eV. We suggest that this result stems from the necessity of including $\hat{T}_2$ amplitudes in the doubly excited manifolds of the effective Hamiltonian, which only the (P–)EOM–MBPT2 methods include compared to CIS(D) and CC2. This hypothesis will be discussed later.

Similar conclusions regarding the performance of the methods tested are reached when comparing to experimental data. For the valence states considered (Table V), the wave function based methods perform poorly compared to the Rydberg states (Table VI). Perhaps more surprisingly is how well B3LYP performs, with a RMS of 0.26 eV, compared to EOM–CCSD which has a RMS twice that at 0.52 eV. However, this may simply be the result of fortuitous cancellation of errors in B3LYP, especially in light of the varied performance of similar hybrid functionals on the same test set.[35] We also note that B3LYP was parameterized to perform well for organic molecules like many of the small molecules tested here. EOM–MBPT2 and P–EOM–MBPT2 perform much worse

than EOM–CCSD or CC2 – consistently overestimating the valence state energies – and we suggest that much of the failure for valence states can be traced back to the total neglect of $\hat{T}_1$ amplitudes.

The single excitation cluster operator has long been understood as an orbital rotation operator, which mixes virtual and occupied orbitals to account for orbital relaxation. Valence states are highly sensitive to the effects of orbital rotation and relaxation. The Thouless theorem[38] says that the effect of the $e^{\hat{T}_1}$ operator is to transform any single determinant into any other single determinant. It is well known that minimization of the energy of a single Slater determinant with respect to the rotation parameters (or t_i^a amplitudes), determines the stability conditions of the Hartree-Fock equations known as Brillouin's condition.[38] The Thouless theorem explains why CCSD and higher methods are so insensitive to reference choice; optimal reference is generated through the $\hat{T}_1$ operator. Because the perturbative approximations considered neglect the effects of orbital rotation, we should expect them to perform much worse for valence states. CC2, which does account for orbital rotation and relaxation, performs quite well for the valence states, which is consistent with this hypothesis. In fact, for the valence states considered CC2 outperformed EOM–CCSD. We wish to note two benchmarking studies of coupled cluster excited state methods, the first by Schreiber *et al.*,[39] and the recent extension by Kánnár

TABLE IV. Mean absolute error (Mean AE), error root mean square (RMS), maximum absolute error (Max AE), and mean signed error (MSE) compared to EOM–CCSD for all the Rydberg states of all the molecules (eV), 39 states total.

All molecules, compared to EOM-CCSD, Rydberg states only			
	Mean AE	RMS	Max AE	MSE
EOM–MBPT2	0.07	0.08	0.25	− 0.04
P–EOM–MBPT2	0.07	0.11	0.42	0.05
CC2	0.48	0.55	0.82	− 0.48
CIS(D)	0.46	0.54	0.95	− 0.44
B3LYP	1.02	1.07	1.59	− 1.02
RPA	0.94	1.17	1.85	0.75
CIS	0.96	1.21	1.86	0.79

TABLE VI. Mean absolute error (Mean AE), error root mean square (RMS), maximum absolute error (Max AE), and mean signed error (MSE) compared to experiment for all the Rydberg states of all the molecules (eV), 39 states total.

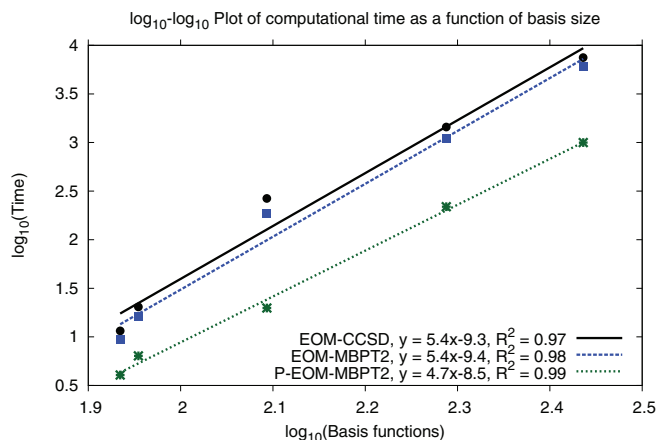| All molecules, compared to experiment, Rydberg states only			
	Mean AE	RMS	Max AE	MSE
EOM–CCSD	0.11	0.14	0.45	0.00
EOM–MBPT2	0.10	0.14	0.34	− 0.05
P–EOM–MBPT2	0.15	0.20	0.55	0.05
CC2	0.50	0.61	1.26	− 0.49
CIS(D)	0.49	0.62	1.32	− 0.44
B3LYP	1.03	1.09	1.82	− 1.03
RPA	0.88	1.11	1.89	0.75
CIS	0.91	1.15	1.94	0.79

FIG. 2. Plot of $\log_{10}$(Time) versus $\log_{10}$(Number basis functions). EOM–CCSD and EOM–MBPT2 have an experimental scaling of $\mathcal{O}(N^{5.4})$, while P–EOM–MBPT2 has an experimental scaling of $\mathcal{O}(N^{4.7})$, nearly an order of magnitude less, as expected.

and Szalay.[40] These studies — which only consider valence states — find that in comparison to CC3 and CASPT2 references, CCSD overestimates valence state energies, whereas the mean deviation for CC2 is near zero. Our results are in agreement with these findings.

Despite the success of CC2 in describing valence states, it is not nearly as robust in describing Rydberg states. Rydberg states are much more diffuse and less sensitive to orbital rotations. The heavy inclusion of the $e^{\hat{T}_2}$ operator in the perturbative EOM methods accounts for the correlation necessary to describe excitations into the excited states, and indeed this is not the first time this has been pointed out.[22] CC2 appears to underestimate Rydberg transition with a negative mean signed error. The perturbative EOM methods tested, along with EOM–CCSD, have RMS errors lower than 0.2 eV — three times less than the nearest-performing method, CIS(D) and CC2. Out of the 39 Rydberg states considered, the P–EOM–MBPT2 was more accurate than CC2 by a factor of three (Table VI). Perhaps even more interesting was that the difference in RMS error between EOM–CCSD and P–EOM–MBPT2 was only 0.06 eV.

While EOM–CCSD is generally the most accurate method considered here, its scaling as $\mathcal{O}(N^6)$ rules it out for use with larger molecular systems. The experimental scaling for the methods tested was demonstrated in Fig. 2, and the re-

TABLE VII. Scaling of EOM–MBPT2 and P–EOM–MBPT2 compared to EOM–CCSD. EOM–MBPT2 has the same scaling as EOM–CCSD, $\mathcal{O}(N^6)$, but with a 23% smaller prefactor. P–EOM–MBPT2 scales an order of magnitude less than the other methods, and its prefactor cannot be compared to EOM–CCSD because the prefactors compare different scaling terms.

	Scaling		Scaling rel. to EOM–CCSD		
	Exp.	Pred.	Exp.	Pred.	Relative prefactor
EOM–CCSD	5.44	6.00	1.00	1.00	1.00
EOM–MBPT2	5.44	6.00	1.00	1.00	0.77
P–EOM–MBPT2	4.72	5.00	0.87	0.83	N/A

sults tabulated in Table VII. Because the calculations are iterative, the timing is relative to one average iteration. All EOM methods converge within one iteration of each other. As is seen, only the P–EOM–MBPT2 method is able to achieve the theoretical reduction of $\mathcal{O}(N^6)$ to $\mathcal{O}(N^5)$, making it a computationally cheaper method which scales along other methods such as CIS(D) and CC2. While EOM–MBPT2 retains the same formal scaling as EOM–CCSD, it does benefit from the reduction of terms which corresponds to a reduced prefactor. Compared to EOM–CCSD, EOM–MBPT2 was found to be 23% cheaper.

CONCLUSION

We have implemented two perturbative approximations to EOM–CCSD, along with CC2, and tested them against a test set of 11 molecules for a total of 69 excited states, all of which have been studied extensively in the gas phase. The methods were also directly compared to EOM–CCSD. The accuracy and timing of the methods was determined, and it was found that the P–EOM–MBPT2 method outperforms both EOM–CCSD and EOM–MBPT2 in terms of computational cost, lowering the formal scaling from $\mathcal{O}(N^6)$ to $\mathcal{O}(N^5)$. For the $\mathcal{O}(N^5)$ methods considered, CC2 performs best in describing valence states compared to both EOM–CCSD and experiments, which is attributable to the flexibility it retains with respect to orbital relaxation. However, it does not perform nearly as well as P–EOM–MBPT2 in the description of Rydberg states, which better accounts for dynamic correlation. Thus on account of their respective approximation, CC2 is the best $\mathcal{O}(N^5)$ method for describing valence states, whereas P–EOM–MBPT2 is the best $\mathcal{O}(N^5)$ method for describing Rydberg states. Together, P–EOM–MBPT2 and CC2 form a complementary pair of low-scaling algorithms that offers predictive power of wave function based excited state methods.

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APPENDIX: DERIVATION OF (P–)EOM–MBPT2 EQUATIONS

We begin our perturbative treatment of the coupled cluster Schrödinger equations by partitioning the normal ordered Hamiltonian into the one-particle component $\hat{F}_N$ and the two-particle component $\hat{V}_N$ as a perturbation, with λ as a scalar ordering parameter

$$\hat{H}_N = \hat{F}_N + \lambda \hat{V}_N. \tag{A1}$$

Similarly, we expand the $\hat{T}$ operator perturbatively

$$\hat{T} = \lambda \hat{T}^{(1)} + \lambda^2 \hat{T}^{(2)} + \lambda^3 \hat{T}^{(3)} + \cdots. \tag{A2}$$

Because of the exponential parameterization, the coupled cluster Schrödinger equation can be written as the infinite series

$$\hat{H}_N e^{\hat{T}}|\Phi_0\rangle$$

$$= \hat{H}_N|\Phi_0\rangle + \hat{H}_N \hat{T}|\Phi_0\rangle + \frac{1}{2}\hat{H}_N \hat{T}^2|\Phi_0\rangle + \cdots \quad (A3)$$

$$= (\hat{F}_N + \lambda \hat{V}_N)|\Phi_0\rangle$$

$$+ (\hat{F}_N + \lambda \hat{V}_N)(\lambda \hat{T}^{(1)} + \lambda^2 \hat{T}^{(2)} + \lambda^3 \hat{T}^{(3)} + \cdots)|\Phi_0\rangle \quad (A4)$$

$$+ \frac{1}{2}(\hat{F}_N + \lambda \hat{V}_N)(\lambda \hat{T}^{(1)} + \lambda^2 \hat{T}^{(2)}$$

$$+ \lambda^3 \hat{T}^{(3)} + \cdots)^2|\Phi_0\rangle + \cdots . \quad (A5)$$

Collecting terms of like order λ yields, with $\bar{H}_N = \hat{H}_N e^{\hat{T}}$

$$\bar{H}_N^{(1)} = \hat{V}_N + \hat{F}_N \hat{T}^{(1)}, \quad (A6)$$

$$\bar{H}_N^{(2)} = \hat{V}_N \hat{T}^{(1)} + \hat{F}_N \hat{T}^{(2)} + \frac{1}{2}\hat{F}_N \hat{T}^{(1)}\hat{T}^{(1)} \cdots . \quad (A7)$$

At this point, we note that the perturbative scheme is formally exact. However, truncating $\hat{T}$ to include only single and double excitations ($\hat{T}_1$ and $\hat{T}_2$, respectively), we have through second order

$$\bar{H}_N^{(1)} = \hat{V}_N + \hat{F}_N \hat{T}_1^{(1)} + \hat{F}_N \hat{T}_2^{(1)}, \quad (A8)$$

$$\bar{H}_N^{(2)} = \hat{V}_N \hat{T}_1^{(1)} + \hat{V}_N \hat{T}_2^{(1)} + \hat{F}_N \hat{T}_1^{(2)} + \hat{F}_N \hat{T}_2^{(2)} + \frac{1}{2}\hat{F}_N \hat{T}_1^{(1)}\hat{T}_1^{(1)}$$

$$+ \frac{1}{2}\hat{F}_N \hat{T}_2^{(1)}\hat{T}_2^{(1)} + \hat{F}_N \hat{T}_1^{(1)}\hat{T}_2^{(1)}. \quad (A9)$$

Assuming canonical Hartree-Fock orbitals, we find that through second order our Hamiltonian matrix elements are, for the singles-singles block

$$\langle\Phi_i^a|\bar{H}\hat{R}_1|\Phi_0\rangle = f_{ac}r_i^c - f_{ki}r_k^a + \langle ak||ic\rangle r_k^c$$

$$- \frac{1}{2}\langle mn||ce\rangle t_{mn}^{ae(1)}r_i^c - \frac{1}{2}\langle km||ef\rangle t_{im}^{ef(1)}r_k^a$$

$$+ \langle km||ce\rangle t_{mi}^{ea(1)}r_k^c, \quad (A10)$$

for the singles-doubles block

$$\langle\Phi_i^a|\bar{H}\hat{R}_2|\Phi_0\rangle = \frac{1}{2}\langle al||cd\rangle r_{il}^{cd} - \frac{1}{2}\langle kl||id\rangle r_{kl}^{ad}, \quad (A11)$$

for the doubles-singles block

$$\langle\Phi_{ij}^{ab}|\bar{H}\hat{R}_1|\Phi_0\rangle$$

$$= P(ij)\langle ab||cj\rangle r_i^c - P(ab)\langle kb||ij\rangle r_k^a$$

$$+ P(ij)P(ab)\langle am||ce\rangle t_{mj}^{eb(1)}r_i^c$$

$$- P(ij)P(ab)\langle km||ie\rangle t_{mj}^{eb(1)}r_k^a$$

$$- \frac{1}{2}P(ab)\langle kb||ef\rangle t_{ij}^{ef(1)}r_k^a + \frac{1}{2}P(ij)\langle mn||cj\rangle t_{mn}^{ab(1)}r_i^c$$

$$+ P(ab)\langle ka||ce\rangle t_{ij}^{eb(1)}r_k^c - P(ij)\langle km||ci\rangle t_{mj(1)}^{ab}r_k^c, \quad (A12)$$

and finally the doubles-doubles block

$$\langle\Phi_{ij}^{ab}|\bar{H}\hat{R}_2|\Phi_0\rangle$$

$$= P(ab)f_{bc}r_{ij}^{ac} - P(ij)f_{kj}r_{ik}^{ab}$$

$$+ \frac{1}{2}\langle ab||cd\rangle r_{ij}^{cd} + \frac{1}{2}\langle kl||ij\rangle r_{kl}^{ab} + P(ij)P(ab)\langle kb||cj\rangle r_{ik}^{ac}$$

$$+ \frac{1}{4}\langle mn||cd\rangle t_{mn}^{ab(1)}r_{ij}^{cd} + \frac{1}{4}\langle kl||ef\rangle t_{ij}^{ef(1)}r_{kl}^{ab}$$

$$+ P(ij)P(ab)\langle km||ce\rangle t_{mi}^{ea(1)}r_{jk}^{bc} - \frac{1}{2}P(ij)\langle km||cd\rangle t_{mj}^{ab(1)}r_{ik}^{dc}$$

$$- \frac{1}{2}P(ij)\langle mk||ef\rangle t_{im}^{fe(1)}r_{kj}^{ab} - \frac{1}{2}P(ab)\langle kl||ce\rangle t_{ij}^{eb(1)}r_{lk}^{ac}$$

$$- \frac{1}{2}P(ab)\langle mn||ec\rangle t_{mn}^{ae(1)}r_{ij}^{cb}, \quad (A13)$$

where $P(pq)$ is an antisymmetric permutation operator,

$$P(pq) = 1 - \mathcal{P}(pq), \quad (A14)$$

where $\mathcal{P}(pq)$ permutes the indices of p and q. These equations define the EOM–MBPT2 method.[22] Terms involving $t_i^{a(1)}$ are always zero when using a canonical Hartree-Fock reference. This, as well as the expression for $t_{ij}^{ab(1)}$, can be determined in the same manner as the so-called $\hat{T}_1$ and $\hat{T}_2$ equations in CCSD, projecting the singly and doubly excited determinant on the CCSD ground state equations. For $t_i^{a(1)}$,

$$\langle\Phi_i^a|\bar{H}^{(1)}|\Phi_0\rangle = 0$$

$$= f_{ab}t_i^{b(1)} - f_{ij}t_i^{a(1)}. \quad (A15)$$

By the diagonal nature of the canonical Fock matrix elements, $t_i^{a(1)} = 0$. In a similar manner,

$$\langle\Phi_{ij}^{ab}|\bar{H}^{(1)}|\Phi_0\rangle = 0$$

$$= \langle ij||ab\rangle - (f_{ii} + f_{jj} - f_{aa} - f_{bb})t_{ij}^{ab(1)},$$

$$t_{ij}^{ab(1)} = \frac{\langle ij||ab\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \quad (A16)$$

This is the expression for $t_{ij}^{ab(1)}$ used in the solution of the EOM–MBPT2 equations. They are completely determined, and therefore no CCSD iterative scheme must be used to compute them prior to the EOM solutions. The working equations may then be solved using non-Hermitian variants of the Davidson algorithm.[23–26]

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