A simple scheme for calculating approximate transition moments within the equation of motion expectation value formalism

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A simple scheme for calculating approximate transition moments within the framework of the equation of motion coupled cluster method is proposed. It relies on a matrix inversion technique to calculate the excited state left eigenvectors and requires no additional cost over that of the excitation energy calculation. The new approximation gives almost identical UV-Vis spectra to that obtained using the standard equation of motion coupled cluster method with single and double excitations for molecules in a standard test set. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4984618>]

I. INTRODUCTION

Energy differences determine many chemical properties, be it thermodynamic quantities like entropy or enthalpy or spectroscopic observables like the ionization potential (IP), electron affinity (EA), or excitation energy (EE). The equation of motion coupled cluster (EOM-CC) method^{1–7} has emerged as one of the most accurate and systematically improvable ways for the calculation of energy differences of all these types. The method is generally used with the inclusion of single and double excitations (EOM-CCSD), which scales as $O(N^6)$ and has a typical error bar of 0.2–0.3 eV, for excited states dominated by a single excitation.

However, the calculation of energy differences, such as EE, is not enough for the simulation of various spectra, which also requires the calculation of transition properties such as transition dipole moments and oscillator strengths. The transition properties in EOM-CCSD are defined using the expectation value approach. Koch *et al.* also introduced a more rigorous linear response (LR) approach,^{8,9} which guarantees the extensivity of the calculated transition properties.^{10,11} However, for most cases, both these approaches give very similar results.¹² Transition properties for generalized coupled cluster wave functions have been implemented by Kállay and Gauss using string-based algorithms.¹³ A very efficient implementation of transition dipole moments within the framework of CC2 theory has been reported by Hättig and Köhn using the density-fitting/resolution of the identity approach¹⁴ and Baudin *et al.*¹⁵ as well as Schütz and co-workers¹⁶ using the local correlation approach. The implementation of transition dipole moments for other variants of coupled cluster or related methods, such as similarity transformed EOMCC (STEOMCC),¹⁷ Fock space multireference coupled cluster (FSMRCC),^{18,19} and symmetry adapted cluster/configuration interaction (SAC-CI),²⁰ has also been reported.

Since the similarity transformed CC Hamiltonian is non-Hermitian, it has different right and left eigenvectors, and calculating transition moments in the EOM-CCSD approach

requires both of these. Thus, such a calculation is roughly twice as costly as one in which only the excitation energy is evaluated, for which the calculation of either one of the eigenvectors is sufficient. Therefore, in almost all the standard quantum chemistry codes, transition moments for EOM-CCSD are not calculated as default when excitation energies are requested, in contrast with configuration interaction singles (CIS) or time dependent density functional theory (TD-DFT) calculations in which the transition moment can also be obtained with almost no additional effort over excitation energy calculations.

There have been various attempts discussed in the literature based on perturbative truncation,^{21–25} density fitting,²⁶ and semi-numerical techniques^{27,28} as well as the local approximation^{29–33} to reduce the computational cost of excitation energy calculations in EOM-CCSD. However, similar efforts to lower the cost of transition moment evaluation have received very much less attention. The aim of this paper is to explore efficient approximate schemes to evaluate EOM-CCSD transition moments without much additional effort beyond the calculation of energy differences and without losing much of the method's inherent accuracy.

II. THEORY AND COMPUTATIONAL DETAILS

A. Notation

Since in the following we will use somewhat unconventional notation, it is necessary to devote a few lines to clarify their exact meaning, although this notation has parallels with that used in linear response theory.^{8,10} Usually, operators are defined as a second quantized string of creators (a^p) and annihilators (a_q), $a^p a^q, \dots, a_r a_s, \dots$. In a spin free formulation, one uses the spin summed generators of the unitary group,

$$E_q^p = \sum_{\sigma=\alpha,\beta} a^{p\sigma} a_{q\sigma}. \quad (1)$$

Then, a triple excitation, for example, can be described as

$$E_i^a E_j^b E_k^c \equiv E_T, \quad (2)$$

where $i, j, k, \dots$ and $a, b, c, \dots$ correspond to some partitioning of the orbital space, and the occupied and virtual

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subspaces in the closed shell case. The single notation E_T may be introduced, to denote a whole excitation class.

In the following, various linear excitation operators ($\hat{R}, \hat{L}, \hat{T}$) will be defined. Again in the closed shell case, such operators, including a constant term L^0 , can be written as

$$\hat{L} = L^0 + L_a^i E_i^a + L_{ab}^{ij} E_i^a E_j^b + \dots \equiv L^0 + L^I E_I, \quad (3)$$

where the Einstein summation convention is used, which in the last term implies also summation over all strings I , i.e., over all excitation classes involved in the operator. Since in the following it will be necessary to distinguish between solutions corresponding to given roots, e.g., $\hat{L}_m$, this allows us to avoid crowded notations, in which the root index (m) has to be denoted along with the excitation labels ($i, j, k, \dots, a, b, c, \dots$).

The notation can of course be further generalized, E_I , and its adjoint $E^I \equiv E_I^\dagger$ can denote in principle any operator string and its adjoint. This may be necessary if ionization operators are involved or in unrestricted formulation, where the spin is explicitly involved, or in open shell restricted spin restricted and multireference theories,³⁴ where more than two orbital spaces are involved. The advantages of normal ordering are not exploited in our formulation either. Depending on these assumptions, some of the details of the derivation below may change, e.g., in a restricted open shell theory, two linear excitation operators do not commute because the set of annihilators and creators overlap. Since our implementation is a closed shell one, the derivation below corresponds to the closed shell case, while equivalent derivations may be obtained for the other cases.

It should be mentioned finally that when calculating scalar products (and expectation values) in a non-orthogonal set of configuration state functions, redundancies can be taken care of by defining a contravariant set of basis functions.³⁵ Thus, for example, for a function Φ , made up only of double excitations acting on the reference $|0\rangle$,

$$\Phi = C_{ab}^{ij} E_i^a E_j^b |0\rangle, \quad \langle \tilde{\Phi} | \Phi \rangle = \tilde{C}_{ij}^{ab} C_{ab}^{ij}, \quad (4)$$

with

$$\tilde{C}_{ij}^{ab} = 2C_{ij}^{ab} - C_{ij}^{ba}, \quad (5)$$

where the tilde denotes the contravariant quantities. This need not be explicitly considered further, since part of the problem is related to the definition of the generic operator E_I , and partly it can be absorbed into an appropriate definition of the scalar product involving linear combinations of coefficients with permuted labels.

B. Ground states

The Schrödinger equation for the molecular Born-Oppenheimer Hamiltonian $\hat{H}$ yields the non-relativistic wave function (Ψ) and energy (E) of the molecular system,

$$\hat{H}|\Psi\rangle = E|\Psi\rangle. \quad (6)$$

In CC theory, the wave function is assumed to have an exponential form

$$|\Psi\rangle = e^{\hat{T}} |0\rangle, \quad (7)$$

where $\hat{T}$ are the CC amplitudes and $|0\rangle$ is a reference Slater determinant, which in the following will refer to the ground state determinant.

For ground states, CC can be neatly summarized by the equations, for the energy (E_0)

$$\langle 0 | \bar{H} | 0 \rangle = E_0, \quad (8)$$

and for the residuals

$$\langle \Phi_{ij}^{ab} \dots | \bar{H} | 0 \rangle = 0, \quad (9)$$

in which $\bar{H}$ is the similarity transformed Hamiltonian,

$$\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}. \quad (10)$$

The CC excitation operator is of the form

$$\hat{T} = T^I E_I. \quad (11)$$

Since they amount to zero, the terms in Eq. (9) may be added to Eq. (8) with some unknown Lagrangian multipliers, to define a more general CC energy functional. Defining a linear excitation operator (for state l),

$$\hat{L}_l = L_l^0 + L_l^I E_I, \quad (12)$$

the ground state CC Lagrangian can be expressed as

$$\mathcal{L} = \langle 0 | \hat{L}_0^\dagger \bar{H} | 0 \rangle = E_0. \quad (13)$$

Here, we used the ground state operator $\hat{L}_0$, in which $L_0^0 = 1$ and L_0^I are Lagrangian multipliers. Thus, it is convenient to introduce the notation $\hat{L}_0 = 1 + \hat{\Lambda}$ exclusively for the ground state, collecting all Lagrangian multipliers into $\hat{\Lambda}$. Obtaining derivatives of the energy and related properties require the solution of the so-called lambda equations,³⁶ which correspond to the following variational condition:

$$\frac{\partial \mathcal{L}}{\partial T^J} = \langle 0 | [\bar{H}, E_J] | 0 \rangle + L_J^0 \langle 0 | E^J [\bar{H}, E_J] | 0 \rangle = 0, \quad (14)$$

where we have used the fact that

$$\frac{\partial \bar{H}}{\partial T^J} = [\bar{H}, E_J]. \quad (15)$$

C. Linear approximation

Here, we will generalize the work of Kollmar and Neese,³⁷ in which they discuss the approximate calculation of the lambda equations for various pair theories. The essence of this approach is that once the CC equations are solved, i.e., $\hat{T}$ is known, the Lagrangian multipliers are not obtained directly from Eq. (14), but from an approach which allows for more insight and also for obtaining approximate solutions. Since the solutions, $\hat{L}_0$, yield zero when substituted into the lambda equations, any linear combination of these equations may be added to the CC Lagrangian. Thus, contracting the lambda equations with an arbitrary nonzero linear excitation operator $\hat{S} \equiv S^I E_I$, the following functional may be defined:

$$\mathcal{F} = \langle 0 | \hat{L}_0^\dagger \bar{H} | 0 \rangle - \langle 0 | \hat{L}_0^\dagger [\bar{H}, \hat{S}] | 0 \rangle. \quad (16)$$

If the ground state CC solution is known, i.e., there is a fixed and nonzero $\hat{T}$ for which $\mathcal{L} = E_0$, then a necessary and sufficient condition to find $\hat{L}_0$ is that $\mathcal{F} = E_0$ for any $\hat{S}$. The critical part of our derivation is that now we are going to set $\hat{S} = \hat{T}$. Note that strictly speaking replacing the arbitrary $\hat{S}$ with the particular $\hat{T}$ will only guarantee in the above setup that the

second term in $\mathcal{F}$ is zero, which means that the lambda residual in Eq. (14) may be zero as desired, or it may be a nonzero vector belonging to the null space of $\hat{T}$. The second case is undesirable and should be avoided if one were to turn this formulation into a practical code, or at least one should check whether the solutions thus obtained indeed satisfy Eq. (14). However, instead of using an arbitrary $\hat{S}$, in a truncated vector space in which all the major operators are defined, it is enough if the second term in $\mathcal{F}$ is zero for a finite set of basis vectors spanning that space. In other words, if the lambda residual is in the null space of all basis vectors, it is zero at the chosen truncation level. If this condition is satisfied, our choice, $\hat{T}$, is also a valid substitution. We will revisit the question of obtaining such a basis in Sec. II F, which will allow us to impose further conditions on approximations to $\hat{\Lambda}$. Here, our primary goal is to obtain a non-iterative approximation, and as will be seen, the particular choice $\hat{S} = \hat{T}$ does have some further advantages beyond the fact that it is readily available. Using the Baker-Campbell-Hausdorff expansion,

$$\bar{H} = \hat{H} + \sum_{k=1}^{\mathcal{N}} \frac{1}{k!} [\bar{H}, \hat{T}]_k \quad (17)$$

and

$$[\bar{H}, \hat{T}] = \sum_{k=1}^{\mathcal{N}} \frac{k}{k!} [\bar{H}, \hat{T}]_k, \quad (18)$$

in which $\mathcal{N}$ is the level where the expansion terminates, $[\hat{H}, \hat{T}]_0 = \hat{H}$ and

$$[\bar{H}, \hat{T}]_k = \underbrace{[[[\hat{H}, \hat{T}], \hat{T}], \dots \hat{T}]}_{k \text{ times}}. \quad (19)$$

Applying the condition $\mathcal{F} = E_0$ with $\hat{S} = \hat{T}$,

$$\langle 0 | \hat{L}_0^\dagger \bar{H} | 0 \rangle - \langle 0 | \hat{L}_0^\dagger [\bar{H}, \hat{T}] | 0 \rangle = \langle 0 | \bar{H} | 0 \rangle, \quad (20)$$

which has to be solved for $\hat{L}_0$. Using the commutator expansions on both sides of the above equation, and noting that in the difference $\bar{H} - [\bar{H}, \hat{T}]$, the onefold commutator, $[\hat{H}, \hat{T}]$, vanishes,

$$\begin{aligned} \langle 0 | \hat{L}_0^\dagger \bar{H} | 0 \rangle + \sum_{k=2}^{\mathcal{N}} \frac{1-k}{k!} \langle 0 | \hat{L}_0^\dagger [\hat{H}, \hat{T}]_k | 0 \rangle \\ = \langle 0 | \hat{H} | 0 \rangle + \sum_{k=1}^{\mathcal{N}} \frac{1}{k!} \langle 0 | [\hat{H}, \hat{T}]_k | 0 \rangle. \end{aligned} \quad (21)$$

Using the notation $\hat{L}_0 = 1 + \hat{\Lambda}$,

$$\begin{aligned} \langle 0 | \hat{\Lambda}^\dagger \hat{H} | 0 \rangle + \sum_{k=2}^{\mathcal{N}} \frac{1-k}{k!} \langle 0 | (1 + \hat{\Lambda}^\dagger) [\hat{H}, \hat{T}]_k | 0 \rangle \\ = \langle 0 | [\hat{H}, \hat{T}] | 0 \rangle + \sum_{k=2}^{\mathcal{N}} \frac{1}{k!} \langle 0 | [\hat{H}, \hat{T}]_k | 0 \rangle. \end{aligned} \quad (22)$$

Since $\hat{T}$ is an excitation operator,

$$\langle 0 | [\hat{H}, \hat{T}] | 0 \rangle = \langle 0 | \hat{H} \hat{T} | 0 \rangle \quad (23)$$

and

$$\langle 0 | \hat{\Lambda}^\dagger \hat{H} | 0 \rangle = \langle 0 | \hat{\Lambda}^\dagger \hat{H} | 0 \rangle^\dagger = \langle 0 | \hat{H} \hat{\Lambda} | 0 \rangle, \quad (24)$$

if the above quantity is a real scalar. In this study, we will assume real quantities so that the above equation is fulfilled. One may also realize that

$$\sum_{k=2}^{\mathcal{N}} \frac{k}{k!} \langle 0 | [\hat{H}, \hat{T}]_k | 0 \rangle = \langle 0 | \hat{H} \hat{T}^2 | 0 \rangle. \quad (25)$$

Then,

$$\langle 0 | \hat{H} (\hat{\Lambda} - \hat{T}) | 0 \rangle = \langle 0 | \hat{H} \hat{T}^2 | 0 \rangle + \sum_{k=2}^{\mathcal{N}} \frac{k-1}{k!} \langle 0 | \hat{\Lambda}^\dagger [\hat{H}, \hat{T}]_k | 0 \rangle. \quad (26)$$

Comparing this to the general case with the arbitrary operator $\hat{S}$,

$$\begin{aligned} \langle 0 | \hat{H} (\hat{\Lambda} - \hat{S}) | 0 \rangle &= \langle 0 | \hat{H} \hat{T} \hat{S} | 0 \rangle \\ &+ \sum_{k=1}^{\mathcal{N}} \frac{1}{k!} \langle 0 | \hat{\Lambda}^\dagger [[\hat{H}, \hat{T}]_{k-1}, (\hat{T} - k\hat{S})] | 0 \rangle, \end{aligned} \quad (27)$$

it is obvious that in the general case, there is no guarantee that either the left or right hand side will be small. For the choice $\hat{S} = \hat{T}$, however, the leading onefold commutator in the right hand side vanishes, and the rest may be considered small since they are higher order in $\hat{T}$ only. Neglecting the right hand side completely in Eq. (26) yields

$$\hat{\Lambda} \approx \hat{T}. \quad (28)$$

This is the approximation Kollmar and Neese obtained for the CCD wave function. In the CCD case, the first term is zero; thus effectively they only neglected the second term in Eq. (26). Note also that for the MP2 or configuration interaction doubles (CID) wave functions, the above relation is exact since we assume a linear excitation operator of the form $1 + \hat{T}$. In the CC case, this is also the lowest order approximation to the exponential wave function, which is consistent with Eq. (28). In the more general case, of the term $\langle 0 | \hat{H} \hat{T}^2 | 0 \rangle$, only the singles amplitude contribution survives. Thus, defining $\hat{\tau} = \hat{T} + \hat{T}^2$,

$$\langle 0 | \hat{H} (\hat{\Lambda} - \hat{\tau}) | 0 \rangle = \sum_{k=2}^{\mathcal{N}} \frac{k-1}{k!} \langle 0 | \hat{\Lambda}^\dagger [\hat{H}, \hat{T}]_k | 0 \rangle, \quad (29)$$

and neglecting the right hand side, which only contains terms of higher order in $\hat{T}$, one obtains the simple approximation,

$$\hat{\Lambda} \approx \hat{\tau}, \quad (30)$$

which, for closed shell CCSD theory, is identical to the usual $\hat{\tau}$ intermediate. Both Eqs. (28) and (30) require only quantities which are available after the ground state CC equations have been solved, thus these approximations are easily obtained. Equation (28) is a linear approximation in terms of $\hat{T}$, while Eq. (30) contains quadratic terms as well. Note that beyond double excitations, the components of $\hat{\Lambda}$ (and $\hat{T}$) do not contribute to the left hand side of Eqs. (26) and (29); thus higher excitation level contributions to $\hat{\Lambda}$ are not well determined if the right hand sides are neglected. However, even in this case one may use Eq. (28) or Eq. (30) as a first approximation with the additional constraints to be discussed in Sec. II F. It remains to be studied below to what extent the assumptions described in this section have enabled us to provide good approximations to Eq. (14).

D. Excited states

For excited states, the EOMCC scheme³ assumes the following form for the excited state wave function:

$$|\Psi_k\rangle = \hat{R}_k e^{\hat{T}} |0\rangle = e^{\hat{T}} \hat{R}_k |0\rangle, \quad (31)$$

since excitation operators commute (in the closed shell case), and $\hat{R}_k$ is a linear excitation operator belonging to the k th state,

$$\hat{R}_k = R_k^0 + R_k^I E_I. \quad (32)$$

With this parametrization, the excited state Schrödinger equation can be written using the similarity transformed Hamiltonian as

$$\bar{H} \hat{R}_k |0\rangle = E_k \hat{R}_k |0\rangle. \quad (33)$$

At this stage, it should be mentioned that $\hat{H}$ and $\bar{H}$ in Eq. (10) have the same eigenspectrum as long as the operator in the exponent is well behaved (e.g., bounded),³⁸ and if in its matrix representation, $\bar{H}$ is projected to the full excitation manifold, i.e., in the full configuration interaction (FCI) limit. The latter condition is rarely satisfied since it would mean that $\hat{R}_k$ must be expanded in the full space. In the next step, the ground state Schrödinger equation may be multiplied from the left to yield

$$\hat{R}_k \bar{H} |0\rangle = E_0 \hat{R}_k |0\rangle. \quad (34)$$

Then, the EOM problem can be directly solved for excitation energies $\omega_k = E_k - E_0$, by projecting to the reference

$$\langle 0 | [\bar{H}, \hat{R}_k] | 0 \rangle = \omega_k R_k^0, \quad (35)$$

with the corresponding projections for excited state amplitudes

$$\langle 0 | E^I [\bar{H}, \hat{R}_k] | 0 \rangle = \omega_k R_k^I. \quad (36)$$

Defining an appropriate $\hat{R}_0$ in Eq. (32), with $R_0^0 = 1$ and all $R_k^I = 0$, the ground state CC equations may also be formally expressed using Eqs. (35) and (36), which may be solved as a non-symmetric eigenvalue problem using a generalized Davidson algorithm.³⁹ Using the operator in Eq. (12) of an arbitrary state l , Eqs. (35) and (36) can be written as

$$\langle 0 | \hat{L}_l^\dagger [\bar{H}, \hat{R}_k] | 0 \rangle = \omega_k \delta_{lk}, \quad (37)$$

in which the biorthonormality condition was imposed,

$$\langle 0 | \hat{L}_l^\dagger \hat{R}_k | 0 \rangle = \delta_{lk}. \quad (38)$$

More specific details on these operators will be given in Sec. II E, where this formalism allows us to treat ground and excited states on an equal footing. So far, the multiroot CC problem has been expressed as a non-symmetric eigenproblem, where left ($\hat{L}_l$) and right ($\hat{R}_k$) solutions differ, although for energies, obtaining one of the two sets is sufficient. If $\hat{R}_k$ is known, $\hat{L}_l$ can be determined from the fact that

$$L_0^I \langle 0 | [\bar{H}, \hat{R}_k] | 0 \rangle + L_I^I \sigma(R_k^I) = \omega_k \delta_{lk} = \sigma(L_0^I) R_k^0 + \sigma(L_I^I) R_k^I, \quad (39)$$

in which

$$\sigma(R)_k^I = \langle 0 | E^I [\bar{H}, \hat{R}_k] | 0 \rangle \quad (40)$$

is the definition of the right hand sigma vector, while $\sigma(L)$ are the unknown left hand sigma vectors. Since the equations are linear in both left and right hand solutions, differentiation with respect to R_k^I yields

$$\sigma(L)_J^I = L_0^I \langle 0 | [\bar{H}, E_J] | 0 \rangle + L_I^I \langle 0 | E^I [\bar{H}, E_J] | 0 \rangle, \quad (41)$$

where we have used the fact that

$$\frac{\partial [\bar{H}, \hat{R}_k]}{\partial R_k^I} = \delta_{lk} [\bar{H}, E_J]. \quad (42)$$

It is similarly easy to see that $\sigma(L)_I^0 = 0$. Here and everywhere in this study, it is assumed that $\hat{T}$, $\hat{R}$, $\hat{L}$ are all truncated at the same excitation level. Comparing Eq. (41) to Eq. (14), the formal similarity is obvious, the difference being in the term involving L_0^I . As we will see, this term is zero for excited states; thus $\sigma(L)_J^I$ can be easily obtained from the ground state lambda equations by canceling the corresponding terms. This may then be evaluated in a subsequent Davidson process. However, it is more common, to evoke a linear equation solver making use of the fact that the exact eigenvalues are known.

E. Matrix formulation

For our purposes, the CC problem may be expressed using the following matrix representation:

$$\bar{H} = \begin{pmatrix} H_0^0 & H_J^0 \\ H_0^I & H_J^I \end{pmatrix}, \quad (43)$$

in which a partitioning was applied distinguishing the reference from higher excitations. The matrix elements are

$$H_J^I = \langle 0 | E^I [\bar{H}, E_J] | 0 \rangle, \quad (44)$$

where the 0 subindex denoting the ground state, and I, J the excitation manifold of singles, doubles, and so on. For $I, J \neq 0$, this matrix is called the Jacobian in the response theory literature. Solving the ground state CC equations ensures that

$$H_0^0 = E_0 - E_0 = 0, \quad H_0^I = 0, \quad (45)$$

in which the latter condition is valid only for the excitation classes I , which are included in $\hat{R}_k$. Since in EOMCC the Hamiltonian is diagonalized only in this truncated subspace, we will consider only the corresponding part of the full Hamiltonian in the following discussion. The left and right hand solutions may be partitioned similarly, and the biorthonormality condition may then be written as

$$\begin{pmatrix} 1 & L_I^0 \\ L_0^I & L_I^I \end{pmatrix} \begin{pmatrix} 1 & R_k^0 \\ 0 & R_k^I \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & I_k^I \end{pmatrix}, \quad (46)$$

in which we have used that $L_0^0 = R_0^0 = 1$ and $R_0^I = 0$, and I_k^I is the unit matrix of the dimension of the number of roots. From this equation, it is immediately obvious that

$$L_0^I = 0, \quad R_k^0 + L_I^0 R_k^I = 0, \quad L_I^I R_k^I = I_k^I. \quad (47)$$

The first equation is the condition that the contribution of the reference function is zero to any excited state left hand state. The second can be used to test the biorthonormality of the ground state left and excited state right vectors, while the last equation is an expression of the biorthonormality of excited state left and right vectors decoupled from the reference state.

Using the fact that Eq. (43) has a zero block, the right hand eigenvalue equation is

$$\begin{pmatrix} 0 & H_J^0 \\ 0 & H_J^l \end{pmatrix} \begin{pmatrix} 1 & R_k^0 \\ 0 & R_k^l \end{pmatrix} = \begin{pmatrix} 1 & R_l^0 \\ 0 & R_l^l \end{pmatrix} \begin{pmatrix} 0 & 0 \\ 0 & \omega_k^l \end{pmatrix}, \quad (48)$$

in which $\omega_k^l \equiv I_k^l \omega_l$. The excited state energies and R_l^l can be obtained simply from the decoupled excited state block

$$H_J^l R_k^l = R_l^l \omega_k^l. \quad (49)$$

This is the equation which is explicitly solved in the Davidson solver. A further equation determines R_k^0 ,

$$H_J^0 R_k^l = R_l^0 \omega_k^l, \quad (50)$$

which can be easily evaluated once R_k^l is known.

For the left hand side,

$$\begin{pmatrix} 1 & L_I^0 \\ 0 & L_I^l \end{pmatrix} \begin{pmatrix} 0 & H_J^0 \\ 0 & H_J^l \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & \omega_k^l \end{pmatrix} \begin{pmatrix} 1 & L_J^0 \\ 0 & L_J^k \end{pmatrix}, \quad (51)$$

which for the ground state yields the lambda equations

$$H_J^0 + L_I^0 H_J^l = 0. \quad (52)$$

These linear equations can be solved in an iterative fashion, and if excited states are calculated, the biorthonormality condition with excited states can be checked for consistency. For L_I^l , the problem is somewhat simpler,

$$L_I^l H_J^l = \omega_k^l L_J^k, \quad (53)$$

and can be written in terms of an eigenvalue problem. This can now be solved using an iterative Davidson or linear equation solver, but in the following we will propose a simple way to approximate left hand solutions without solving this equation.

F. Matrix inverse approximation

It is possible to obtain an approximate solution for the excited state left vectors without another iterative procedure and computation of sigma vectors. We begin by the simple observation that if *all* the eigenvectors of H_J^l within the truncated manifold were available, then the left hand sides could simply be obtained as $L_I^l = (R^{-1})_I^l$ from the biorthonormality condition. Since the number of excitations (N_I) denoted by the string I is much larger than the number of computed roots (N) labeled by l , this inversion problem is usually underdetermined. Still, it is possible to find a simple non-iterative solution for such a system of equations, i.e., the minimum norm solution, which has been beneficially used in other areas of quantum chemistry before.⁴⁰ Defining R_N and L_N as $N_I \times N$ matrices containing N roots, each of which has N_I elements, one may drop the tensor indices and obtain

$$L_N^\dagger R_N = I_N \Rightarrow L_N^\dagger \approx (R_N^\dagger R_N)^{-1} R_N^\dagger \equiv S_N. \quad (54)$$

This solution satisfies the biorthonormality condition for the corresponding right vectors by construction. The approximation lies in the fact that biorthonormality is not satisfied for any other roots than the ones for which the right hand solutions are available. To be more explicit about the

approximations involved in Eq. (54), L_N will be expressed *exactly* using the full biorthonormality condition. The analysis described below does not aim to improve the pseudoinverse S_N in practice since that would require the determination of further roots.

One may denote the matrix of all right solutions as R and introduce a partitioning into known and unknown roots, (R_N , R_M), in which $N + M = N_I$. We may do the same for L and write the exact solution as

$$\begin{pmatrix} L_N^\dagger \\ L_M^\dagger \end{pmatrix} \equiv L^\dagger = R^{-1} = (R^\dagger R)^{-1} R^\dagger = \begin{pmatrix} R_N^\dagger R_N & R_N^\dagger R_M \\ R_M^\dagger R_N & R_M^\dagger R_M \end{pmatrix}^{-1} \begin{pmatrix} R_N^\dagger \\ R_M^\dagger \end{pmatrix}. \quad (55)$$

To select the exact solutions $L_N^\dagger$, one may employ a rectangular projector ($I_N, 0$) and use the matrix block inversion rule,

$$L_N = (I_N - S_N P_M R_N)^{-1} S_N (I - P_M), \quad (56)$$

in which

$$P_M = R_M (R_M^\dagger R_M)^{-1} R_M^\dagger \quad (57)$$

is a projector to the complementary space. The expression in Eq. (56) is the exact expression for the N left eigenstates, which contains our approximate solution S_N , from which the complementary components are projected and the result is renormalized with respect to R_N . If we define the offdiagonal overlap of states, it can be seen that

$$\epsilon_{NM} = R_N^\dagger R_M, \quad \epsilon_{NM} = 0 \Rightarrow L_N = S_N, \quad (58)$$

which is what one expects, since, if this overlap is zero, then the first N solutions are decoupled from the remaining ones. It can be shown by expanding Eq. (56) in a series that using the matrix inverse approximation yields an error in which the leading term is linear in ϵ_{NM} . The quality of the obtained result using S_N relies on the fact that for CC left and right hand states, the overlap is nearly unity, and the nondiagonal elements are in general very small. This also means that the quality of such an approximate EOM-CCSD left vector is expected to improve with the number of roots requested in the calculation, recovering the exact result if all roots are involved. One practical aspect of this process is that it requires the calculation of an inverse matrix, which involves the definition of a numerical threshold below which the eigenvalues of the matrix are considered zero. Using such threshold, numerical noise can be effectively reduced.

On a final note, we remark that even the approximate ground state solution can be improved using this procedure. In Sec. II C, it was discussed that a complete basis, spanning the space of which $\hat{S}$ is an arbitrary element, is needed to satisfy Eq. (16). Within the truncated excitation space, the complete set of solutions $\hat{R}_k$ (with $k \neq 0$ and the constant component may be projected out) and also $\hat{L}_k$ (with $k \neq 0$, all of which have a zero constant component) are both such non-orthonormal basis sets. Thus, if in Eq. (16) we substitute $\hat{S} = \hat{R}_k$ (the constant component vanishes in the commutator), it reduces to

$$\mathcal{F} = \langle 0 | \hat{L}_0^\dagger \hat{H} | 0 \rangle - \omega_k \langle 0 | \hat{L}_0^\dagger \hat{R}_k | 0 \rangle, \quad (59)$$

which, if $\mathcal{F} = E_0$ is to hold, leads to the condition also expressed in Eq. (47) that the ground state left and the excited

state right vectors should be biorthonormal. This condition is normally used as a consistency check, since all the terms appearing in a conventional calculation are obtained independently. On the other hand, for an approximate solution, enforcing it should improve the ground state solution. This is clear since both $\hat{T}$ and $\hat{\Lambda}$ can be produced as a linear combination of $\hat{L}_k$; in fact for the latter, the coefficients are simply $-R_k^0$, yielding $\Lambda_I = -R_k^0 L_I^k$ due to biorthonormality. If the excited state left vectors are determined in some manner, then any approximation of the ground state $\hat{\Lambda}$ mentioned in Sec. II C can be improved by defining a new ground state left vector as

$$L_I^0 = \Lambda_I - (R_k^0 + \Lambda_I R_k^I) L_I^k. \quad (60)$$

As for the excited states, if all $\hat{R}_k$ were available, the process described here and in Sec. II C would yield the exact ground state lambda vector as well. Of course, since usually only a few excited state solutions are available, it is important that the approximation for $\hat{\Lambda}$ is already a reasonable one, which we tried to argue in Sec. II C. It remains to investigate to what extent these approximations affect calculated properties.

G. Transition properties in EOMCC

After the solution of right and left EOMCC eigenvectors and the ground state left vector, one can calculate the transition properties³ between the ground state and any k -th excited state is given by using the following formula:

$$|T^k|^2 = \langle 0 | (1 + \hat{\Lambda}^\dagger) \bar{D} \hat{R}_k | 0 \rangle \langle 0 | \hat{L}_k^\dagger \bar{D} | 0 \rangle, \quad (61)$$

in which $|T^k|^2$ is the square modulus of the transition moment T^k and the notation $\bar{D} = e^{-\hat{T}} \hat{D} e^{\hat{T}}$ was introduced for the corresponding property operator $\hat{D}$. The quantity $|T^k|^2$ can be written in terms of right and left transition moments

$$T_R^k = \langle 0 | (1 + \hat{\Lambda}^\dagger) \bar{D} \hat{R}_k | 0 \rangle, \quad (62)$$

$$T_L^k = \langle 0 | \hat{L}_k^\dagger \bar{D} | 0 \rangle. \quad (63)$$

Individually left and right transition moments have little significance because the left ground and excited states are not normalized. However, the biorthonormality relation ensures the combined normalization of the product $|T^k|^2$, since

$$\langle 0 | (1 + \hat{\Lambda}) e^{-\hat{T}} | e^{\hat{T}} | 0 \rangle = \langle 0 | \hat{L}_k e^{-\hat{T}} | e^{\hat{T}} \hat{R}_k | 0 \rangle = 1. \quad (64)$$

Transition moments can then be used to calculate experimentally observable oscillator strength values in the dipole length approximation. If $\hat{D}$ is the dipole operator, then the corresponding oscillator strength is defined (in atomic units) as

$$f_k = \frac{2}{3} \omega_k |T^k|^2. \quad (65)$$

H. Transition properties in CCLR

In the framework of response theory,^{8,10,41} periodically time dependent perturbation terms are added to the Hamiltonian, and their effect is evaluated in an appropriate time dependent formulation. Here, only the most important results will be quoted for CC properties to enable comparison between EOMCC and CCLR results.

For excitation energies, EOMCC and CCLR give identical results, as is the case for the right transition moments. The left

transition moment on the other hand contains the response of the ground state cluster amplitudes. This can be circumvented by solving an additional set of equations for perturbation independent parameters expressed as a linear excitation operator $\hat{\zeta}_k$,

$$\begin{aligned} &\langle 0 | (1 + \hat{\Lambda}^\dagger) [\bar{H}, E_I], \hat{R}_k | 0 \rangle + \langle 0 | \hat{\zeta}_k^\dagger [\bar{H}, E_I] | 0 \rangle \\ &+ \omega_k \langle 0 | \hat{\zeta}_k^\dagger E_I | 0 \rangle = 0, \end{aligned} \quad (66)$$

in which $\hat{\zeta}_0^k = 0$, $k \neq 0$, and the last term appears for dynamic properties. Using these parameters, the CCLR right transition moment is

$$T_R^k = \langle 0 | (1 + \hat{\Lambda}^\dagger) [\bar{D}, \hat{R}_k] | 0 \rangle + \langle 0 | \hat{\zeta}_k^\dagger \bar{D} | 0 \rangle. \quad (67)$$

Comparing this with a slightly rearranged EOM-CC right transition moment,

$$T_R^k = \langle 0 | (1 + \hat{\Lambda}^\dagger) [\bar{D}, \hat{R}_k] | 0 \rangle + \langle 0 | (1 + \hat{\Lambda}^\dagger) \hat{R}_k \bar{D} | 0 \rangle. \quad (68)$$

Following Koch *et al.*,¹⁰ it can be shown (see the [supplementary material](#)) that the CCLR solution reduces to the EOM one at the FCI limit, while our approximate left vectors coincide with the EOM one if all roots are considered in the truncated manifold. It has also been demonstrated by Koch *et al.*¹⁰ that CCLR transition moments are size-intensive unlike the EOM ones, which may lead to spurious results in certain cases. Thus, at the usual singles and doubles truncation level, CCLR may be considered superior in quality, although it is more costly as will be discussed below.

I. The cost of transition moment calculations

The cost of calculating ground to excited state transition properties for n roots in the CCLR formulation¹² is

$$T_{Total}^{LR} = T_{\hat{T}} + T_{\hat{\Lambda}} + nT_{\hat{R}} + nT_{\hat{L}} + nT_{\hat{\zeta}}, \quad (69)$$

where T_{Total}^{LR} is the total time required for calculating the CCLR transition moment and $T_{\hat{T}}, T_{\hat{\Lambda}}, T_{\hat{R}}, T_{\hat{L}}$ and $T_{\hat{\zeta}}$ denote the required amount of time to determine $\hat{T}, \hat{\Lambda}, \hat{R}, \hat{L}$, and $\hat{\zeta}$. The corresponding equations all scale as $O(N^6)$ with the basis set size in the singles and doubles truncation, albeit with a different pre-factor.

The time required for transition properties for the same n roots in EOMCC is

$$T_{Total}^{EOM} = T_{\hat{T}} + T_{\hat{\Lambda}} + nT_{\hat{R}} + nT_{\hat{L}}. \quad (70)$$

Assuming identical pre-factors in the above quantities, the EOMCC transition properties should be between a fifth to a third of the CCLR cost cheaper especially as the number of roots increases. Note that it is usually the evaluation of the $\hat{T}$ amplitudes which has the largest pre-factor, and unless these are evaluated in some approximate manner, it may take a good number of roots before savings in the excited state part become appreciable or dominating. While CCLR transition properties are superior, for a large array of practical purposes, both approaches yield similar results. As for EOM itself, the calculation of transition properties is 50% more costly than a corresponding EOM-CC energy calculation since in this case it is enough to calculate one set of amplitudes ($\hat{T}$ and $\hat{R}$). Due to the significant additional cost, almost no quantum chemistry program calculates transition properties by default, which

also means that spectroscopic properties are relatively hard to obtain within CC based theoretical models.

In this paper, we present three approaches for the approximate calculation of EOM-CCSD transition properties. In the first approach, the EOM-CC excited state left eigenvectors are calculated using the matrix inverse approximation, as described in Sec. II F. We will refer to this method as EOM-CCSD-inv, the cost of which can be estimated as follows:

$$T_{Total}^{EOM-inv} = T_{\hat{T}} + T_{\hat{\Lambda}} + nT_{\hat{R}}. \quad (71)$$

This saves about half the time spent in the excited state part since as compared to an energy evaluation, only the ground state lambda equations need to be solved.

One may propose further simplifications for the ground state part. One of them is to approximate $\hat{\Lambda}$ by $\hat{\tau}$, obtained as a generalization of Kollmar and Neese's approximate scheme³⁷ for CCD as described in Sec. II C. We will label this approach as EOM-CCSD-simp. Finally, $\hat{\Lambda}$ may simply be equated with $\hat{T}$ in the linear approximation, which will be referred to as EOM-CCSD-lin. The cost of evaluating transition properties in these approaches can be estimated to be

$$T_{Total}^{EOM-simp} = T_{\hat{T}} + nT_{\hat{R}}, \quad (72)$$

which represent no significant additional costs over the energy calculation. Using EOM-CCSD-lin approximation, it is easy to generate transition properties in EOMCC, for any arbitrary truncation level of $\hat{T}$ and $\hat{R}$. This has a special significance if $\hat{T}$ or $\hat{R}$ can also be obtained in some low cost approximate manner. We have calculated transition properties in the recently reported back transformed pair natural orbital or bt-PNO-EOM-CCSD approximation of Izsák and co-workers,³¹ which reduces the cost of the calculation of the ground state $\hat{T}$ amplitudes to an extent that the remaining bottleneck is definitely the evaluation of the $\hat{R}$ amplitudes. For this part, the chain of spheres approximation (COSX)^{40,42,43} has been implemented for the most time consuming four external exchange terms.²⁸ While this does not improve the overall scaling of the method, it does reduce the pre-factor, enabling the calculations for medium sized molecules.

The performance of the three approximate variants and the bt-PNO-EOM-CCSD is tested in Sec. III by calculating oscillator strengths. All EOM-CCSD calculations were performed using the quantum chemistry package ORCA.⁴⁴ The frozen core approximation has been used with normal PNO settings⁴⁵ for the bt-PNO-EOM-CCSD calculations.

III. RESULTS AND DISCUSSIONS

A. Dependence of oscillator strength on the number of roots

As described in Sec. II F, the quality of left vectors calculated by the matrix inverse technique depends upon the number of calculated roots. Table I presents the dependence of EOM-CCSD-inv oscillator strengths for the first two valence excited states of ethene using the triple zeta valance polarized (TZVP) basis set. The excitation energy for the states is 8.506 eV (${}^1B_{1u}$) and 8.781 eV (${}^1B_{1g}$), respectively. It can be seen that even with one root, EOM-CCSD-inv oscillator

TABLE I. Dependence of EOM-CCSD-inv oscillator strengths (f) on the number of calculated roots for the first two valence excited states of ethene using the TZVP basis set. Oscillator strengths obtained from T_L^k only are denoted as f^L .

States	Exact	1 Root	4 Root	20 Root	50 Root	100 Root
$f^L({}^1B_{1u})$	0.4482	0.4217	0.4217	0.4227	0.4344	0.4429
$f^L({}^1B_{1g})$	0.0225	0.0226	0.0226	0.0221	0.0226	0.0224
$f({}^1B_{1u})$	0.4182	0.4057	0.4057	0.4062	0.4117	0.4158
$f({}^1B_{1g})$	0.0219	0.0220	0.0220	0.0217	0.0219	0.0219

strengths (0.4057 and 0.0220) are in very good agreement with the exact EOM-CCSD values of 0.4182 eV and 0.0219 eV. Since the left transition moment is the sensitive quantity in our approaches; in Table I, the “left” oscillator strengths are also presented corresponding to replacing T^k with T_L^k in Eq. (65). The error in oscillator strengths for these is slightly higher than the proper one since the latter contains both T_L^k and T_R^k . Although oscillator strengths depend on the number of calculated roots, they converge towards the exact value as the number of roots increases, in accordance with our expectation. However, the rate of convergence is very slow, and consequently large differences are expected only if the number of roots involved varies significantly. The change in the left oscillator strength values obtained from the EOM-CCSD-inv approach by including 1 as opposed to 100 roots in the inversion is below 5% for both roots in Table I. For the total oscillator strength, this change is even less, below 3%. The EOM-CCSD-simp and EOM-CCSD-lin should follow the same trend.

The problem of the dependence of the oscillator strength on the number of calculated roots could be avoided by inverting the right hand vector for each root individually rather than inverting the whole space of available right hand EOM vectors together. This essentially ensures that for each root the resulting vector left vector is normalized to the right vector in question. However, the resulting left vector would not be bi-orthogonal to the other right vectors involved in a calculation. Thus, even if one solves the EOM right eigenproblem one state at a time, the left vectors should be obtained once all the requested right hand states are available. All results reported in the present study are calculated in this fashion.

B. Error analysis

Before turning to a detailed analysis of errors, we start our discussion with the simplest two-electron system, H_2 , since in this case the CCSD wave function is identical to the FCI one. Two roots of the H_2 molecule were calculated using the def2-TZVP basis set (12 basis functions), the excitation energies being 13.535 eV and 25.389. The transition moments for the EOM-CCSD and EOM-inv levels were, respectively, 0.483 and 0.186, while the EOM-CCSD-lin approximation yielded 0.487 and 0.182. Thus, in this small test system, the inversion approach for the excited states leads to virtually no errors with respect to FCI. The results are more sensitive to approximating the ground state, but again they are small in the present case.

Table II contains selected oscillator strength values for molecules in Thiel's test set⁴⁶ obtained from various

TABLE II. Oscillator Strength calculated from different approximations to EOM-CCSD.

Molecule	States	E(CC3)	$f(\text{CC3})$	E(CCLR)	$f(\text{CCLR})$	$f(\text{EOMCC})$	$f(\text{EOM-inv})$	$f(\text{EOM-simp})$	$f(\text{EOM-lin})$	$E(\text{bt-PNO})$	$f(\text{bt-PNO})$
Naphthalene	$1^1\text{B}_{2u}(\pi - \pi^*)$	5.03	0.085	5.21	0.083	0.092	0.082	0.088	0.082	5.196	0.084
	$\text{B}_{3u}(\pi - \pi^*)$	6.33	1.325	6.55	1.461	1.563	1.544	1.560	1.551	6.520	1.556
	$\text{B}_{2u}(\pi - \pi^*)$	6.57	0.239	6.77	0.294	0.325	0.330	0.322	0.333	6.762	0.324
	$3^1\text{B}_{3u}(\pi - \pi^*)$	8.12	0.005	9.03	0.014	0.015	0.013	0.015	0.013	9.017	0.012
	$3^1\text{B}_{2u}(\pi - \pi^*)$	8.44	0.498	8.77	0.538	0.570	0.550	0.560	0.555	8.760	0.572
Furan	$1^1\text{B}_2(\pi - \pi^*)$	6.6	0.155	6.8	0.159	0.167	0.161	0.161	0.161	6.784	0.162
	$2^1\text{A}_1(\pi - \pi^*)$	6.62	0.001	6.89	0.001	0.002	0.001	0.001	0.001	6.873	0.001
	$3^1\text{A}_1(\pi - \pi^*)$	8.53	0.45	8.83	0.500	0.525	0.508	0.513	0.514	8.813	0.519
Pyridazine	$1^1\text{B}_1(n - \pi^*)$	3.93	0.006	4.12	0.007	0.007	0.007	0.007	0.007	4.089	0.007
	$1^1\text{A}_2(n - \pi^*)$	5.22	0.014	5.35	0.014	0.015	0.014	0.014	0.014	5.333	0.014
	$2^1\text{B}_1(n - \pi^*)$	6.42	0.005	6.7	0.005	0.005	0.005	0.005	0.005	6.672	0.005
	$1^1\text{B}_2(\pi - \pi^*)$	6.93	0.012	7.09	0.006	0.006	0.004	0.004	0.004	7.071	0.006
	$2^1\text{B}_2(\pi - \pi^*)$	7.55	0.34	7.79	0.458	0.491	0.476	0.485	0.485	7.770	0.484
	$3^1\text{A}_1(\pi - \pi^*)$	7.82	0.433	8.11	0.493	0.529	0.507	0.512	0.512	8.093	0.516
s-tetrazine	$1^1\text{B}_{3u}(n - \pi^*)$	2.54	0.007	2.72	0.009	0.009	0.009	0.008	0.008	2.681	0.008
	$1^1\text{B}_{2u}(\pi - \pi^*)$	5.12	0.044	5.27	0.047	0.050	0.047	0.048	0.048	5.247	0.048
	$2^1\text{B}_{3u}(n - \pi^*)$	6.68	0.011	7	0.012	0.013	0.012	0.012	0.012	6.969	0.012
	$1^1\text{B}_{1u}(\pi - \pi^*)$	7.45	0.002	7.66	0.003	0.003	0.002	0.003	0.003	7.642	0.003
	$2^1\text{B}_{1u}(\pi - \pi^*)$	7.79	0.349	8.06	0.381	0.413	0.394	0.404	0.407	8.041	0.407
	$2^1\text{B}_{2u}(\pi - \pi^*)$	8.51	0.307	8.88	0.333	0.362	0.341	0.345	0.362	8.856	0.347
Formaldehyde	$1^1\text{B}_1(\sigma - \pi^*)$	9.19	0.003	9.26	0.003	0.003	0.003	0.003	0.003	9.254	0.003
	$3^1\text{A}_1(\pi - \pi^*)$	10.45	0.348	10.54	0.373	0.382	0.382	0.370	0.370	10.528	0.421
Formamide	$1^1\text{A}''(n - \pi^*)$	5.66	0.001	5.66	0.001	0.001	0.001	0.001	0.001	5.641	0.001
	$2^1\text{A}'(\pi - \pi^*)$	7.24	0.03	7.51	0.067	0.070	0.069	0.069	0.069	7.502	0.072
	$3^1\text{A}'(n - R)$	8.27	0.386	8.52	0.373	0.387	0.392	0.361	0.361	8.488	0.352
	$4^1\text{A}'(n - R)$	8.47	0.125	8.73	0.132	0.134	0.136	0.126	0.126	8.716	0.123
	$7^1\text{A}'(\pi - \pi^*)$	10.94	0.11	11.33	0.102	0.105	0.103	0.101	0.100	11.321	0.102
	$8^1\text{A}'(n - R)$	11.77	0.021	11.98	0.037	0.038	0.037	0.035	0.035	11.961	0.035
Cytosine	$2^1\text{A}'(\pi - \pi^*)$	4.72	0.046	4.98	0.058	0.062	0.063	0.060	0.060	4.936	0.059
	$1^1\text{A}''(n - \pi^*)$	5.16	0.001	5.45	0.002	0.002	0.002	0.002	0.002	5.409	0.002
	$2^1\text{A}''(n - \pi^*)$	5.52	0.001	6	0.000	0.000	0.000	0.000	0.000	5.961	0.000
	$3^1\text{A}'(\pi - \pi^*)$	5.61	0.13	5.95	0.177	0.186	0.191	0.181	0.181	5.908	0.179
	$4^1\text{A}'(\pi - \pi^*)$	6.61	0.52	6.81	0.607	0.641	0.622	0.594	0.594	6.766	0.616
	$6^1\text{A}''(n - \pi^*)$	6.83		7.16	0.001	0.001	0.001	0.001	0.001	7.126	0.001
Thymine	$2^1\text{A}'(\pi - \pi^*)$	5.34	0.172	5.6	0.222	0.235	0.233	0.225	0.225	5.569	0.296
	$3^1\text{A}'(\pi - \pi^*)$	6.34	0.072	6.78	0.071	0.075	0.074	0.069	0.069	6.748	0.072
	$4^1\text{A}'(\pi - \pi^*)$	6.71	0.197	7.05	0.285	0.297	0.293	0.275	0.275	7.023	0.280
Uracil	$2^1\text{A}'(\pi - \pi^*)$	5.44	0.174	5.7	0.224	0.237	0.236	0.228	0.228	5.669	0.229
	$3^1\text{A}'(\pi - \pi^*)$	6.29	0.046	6.76	0.061	0.064	0.062	0.058	0.058	6.726	0.059
	$4^1\text{A}'(\pi - \pi^*)$	6.84	0.152	7.19	0.209	0.220	0.218	0.205	0.205	7.170	0.210
	$5^1\text{A}''(n - \pi^*)$	6.87		7.69	0.001	0.001	0.001	0.001	0.001	7.653	0.001
Adenine	$2^1\text{A}'(\pi - \pi^*)$	5.18		5.37	0.002	0.003	0.004	0.003	0.003	5.331	0.005
	$1^1\text{A}''(n - \pi^*)$	5.34	0.001	5.58	0.001	0.001	0.001	0.001	0.001	5.544	0.001
	$3^1\text{A}'(\pi - \pi^*)$	5.39		5.61	0.297	0.315	0.314	0.302	0.303	5.568	0.301
	$2^1\text{A}''(n - \pi^*)$	5.96	0.002	6.19	0.002	0.002	0.002	0.002	0.002	6.159	0.002
	$4^1\text{A}'(\pi - \pi^*)$	6.53		6.83	0.513	0.552	0.546	0.527	0.528	6.807	0.538

EOM-CCSD approaches, along with the LR-CCSD and LR-CC3 results for comparison using the TZV basis set. The latter values were taken from the work of Szalay and Kánár;⁴⁷ only states with oscillator strengths larger than 0.005 are presented. The oscillator strengths for different excited states, sometimes even in the same molecule, may differ by orders

of magnitude; therefore it only makes sense to compare deviations expressed as a percentage of the oscillator strength of a given reference. Similar data are available for all the molecules in Thiel's test set as the [supplementary material](#).

Table III presents the mean absolute deviation (MAD) relative to the CC3 reference value for oscillator strengths using

TABLE III. Mean absolute deviation (MAD) values in % for oscillator strengths using various approximations to EOM-CCSD with respect to difference reference values.

Method	Ref. CC3	Ref. CCSD-LR	Ref. EOM-CCSD
CCSD-LR	16.82		
EOM-CCSD	21.84	5.30	
EOM-CCSD-inv	19.63	4.14	4.16
EOM-CCSD-simp	17.86	4.10	5.44
EOM-CCSD-lin	18.06	4.15	5.56
bt-PNO-EOM-CCSD	19.14	5.60	6.28

different approximations to EOM-CCSD. Only states dominated by single excitation (80% singles character) have been considered for the numerical analysis to make sure that only cases for which EOM-CCSD or LR-CCSD provides a reasonable description are studied. It can be seen that all the methods in the CCSD truncation perform only moderately well. All of them show MAD values of about 20%, the LR-CCSD value being the smallest at 18.82%, while the error in CCSD-LR and in all the variants of EOM-CCSD follows very similar trends. For all methods, the largest relative errors are mainly due to either inaccuracy in predicting small oscillator strengths or due to a large mixing of states in the case of the

$2^1A'$ and $8^1A'$ states of formamide. However, large errors are also observed for states, for example, the 2^1B_2 state of pyridazine which has a relatively large oscillator strength and is dominated by a single excitation to a degree more than 90% singles and which still exhibits a quite large absolute deviation. The deviation in the excitation energy going from CCSD to CC3 for that particular state is 0.16 eV, which is smaller than the mean absolute errors observed in EOM-CCSD for Thiel's test set. Therefore, the transition properties seem to be more sensitive to the effects of triples correction than the energy itself.

One may also compare the EOM-CCSD errors for oscillator strengths in Table II with CCSD-LR, which has a more complete treatment for the left vector. The outlier $1^1A''$ state of adenine has been removed from the analysis, since in this case the large relative error corresponds to a small absolute error in calculating a small oscillator strength. The standard EOM-CCSD method has an MAD of 5.30%, while EOM-CCSD-inv, EOM-CCSD-simp, and EOM-CCSD-lin perform very similarly, all three of them have an MAD of about 4.1. The *bt*-PNO-EOM-CCSD method also gives very reasonable performance with an MAD value of 5.30% for oscillator strengths.

It should be noted that since all the new methods proposed for the transition properties in this paper are approximations

FIG. 1. The comparison of oscillator strengths in different approximations to EOM-CCSD. (a) Approximate EOM-CCSD Oscillator Strength vs Exact EOM-CCSD Oscillator Strength. (b) Relative Error of the Calculated Oscillator Strength as the Function of the EOM-CCSD Oscillator Strength.

to the standard EOM-CCSD method, it is appropriate to compare them to the latter because such a comparison provides information about the errors due exclusively to the approximations involved. In Fig. 1(a), the approximate oscillator strength is plotted against those obtained from the standard method. In general, the approximations are in very good agreement with the reference, since the plots are almost straight lines with a slope about one, with some small bumps in the lower oscillator strength region. The bt-PNO-EOM-CCSD curve exhibits the largest number of outliers. This is also manifest in the MAD value of 6.28% for this method, the highest among all the approximations. For excitation energies, the corresponding MAD in bt-PNO-EOM-CCSD is 0.027 eV. The

EOM-CCSD-inv approximation shows the smallest MAD of 4.16%, since in this case only the excited state left vectors are approximated. Both EOM-CCSD-simp and EOM-CCSD-lin, which also approximate both ground and excited state left vectors, have slightly larger MADs, 5.44% and 5.66%, respectively, which is still in good agreement with the standard method. Figure 1(b) illustrates the fact that large relative errors mostly correspond to excited states with small transition moments, which should have little effect on calculated spectra. However, it is also evident from Fig. 1(b) that in some cases the errors in bt-PNO-EOM-CCSD are more significant even for states with larger transition moments, e.g., the 2 $^1A'$ state of thymine. It is readily seen that the

FIG. 2. UV-Vis spectra obtained from CC-LR and various EOM-CCSD schemes. The spectra are convoluted using Lorentzian broadening. (a) Formamide, (b) naphthalene, (c) imidazole, (d) tetrazine.

difference between approximating the ground state left vector by $\hat{\tau}$ or by $\hat{T}$ following Kollmar and Neese³⁷ makes very little difference in terms of accuracy. Therefore, the EOM-CCSD-lin approximation can be used as a general approach to calculate approximate transition moments in EOM-CCSD in Sec. III C.

C. Comparison with CC3 spectrum

Simulating actual spectra is the real test of accuracy for any method used to calculate oscillator strengths. Figure 2 presents UV-Vis spectra for a variety of species in using CC-LR and various EOM-CCSD approaches. The data used for plot are tabulated in Table II. As the EOM-CCSD-inv, EOM-CCSD-simp, and EOM-CCSD-lin schemes were shown to behave similarly in Sec. III B, we only plotted the spectra using the EOM-CCSD-lin method.

Different approximations to EOM-CCSD and LR-CCSD give almost identical performance for formamide. The excitation energies in EOM-CCSD or LR-CCSD are overestimated as compared to LR-CC3. However, the discrepancy is systematic, and the error in the CCSD approximations can be considered as a constant blue shift from the CC3 result. The transition moments are more sensitive to electron correlation. The peaks corresponding to the $3^1A'$, $4^1A'$, and $7^1A'$ states (see Table II) in the CC3 calculated spectrum are well reproduced using both EOM-CCSD and LR-CCSD. However, the peaks assigned to the $2^1A'$ and $8^1A'$ excited states in either EOM-CCSD or LR-CCSD are almost double in height than their corresponding CC3 counterpart. The oscillator strength values of the last two peaks are small; thus the spectrum using LR-CCSD or any of the EOM-CCSD variants is in good agreement with the CC3 one in general. The EOM-CCSD-lin method yields

FIG. 3. The UV-Vis spectra using different approximations to EOM-CCSD. The spectra are convoluted using Lorentzian broadening. (a) Pyridine, (b) tetrazine, (c) formaldehyde, (d) furan.

an almost identical spectrum as the standard EOM-CCSD method. The bt-PNO-EOM-CCSD method also performs very well as compared to the LR-CCSD or standard EOM-CCSD. The oscillator strengths for the peaks corresponding to the 3 $^1A'$ and 4 $^1A'$ states are slightly underestimated in bt-PNO-EOM-CCSD, and overall the spectrum is slightly red shifted from the corresponding EOM-CCSD or LR-CCSD spectrum.

The EOM-CCSD/CCSD-LR spectrum for naphthalene is in good agreement with the CC3 method except for the peaks corresponding to the excited states, 2 $^1B_{3u}$ and 2 $^1B_{2u}$, where the oscillator strengths are overestimated as compared to CC3. CCSD-LR performs slightly better for these two peaks than the EOM-CCSD method, although the two methods are in very good agreement with one another in general. The EOM-CCSD and EOM-CCSD-lin approaches perform equally well and give almost indistinguishable spectra for naphthalene. The bt-PNO-EOM-CCSD method is in very good agreement with standard EOM-CCSD except the peaks corresponding to 2 $^1B_{3u}$ and 2 $^1B_{2u}$, where it is slightly red shifted compared to EOM-CCSD.

For imidazole, CC-LR and EOM-CCSD spectra are again in very good agreement, both blue shifted from the CC3 spectrum with a constant amount. The EOM-CCSD-lin method performs almost as well as standard EOM-CCSD, while the bt-PNO-EOM-CCSD result is red shifted compared to EOM-CCSD, but otherwise they are in very good agreement.

Finally, the EOM-CCSD spectrum for tetrazine agrees very well with CC3 apart from an almost constant blue shift and the two most intense peaks, the intensity of which is slightly overestimated in EOM-CCSD. CCSD-LR is slightly in better agreement with CC3 for these two peaks, while in general it predicts a similar spectrum to that obtained from EOM-CCSD. The EOM-CCSD-lin, bt-PNO-EOM-CCSD, and standard EOM-CCSD spectra are also almost identical.

D. Comparison with EOM-CCSD spectrum

So far the CC3 method was used as a reference for our calculations, while only a few optical spectra were reported⁴⁷ for the molecules in Thiel's test set⁴⁶ using this method. As the difference between CC3 and EOM-CCSD has been discussed in Sec. III C, we will now change the reference to standard EOM-CCSD, all the more so since the approximations discussed here aim at that accuracy. This choice will allow us to carry out more costly calculations. Figure 3 presents UV-Vis spectra using the various approximations to EOM-CCSD for pyridine, tetrazine, formaldehyde, and furan. For each molecule, 40 roots have been calculated using the TZVP basis set. To get a proper description of the Rydberg states, additional 5s, 5p, and 4d functions were added to the center of symmetry. Excitation energies and oscillator strengths used for plotting these spectra are provided in the [supplementary material](#). These spectra demonstrate that EOM-CCSD-inv, EOM-CCSD-simp, and EOM-CCSD-lin give almost indistinguishable results from standard EOM-CCSD for all the four molecules. The bt-PNO spectrum is generally a constant red shift away from the EOM-CCSD one, with occasional small deviations in the peak intensity.

IV. CONCLUSIONS

We have presented efficient approximations for the calculation of transition properties using a matrix inversion technique. The accuracy of the transition properties is demonstrated by calculating the oscillator strength of the molecules in Thiel's test set⁴⁶ at the EOM-CCSD level. The calculated left vectors and the oscillator strengths depend on the number of calculated roots; however, the variation in the calculated oscillator strengths is, in general, small and expected to be insignificant for most practical purposes. The three approximate variants investigated in the paper are in much closer agreement with the standard EOM-CCSD values than the difference between EOM-CCSD and the LR-CCSD or LR-CC3 reference for Thiel's test set. The bt-PNO-EOM-CCSD variant shows a slightly larger error but it is still in good agreement with canonical EOM-CCSD oscillator strengths, which demonstrates its suitability for predicting UV-Vis spectra. EOM-CCSD-inv, EOM-CCSD-lin, and EOM-CCSD-simp perform very similar to each other and provide almost indistinguishable UV-VIS spectra. EOM-CCSD-lin, which calculates the EOM-CCSD left vector by the matrix inversion technique and approximates the ground state left vector using the ground state $\hat{T}$ amplitudes, is the simplest and most efficient among them and can be used in principle to obtain transition properties for arbitrary truncation levels in the excitation operators. It requires almost no additional computational cost over that of an EOM-CCSD energy calculation and can be used as an inexpensive way to calculate transition properties.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for details on some of the derivations and further data on the performance of the various methods for Thiel's test set are provided in the [supplementary material](#).

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