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Kaushik D. Nanda,[1] Anna I. Krylov,[1,2] and Jürgen Gauss[2]
[1]*Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482, USA*
[2]*Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany*

In this letter, we investigate the pole structure of dynamical polarizabilities computed within the equation-of-motion coupled-cluster (EOM-CC) theory. We show, both theoretically and numerically, that approximate EOM-CC schemes such as, for example, the EOM-CC singles and doubles model exhibit an incorrect pole structure in which the poles that reflect the excitations from the target state (i.e., the EOM-CC state) are supplemented by artificial poles due to excitations from the CC reference state. These artificial poles can be avoided by skipping the amplitude response and reverting to a sum-over-states formulation. While numerical results are generally in favor of such a solution, its major drawback is that this scheme violates size extensivity. *Published by AIP Publishing.*
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Equation-of-motion coupled-cluster (EOM-CC) theory[1–6] was originally designed for the computation of electronic excitation energies, ionization potentials, and electron affinities. However, nowadays, EOM-CC theory is more and more often applied also in cases where the focus is not on energy differences but, rather, on a specific manifold of electronic states. Examples include the treatment of open-shell states by the ionization-potential (IP) or electron-attachment (EA) variants[7–10] or the description of polyradicals by the spin-flip[11,12] (SF) or double-ionization potential[13] (DIP) variants. In this way, EOM-CC offers a practical (albeit only partial) solution to the notorious multireference problem in coupled-cluster (CC) theory.[3,6,14,15]

Whenever EOM-CC theory is used to describe a specific target state, the issue of computing properties is raised. Analytic schemes for the computation of first- and second-order properties have been reported for various EOM-CC variants.[7,16–24] In this letter, we extend those schemes for the computation of frequency-dependent properties and analyze the pole structure of the EOM-CC response functions. Closely related to the present work is the one reported in Ref. 25, in which the authors reported on the implementation of static and dynamical excited-state polarizabilities within a CC linear-response framework. The theory was derived there by focusing on the difference between the ground- and excited-state polarizabilities, and no rigorous analysis of the pole structure was carried out.[26]

The pole structure of a response function, e.g., the dynamical polarizability, is determined by the spectral properties of the Hamiltonian. For the exact solution of the Schrödinger equation, the poles of the response functions occur at the corresponding excitation energies. Likewise, the poles of the response functions for approximate quantum-chemical treatments reflect the spectral structure of the underlying model, thus offering a route toward the computation of excitation energies, as exploited, for example, in coupled-cluster (CC)

theory.[27–29] However, in the case of approximate quantum-chemical approaches, the pole structure of the response function might be contaminated by spurious poles. It is, for example, well known that the relaxation of the Hartree-Fock (HF) reference spoils the pole structure of the CC response functions, and this is the reason why the orbital response is usually omitted within CC response theory.[30]

Focusing on the treatment of electrical properties using response theory,[31] the dipole moment ($\mu_i$) and dynamical polarizability tensor ($\alpha_{ij}$) are given as the first and second derivatives of the time-averaged quasi-energy[30] with respect to the components of the oscillating electric field $\epsilon_i(\omega)$,

$$\mu_i^k = -\left(\frac{d\{Q^k\}_T}{d\epsilon_i(0)}\right)_{\epsilon_i=0}, \tag{1}$$

$$\alpha_{ij}^k(\omega) = -\frac{1}{2}C^{\pm\omega}\left(\frac{d^2\{Q^k\}_T}{d\epsilon_i(\omega)d\epsilon_j(-\omega)}\right)_{\epsilon_i,\epsilon_j=0}, \tag{2}$$

with the quasi-energy defined as

$$Q^k(t) = \langle\Psi_k(t)|H(t) - i\frac{\partial}{\partial t}|\Psi_k(t)\rangle \tag{3}$$

for the phase-isolated wave function $\Psi_k(t)$ of the considered state $k$ and time averaging carried out via

$$\{Q^k\}_T = \lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T}Q^k(t)dt. \tag{4}$$

The operator $C^{\pm\omega}$ ensures symmetry with respect to complex conjugation and involves a simultaneous sign reversal of all frequencies. For a detailed definition of this operator, we refer, for example, to Eq. (3.35) in Ref. 30.

For variational approaches, the above derivative expressions can be also expressed in terms of the unperturbed (i.e., time-independent) wave functions. For the dipole moment, this yields the expectation value

$$\mu_i^k = \langle\Psi_k|\hat{\mu}_i|\Psi_k\rangle, \tag{5}$$

with $\hat{\mu}_i$ as the $i$th component of the dipole operator. For the polarizability tensor, one obtains a sum-over-states expression

$$
\begin{aligned}
&\alpha_{ij}^k(\omega) \\
&= \sum_{n \neq k} \left( \frac{\langle \Psi_k | \hat{\mu}_i | \Psi_n \rangle \langle \Psi_n | \hat{\mu}_j | \Psi_k \rangle}{E_n - E_k + \omega} + \frac{\langle \Psi_k | \hat{\mu}_i | \Psi_n \rangle \langle \Psi_n | \hat{\mu}_j | \Psi_k \rangle}{E_n - E_k - \omega} \right),
\end{aligned}
\tag{6}
$$

with $\Psi_n$ and $E_n$ denoting the wave functions and energies for all states that are different from the considered state with wave function $\Psi_k$ and energy $E_k$. Equation (6) shows that the dynamical polarizability tensor has poles whenever the frequency $\omega$ of the oscillating electric field matches an excitation energy given by $E_n - E_k$.

However, for non-variational approaches such as CC and EOM-CC theory, the given expressions are no longer valid and the properties of interest need to be computed as the derivatives of the time-averaged quasi-energy Lagrangian.[30] Within CC theory, the quasi-energy Lagrangian is given in terms of the cluster operator $T$, the reference determinant $\Phi_0$, and the $\Lambda$ operator from CC gradient theory[27,32] according to[30]

$$
\begin{aligned}
L_{CC}(t) &= \langle \Phi_0 | e^{-T} \left( H - i \frac{\partial}{\partial t} \right) e^T | \Phi_0 \rangle \\
&\quad + \langle \Phi_0 | \Lambda e^{-T} \left( H - i \frac{\partial}{\partial t} \right) e^T | \Phi_0 \rangle.
\end{aligned}
\tag{7}
$$

This choice of the Lagrangian implies that the unperturbed equations for the cluster operator are

$$
\langle \Phi_\mu | e^{-T} \hat{H} e^T | \Phi_0 \rangle = 0
\tag{8}
$$

with projection on all determinants $\Phi_\mu$ within the given excitation manifold.

In the case of EOM-CC theory, the quasi-energy Lagrangian takes the form

$$
\begin{aligned}
L_{EOM-CC}(t) &= E + \langle \Phi_0 | \mathcal{L} e^{-T} \left( H - E - i \frac{\partial}{\partial t} \right) e^T \mathcal{R} | \Phi_0 \rangle \\
&\quad + \langle \Phi_0 | \mathcal{Z} e^{-T} \left( H - i \frac{\partial}{\partial t} \right) e^T | \Phi_0 \rangle,
\end{aligned}
\tag{9}
$$

where we have dropped the index $k$ at $\mathcal{R}$ and $\mathcal{L}$ for brevity. In the unperturbed limit, $\mathcal{R}$ and $\mathcal{L}$ are the right and left solutions

of the EOM-CC eigenvalue problem

$$
\langle \Phi_\mu | \bar{H} \mathcal{R} | \Phi_0 \rangle = E \langle \Phi_\mu | \mathcal{R} | \Phi_0 \rangle,
\tag{10}
$$

$$
\langle \Phi_0 | \mathcal{L} \bar{H} | \Phi_\mu \rangle = E \langle \Phi_0 | \mathcal{L} | \Phi_\mu \rangle,
\tag{11}
$$

with $E$ as the energy of the state of interest. Here, we have introduced the similarity-transformed Hamiltonian

$$
\bar{H} = e^{-T} \hat{H} e^T.
\tag{12}
$$

By gathering the Lagrange multipliers for the constraints imposed by the CC amplitude equations, the unperturbed operator, $\mathcal{Z}$, is determined via[7,16,17,21]

$$
\langle \Phi_0 | \mathcal{Z} [\bar{H}, \tau_\mu] | \Phi_0 \rangle = -\langle \Phi_0 | \mathcal{L} [\bar{H}, \tau_\mu] \mathcal{R} | \Phi_0 \rangle,
\tag{13}
$$

where the bare excitation operator, $\tau_\mu$, connects the reference determinant to the excited determinant $\Phi_\mu$. Note that our choice for the EOM-CC Lagrangian assumes that $\mathcal{R}$ and $\mathcal{L}$ satisfy the normalization condition[2]

$$
\langle \Phi_0 | \mathcal{L} \mathcal{R} | \Phi_0 \rangle = 1.
\tag{14}
$$

With the above Lagrangian, the expressions for the EOM-CC dipole moment and frequency-dependent polarizability tensor, now defined as the corresponding derivatives of the time-averaged quasi-energy Lagrangian $\{L_{EOM-CC}\}_T$, read as

$$
\mu_i = \langle \Phi_0 | \mathcal{L} e^{-T} \hat{\mu}_i e^T \mathcal{R} | \Phi_0 \rangle + \langle \Phi_0 | \mathcal{Z} e^{-T} \hat{\mu}_i e^T | \Phi_0 \rangle
\tag{15}
$$

and

$$
\begin{aligned}
\alpha_{ij}(\omega) = \frac{C^{\pm \omega}}{2} \Big( &\langle \Phi_0 | \mathcal{L}^j(\omega) \bar{\mu}_i \mathcal{R} | \Phi_0 \rangle + \langle \Phi_0 | \mathcal{L} [\bar{\mu}_i, T^j(\omega)] \mathcal{R} | \Phi_0 \rangle \\
&+ \langle \Phi_0 | \mathcal{L} \bar{\mu}_i \mathcal{R}^j(\omega) | \Phi_0 \rangle + \langle \Phi_0 | \mathcal{Z}^j(\omega) \bar{\mu}_i | \Phi_0 \rangle \\
&+ \langle \Phi_0 | \mathcal{Z} [\bar{\mu}_i, T^j(\omega)] | \Phi_0 \rangle \Big),
\end{aligned}
\tag{16}
$$

where $\bar{\mu}$ is the similarity-transformed dipole operator

$$
\bar{\mu}_i = e^{-T} \hat{\mu}_i e^T.
\tag{17}
$$

Whereas the dipole moment can be obtained by using only unperturbed quantities, the determination of the polarizability tensor requires the knowledge of the perturbed quantities, which are denoted in Eq. (16) by superscripts $i$ and $j$ and an additional specification of the frequency as the argument. Thus, $T^i(\omega)$ stands for the first-order response of the cluster operator to an electric-field perturbation $\epsilon_i$ with frequency $\omega$ and so on. The first-order responses of $T$, $\mathcal{R}$, $\mathcal{L}$, and $\mathcal{Z}$ are determined via the following equations:

$$
\langle \Phi_\mu | [\bar{H}, T^i(\omega)] - \omega T^i(\omega) | \Phi_0 \rangle = \langle \Phi_\mu | \bar{\mu}_i | \Phi_0 \rangle,
\tag{18}
$$

$$
\langle \Phi_\mu | (\bar{H} - E - \omega) \mathcal{R}^i(\omega) | \Phi_0 \rangle = \langle \Phi_\mu | (\bar{\mu}_i - \mu_i) \mathcal{R} | \Phi_0 \rangle - \langle \Phi_\mu | [\bar{H}, T^i(\omega)] \mathcal{R} | \Phi_0 \rangle + \omega \langle \Phi_\mu | T^i(\omega) \mathcal{R} | \Phi_0 \rangle,
\tag{19}
$$

$$
\langle \Phi_0 | \mathcal{L}^i(\omega) (\bar{H} - E + \omega) | \Phi_\mu \rangle = \langle \Phi_0 | \mathcal{L} (\bar{\mu}_i - \mu_i) | \Phi_\mu \rangle - \langle \Phi_0 | \mathcal{L} [\bar{H}, T^i(\omega)] | \Phi_\mu \rangle + \omega \langle \Phi_0 | \mathcal{L} T^i(\omega) | \Phi_\mu \rangle,
\tag{20}
$$

$$
\begin{aligned}
\langle \Phi_0 | \mathcal{Z}^i(\omega) ([\bar{H}, \tau_\mu] + \omega \tau_\mu) | \Phi_0 \rangle = &\langle \Phi_0 | \mathcal{Z} [\bar{\mu}_i, \tau_\mu] | \Phi_0 \rangle - \langle \Phi_0 | \mathcal{Z} [[\bar{H}, T^i(\omega)], \tau_\mu] | \Phi_0 \rangle - \langle \Phi_0 | \mathcal{L}^i(\omega) [\bar{H}, \tau_\mu] \mathcal{R} | \Phi_0 \rangle \\
&- \langle \Phi_0 | \mathcal{L} [\bar{H}, \tau_\mu] \mathcal{R}^i(\omega) | \Phi_0 \rangle + \langle \Phi_0 | \mathcal{L} [\bar{\mu}_i, \tau_\mu] \mathcal{R} | \Phi_0 \rangle - \langle \Phi_0 | \mathcal{L} [[\bar{H}, T^i(\omega)], \tau_\mu] \mathcal{R} | \Phi_0 \rangle \\
&- \omega \langle \Phi_0 | \mathcal{L}^i(\omega) \tau_\mu \mathcal{R} | \Phi_0 \rangle - \omega \langle \Phi_0 | \mathcal{L} \tau_\mu \mathcal{R}^i(\omega) | \Phi_0 \rangle,
\end{aligned}
\tag{21}
$$

which can be derived from the original time-dependent equations [Eqs. (8), (10), (11), and (13), respectively] via an order-by-order expansion and a Fourier-component analysis (see Ref. 30 for details). Using the amplitude-response equation

[Eq. (18)], the response equations for $\mathcal{R}$ and $\mathcal{L}$ [Eqs. (19) and (20)] can be recast in a sometimes more convenient form with commutators,

$$\langle\Phi_\mu|(\bar{H}-E-\omega)\mathcal{R}^i(\omega)|\Phi_0\rangle = \langle\Phi_\mu|[\bar{\mu}_i,\mathcal{R}]|\Phi_0\rangle - \left(\mu_i-\mu_i^0\right)\langle\Phi_\mu|\mathcal{R}|\Phi_0\rangle - \langle\Phi_\mu|[[\bar{H},T^i(\omega)],\mathcal{R}]|\Phi_0\rangle, \tag{22}$$

$$\langle\Phi_0|\mathcal{L}^i(\omega)(\bar{H}-E+\omega)|\Phi_\mu\rangle = \langle\Phi_0|\mathcal{L}[\bar{\mu}_i,\tau_\mu]|\Phi_0\rangle - \left(\mu_i-\mu_i^0\right)\langle\Phi_0|\mathcal{L}|\Phi_\mu\rangle - \langle\Phi_0|\mathcal{L}[[\bar{H},T^i(\omega)],\tau_\mu]|\Phi_0\rangle, \tag{23}$$

with $\mu_i^0$ denoting the dipole moment of the CC reference state.

By setting the frequency $\omega$ to zero, the given equations reduce to those in the static case ($\omega = 0$) in which the first-order responses of $T$, $\mathcal{R}$, $\mathcal{L}$, and $\mathcal{Z}$ are the corresponding first derivatives.[22,24] It should be noted here that in order to fulfill the first-order perturbed biorthogonality conditions, it is necessary to project out the unperturbed contributions in the $\mathcal{R}$- and $\mathcal{L}$-response equations, as described in Ref. 22. We note that the given expression for the polarizability tensor is referred to as asymmetric (see Ref. 19) and that the corresponding symmetric and mixed symmetric-asymmetric expressions can be derived as outlined in Ref. 19 and in Ref. 22 (for the static case), respectively. A detailed derivation of the working equations is given in the supplementary material.

The given equations enable an analysis of the pole structure of the EOM-CC linear-response function. Whereas the contributions due to $\mathcal{R}^i(\omega)$ and $\mathcal{L}^i(\omega)$ lead to a pole whenever $\omega$ hits an excitation-energy difference, i.e., an excitation energy for the state of interest, the contributions due to $T^i(\omega)$ and $\mathcal{Z}^i(\omega)$ yield poles whenever $\omega$ matches any of the ground-state excitation energies. Our theoretical analysis thus indicates that the EOM-CC linear-response function contains spurious poles arising due to the consideration of the amplitude response. Obviously, these spurious poles can be avoided by skipping the amplitude-response terms and only considering terms with the $\mathcal{R}$ and $\mathcal{L}$ response. The expression for the polarizability tensor then reduces to

$$\alpha_{ij}(\omega) = \frac{\mathcal{C}^{\pm\omega}}{2}\left(\langle\Phi_0|\mathcal{L}^j(\omega)\bar{\mu}_i\mathcal{R}|\Phi_0\rangle + \langle\Phi_0|\mathcal{L}\bar{\mu}_i\mathcal{R}^j(\omega)|\Phi_0\rangle\right). \tag{24}$$

However, in the case of the response equations for $\mathcal{R}$ and $\mathcal{L}$, the skipping of the amplitude response is not unique and depends on whether one starts from Eqs. (22) and (23) or Eqs. (19) and (20). The first choice leads to size-extensive results for the non-amplitude-relaxed polarizabilties, but does not recover the proper full configuration-interaction (FCI) limit in the untruncated case. By contrast, the second choice ensures the correct FCI limit. Furthermore, Eq. (24) can be recast with this choice in a sum-over-states form

$$\alpha_{ij}^k(\omega) = \frac{\mathcal{C}^{\pm\omega}}{2}\sum_{n\neq k}\left(\frac{\langle\Phi_0|\mathcal{L}_k\bar{\mu}_j\mathcal{R}_n|\Phi_0\rangle\langle\Phi_0|\mathcal{L}_n\bar{\mu}_i\mathcal{R}_k|\Phi_0\rangle}{E_n-E_k+\omega}\right.$$
$$\left. + \frac{\langle\Phi_0|\mathcal{L}_k\bar{\mu}_i\mathcal{R}_n|\Phi_0\rangle\langle\Phi_0|\mathcal{L}_n\bar{\mu}_j\mathcal{R}_k|\Phi_0\rangle}{E_n-E_k-\omega}\right), \tag{25}$$

where $\mathcal{R}_n$, $\mathcal{L}_n$, and $E_n$ denote the right and left EOM-CC solutions and the corresponding EOM-CC energy of the states $n$ and $\mathcal{R}_k$, $\mathcal{L}_k$, and $E_k$ denote those for the state of interest. The only drawback of this choice for skipping the amplitude

response is that it violates size-extensivity. We note that different choices of formulating second-order properties were also discussed in Ref. 20 in the context of CC ground-state polarizabilities.

For the computation of frequency-dependent polarizabilities at the EOM-CC singles and doubles (EOM-CCSD) level, we extended the already existing implementation for the calculation of static polarizabilities[22] within the Q-Chem program package.[33,34] The required modifications entail adding the frequency-dependent terms to the response equations.

To investigate numerically the pole structure of EOM-CCSD polarizabilities, we computed the frequency-dependent polarizabilities of water ($H_2O$) in the lowest singlet $A_1$ excited state ($2A_1$). We carried out the calculations using the aug-cc-pVDZ basis[35,36] within the frozen-core approximation at the CCSD/aug-cc-pVDZ optimized geometry ($r_{OH} = 0.965$ Å and $\theta_{HOH} = 104.16°$; the molecule is in the $YZ$ plane with the dipole moment along the $Z$ axis). At the considered computational level, the $2A_1$ state lies 9.80 eV above the ground state; the excitation energies for the lowest $B_1$ excited states are 7.41 eV, 11.07 eV, 11.87 eV, 13.60 eV, 13.90 eV, 15.73 eV, and 18.91 eV. Panel (a) of Fig. 1 shows the dispersion of the $xx$ component of the ground-state polarizability tensor computed at the CCSD/aug-cc-pVDZ level. As expected, poles are observed at 7.41 eV and 11.07 eV, corresponding to the first two excited states of $B_1$ symmetry. No poles appear for the $A_1$, $A_2$, and $B_2$ excited states due to obvious symmetry reasons.[37] Panel (b) of Fig. 1 displays the corresponding dispersion curve for the $xx$ component of the EOM-CCSD polarizability. Poles appear at 1.23 eV, 2.03 eV, 2.43 eV, 3.77 eV, 4.06 eV, 5.90 eV, and 9.08 eV; all of them correspond to excitations out of the $2A_1$ state to excited states of $B_1$ symmetry. However, there are additional poles at 7.41 eV and 11.07 eV, that is, at energies that correspond to excitations from the $1A_1$ ground state to the $B_1$ excited states. These are clearly unphysical poles, and indeed, they are not present in the dispersion curve obtained by using the sum-over-states expression, i.e., Eq. (25).

The presented example illuminates an important aspect of EOM-CC theory (and, likewise, also of CC linear-response theory), namely, that the corresponding response function is affected by spurious poles due to the response of the CC amplitudes. These poles persist for all approximate EOM-CC treatments and only disappear in the FCI limit, when the amplitude response no longer contributes. These artificial poles can be avoided by ignoring the amplitude response. However, this either violates size-extensivity or the proper FCI limit is not reached within the complete cluster expansion. One thus faces the choice between (I) a size-extensive scheme with an incorrect pole structure, (II) a scheme with a correct pole structure that is no longer size extensive, or (III) a size-extensive scheme
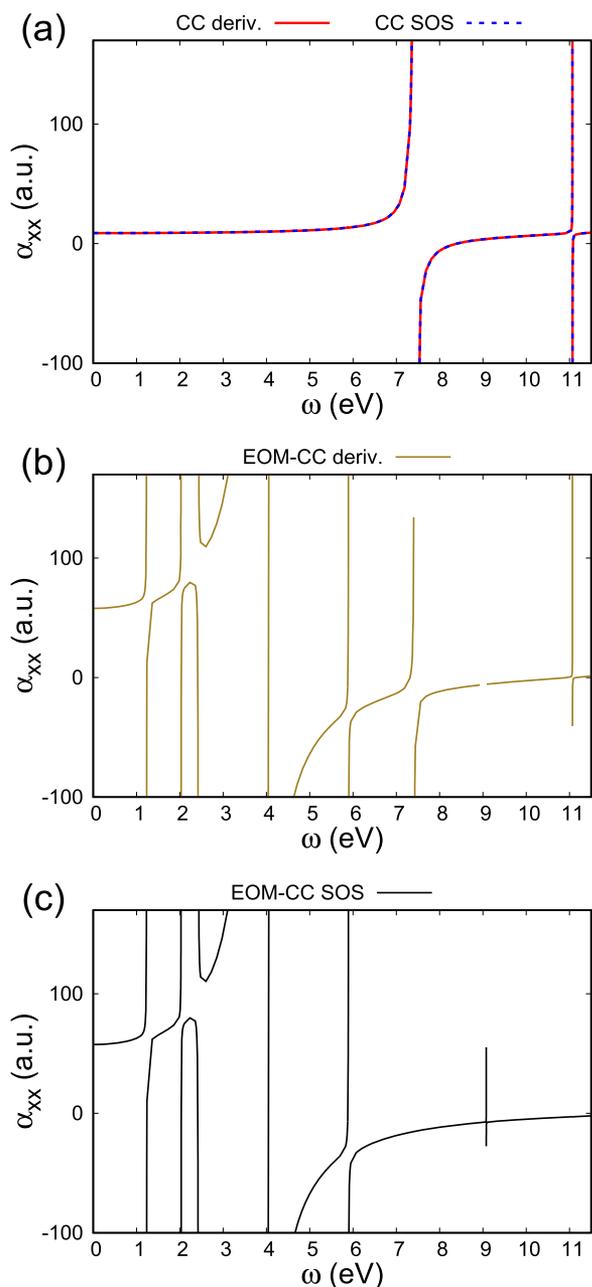
FIG. 1. CCSD and EOM-EE-CCSD polarizabilities (*xx* component) for (a) the ground state and [(b) and (c)] the $2A_1$ state of water calculated using (b) the derivative and (c) the sum-over-states approach as a function of the frequency $\omega$.

results obtained with the sum-over-states approach for static polarizabilities and interstate properties, such as two-photon absorption transition moments[38] or spin-orbit coupling constants,[39–41] seem to confirm that expectation. However, the comparison between sum-over-states results and those with the amplitude response in the case of polarizabilities also reveals some cases with differences as large as 30% (Ref. 22).

While our findings reveal some limitations on the applicability of EOM-CC theory, in particular, within single-state applications, we also stress that EOM-CC is not the only scheme that exhibits an incorrect pole structure. Other famous examples are CCSD with perturbative triples corrections, CCSD(T), and several multireference CC schemes.[42,43] Problems with the pole structure always seem to appear when a two- or multi-step strategy is used in the CC treatment. While such schemes are often ingenious and useful for the treatment of challenging problems in electronic-structure theory, they are more prone to deficiencies such as the appearance of artificial poles.

We provide derivations of Eqs. (19)–(23) and details of our implementation in the supplementary material.

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with a correct pole structure that does not converge to the FCI limit. The last one should, most likely, be dismissed as the recovery of the proper FCI limit is a rather strong argument, in particular, considering that these deviations persist even when using the complete (de-)excitation manifold for $T$, $\mathcal{R}$, and $\mathcal{L}$. Concerning the other two options, one can argue in favor of the first one by pointing out that the artificial poles typically appear at higher frequencies (see Fig. 1 as well as the example discussed in Ref. 25 in which no spurious pole was observed), as the ground-state excitation energies in many cases are higher in energy than the corresponding excited-state excitation energies. A good argument for the second approach is that the size-extensivity error in most cases is not too large and actually should decrease when including higher excitations. Numerical

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