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# Similarity transformed equation-of-motion coupled-cluster theory: Details, examples, and comparisons

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The similarity transformed equation-of-motion coupled-cluster (STEOM-CC) method is presented in full detail. Comparisons are made with the Fock space coupled-cluster (FSCC) method and the equation-of-motion coupled-cluster (EOM-CC) scheme. The role of implicit triple excitations and, relatedly, charge transfer separability in STEOM is discussed. The dependence on the choice of active space in STEOM is addressed and criteria for the selection of the active space are given. The evaluation of properties within STEOM is outlined and a large number of illustrative examples of STEOM is presented. © 1997 American Institute of Physics. [S0021-9606(97)02841-9]

## I. INTRODUCTION

Recently we developed an alternative strategy to obtain a manifold of electronic eigenstates at a given nuclear geometry that proved particularly effective, yet accurate.<sup>1,2</sup> The idea behind the approach is rather different from the conventional wave function optimization approaches. In the similarity transformed equation-of-motion coupled-cluster (STEOM-CC) method<sup>1,2</sup> a sequence of two similarity transformations of the second quantized Hamiltonian is performed, such that the one- and (a selection of most important) two-body components of the new Hamiltonian that net increase the excitation level are transformed to zero. The first transformation in STEOM uses the singles and doubles connected excitation operator  $\hat{T} = \hat{T}_1 + \hat{T}_2$  that is obtained from a standard CCSD calculation.<sup>3</sup> The transformed Hamiltonian

$$\hat{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}, \quad (1)$$

is familiar from equation-of-motion coupled-cluster (EOM-CC) theory<sup>4-7</sup> [or coupled-cluster linear response (CCLR)<sup>8-10</sup>] and has the property that one- and two-particle pure excitation operators (the  $1h1p-2h2p$  operators) in  $\hat{H}$  vanish. In the second transformation we use a normal ordered exponential operator  $\{e^{\hat{S}}\}$ <sup>11</sup> as introduced by Lindgren,<sup>12</sup> and which is familiar from Fock space coupled-cluster theory.<sup>12-29</sup> The operator  $\hat{S}$  is determined such that a selection of the most important remaining excitation operators of  $hhh$  and  $hpps$  form that net increase the excitation level by one, but which give a vanishing result when acting on the reference determinant, are transformed to zero. In this step we introduce a set of active orbitals. Only integrals that have an active quasi-particle annihilation operator are transformed to zero.

To a good approximation the final transformed Hamiltonian  $\hat{G}$  attains a block form that makes it very easy to extract a subset of its eigenvalues: Each subblock of the transformed Hamiltonian corresponding to a definite excitation level can be diagonalized separately. It follows that excitation energies corresponding to dominantly singly excited states can be obtained by diagonalizing  $\hat{G}$  over the subspace of singly excited determinants. Operationally the final step in

a STEOM calculation for excitation energies amounts to a CI singles calculation with modified matrix elements. This step is almost trivial and gives the scheme enormous computational and conceptual appeal: A large number of electronic states can be calculated at virtually no cost.

Moreover, since the transformed Hamiltonian is given in second quantization the convenient block form holds for all sectors in Fock space, corresponding to  $N$ ,  $N \pm 1$ ,  $N \pm 2$  particles and so forth. Principal ionization energies are obtained by diagonalizing over the one hole configurations, electron affinities derive from diagonalization over the one particle configurations, while double ionization potentials (for example to interpret Auger spectra) are obtained by diagonalizing over two hole determinants and so forth.

In the first applications of the STEOM-CC scheme we considered the excitation spectra of the pyridine molecule<sup>1</sup> and free base porphyrin.<sup>2</sup> The accuracy of the STEOM results were found to be comparable to state-of-the-art methods like MRCI,<sup>30</sup> CASPT2,<sup>31,32</sup> EOM-CC<sup>33</sup> and SAC-CI,<sup>34,35</sup> while the computational requirements are much reduced compared to the above methods. We also introduced the so-called STEOM-PT method in which the CCSD coefficients were replaced by their first-order analogs, and which yielded very satisfactory results for the pyridine molecule. The results for free base porphyrin were less accurate, due to higher order correlation effects needed for the description of the ground state. In STEOM-PT the most expensive CCSD step is eliminated, which scales with the sixth power of the basis set. The calculation of  $\hat{H}$  matrix-elements also scales with the sixth power of the basis set, but contrary to CCSD, this step is noniterative. The formation of  $\hat{H}$  for larger systems is the most expensive step in a STEOM-PT calculation. The calculation of the  $S$ -amplitudes and the second similarity transform scale with the fifth power of the basis set and this step scales linearly with the size of the active space. The final diagonalization step in STEOM scales with only the fourth power of the basis set. This favorable scaling was demonstrated in our calculations on pyridine and free base porphyrin.

In STEOM many elements are combined that have their roots in various developments in open-shell coupled-cluster theory. The concept of many-body similarity transformations

and a subsequent diagonalization of the transformed Hamiltonian over small subspaces goes back to Stolarczyk and Monkhorst.<sup>21–24</sup> In a recent paper the use of many-body similarity transformations were revived and a number of problems with the original formulation of Stolarczyk and Monkhorst were resolved.<sup>11</sup> Specifically, it was shown that the transformed Hamiltonian could be obtained without explicit use of the cumbersome inverse of the transformation operator  $\{e^{\hat{S}}\}$ . In addition we allowed for the use of a subset of active orbitals which is necessary to make the approach practical. Furthermore, the intimate relation between the Stolarczyk–Monkhorst approach and the Fock space coupled–cluster method developed by Lindgren, Mukherjee, and others<sup>12,14,15,19,25</sup> was demonstrated.<sup>11</sup> The idea of many-body similarity transformations has also been the basis for a simple and general formulation of spin-adapted open-shell coupled-cluster theory,<sup>36</sup> which is yet to be implemented.

Another important aspect of STEOM derives from the relations between STEOM and FSCC on the one hand, and EOM-CC theory for the IP- and EA-sectors on the other.<sup>37,38</sup> This allows us to formulate all steps in a STEOM calculation, except for the initial solution of the CCSD equations, as eigenvalue problems. This is stable numerically and has important advantages over the solution of nonlinear equations as in FSCC.

In this paper we give a detailed exposition of the STEOM method for excitation energies, doubly ionized and doubly attached states. A number of subtleties in the formulation of STEOM will be addressed. The relationship with other developments in open-shell coupled-cluster theory will be clarified and illustrated with numerical results. The outline of this paper is as follows.

In Sec. II A we present a derivation of the amplitude equations. We start from the point of view of the many-body similarity transformation, and provide the connection with amplitude equations in FSCC and the eigenvalue problems of the IP-EOM-CC and EA-EOM-CC methods. We also discuss the rôle of active orbitals in this section. In Sec. II B we present detailed formulas for the matrix elements of the transformed Hamiltonian at the orbital level.

In Sec. III we present the first applications of STEOM to doubly ionized and doubly attached states. The DIP-STEOM scheme can straightforwardly be used to interpret Auger spectra, and we discuss an elementary application to the HF molecule. DIP-STEOM also provides a means to obtain the ionized states of doublet radicals. In this case we start from the closed shell anion and delete two electrons to arrive at the cation states. As an example we discuss the ionized states of the F-atom which are obtained as the doubly ionized states of the closed shell  $F^-$  anion. The double attachment scheme can be used to calculate excitation spectra of open-shell systems like oxygen or the carbon atom, which in their ground state have two open-shell electrons out of a closed shell configuration.

Both the DIP- and DEA-STEOM method show great promise to be applicable to systems that require a traditional multireference description.<sup>39,40</sup> The DIP method can be used

to describe systems that have two electrons in two active spatial orbitals, or four electrons in three orbitals, i.e., two holes in a closed-shell configuration. Similarly the DEA method can be used to describe systems that have two electrons on top of a closed shell. This includes a surprising number of difficult transition states, bi-radicals etc. As an example we will discuss the vibrational frequencies of ozone, a notorious multireference problem.<sup>41,42</sup>

In Sec. IV we further discuss the relation of FSCC and STEOM with particular emphasis on the rôle of the active space. If the active space is exhaustive the two methods will give identical results, although the numerical convergence behavior of the two schemes will be different. We provide a direct comparison of the two methods by considering the *s*-tetrizine molecule using the same computational parameters as in an earlier FSCC calculation.<sup>43</sup> The dependence of STEOM results on the size and character of the active space is illustrated with a calculation of the excitation spectrum of the CO molecule.

In Sec. V we compare the STEOM-CC and EOM-CC methods for excitation energies. In STEOM there is an implicit contribution from “disconnected” triple excitations if we transform back to the EOM picture. This triple contribution has been considered by Meissner and Bartlett<sup>44</sup> in a comparison of FSCC and EOM-CC, and they suggested a dressing of the EOM-CC method to incorporate this effect.<sup>45</sup> Interestingly, STEOM and EOM-CC can be viewed as different approximations to this dressed EOM-CC method. An important motivation to consider the triples correction was that FSCC (and also STEOM) eigenvalues and right-hand eigenvectors satisfy the proper separability conditions, since they are fully linked, extension theories, EOM-CC (or its CCLR twin) does not. In particular the excitation energies in FSCC/STEOM are charge transfer separable. By this we mean that in the limit of a system consisting of two noninteracting closed shell subsystems, the excitation energy of a charge transfer excitation (from one subsystem to the other) is precisely equal to the sum of the relevant electro-affinity on one subsystem and the ionization potential on the other. Due to the truncated CI structure this charge transfer separability is not satisfied in EOM-CC. We illustrate these concepts by considering the charge transfer excitation from Be to  $C_2$  at large separation of the Be and  $C_2$  moieties. Triple corrections to EOM-CC<sup>46–51</sup> have been shown to be important also for less exotic systems, in particular, for valence excited states. To gauge the effect of triples we make a comparison between STEOM and EOM-CC for the  $N_2$ ,  $H_2O$ , and  $C_2$  molecules for which full CI results have recently been presented.<sup>51</sup> We also discard the triples correction from STEOM and compare results from the resulting “STEOM-no-T” model to EOM-CCSD results.

In Sec. VI we discuss the evaluation of properties and transition moments in the STEOM framework, using the convenient biorthogonal expectation value approach that has been used in the equation-of-motion coupled-cluster method.<sup>6</sup> We compare STEOM results with EOM-CC results for the CO molecule, and also consider excited-state proper-

ties calculated as energy derivatives through finite difference techniques.

Our findings are summarized in the final section.

## II. SIMILARITY TRANSFORMED EQUATION-OF-MOTION COUPLED-CLUSTER THEORY (STEOM-CC)

In this section we will discuss and derive the STEOM equations at various levels. In the first subsection we will discuss the ideas behind the approach and the amplitude equations in general terms. We will also show how the amplitudes for the second transformation can be obtained from IP-EOM-CC and EA-EOM-CC eigenvalue problems and a suitable normalization. In the second subsection we provide detailed equations for the transformed matrix elements at the orbital level.

Some remarks about notation are in order. The orbitals are partitioned into occupied orbitals,  $i, j, k, l$ , unoccupied orbitals  $a, b, c, d$ , while general orbitals are denoted  $p, q, r, s$ . In addition active occupied orbitals will be labeled  $m, n$ , while active virtual orbitals are indicated by  $e, f$ . Finally we will use a prime to indicate orbitals that are explicitly inactive, i.e.,  $i', j'$  and  $a', b'$ .

### A. Amplitude equations

In STEOM-CCSD theory we perform a sequence of two many-body similarity transformations, such that the most important one- and two-body net-excitation operators in the resulting transformed Hamiltonian  $\hat{G}$  vanish. The first transformation is familiar from equation-of-motion coupled-cluster theory and is given by

$$\hat{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}. \quad (2)$$

The operator  $\hat{T}$  consists of single and double pure excitation operators

$$\hat{T} = \hat{T}_1 + \hat{T}_2 = \sum_{i,a} t_i^a \{\hat{a}^\dagger \hat{i}\} + \frac{1}{4} \sum_{i,j,a,b} t_{ij}^{ab} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\}, \quad (3)$$

where the brackets indicate normal order with respect to a predetermined reference determinant  $|\Phi_0\rangle$ . Given the amplitudes of the operator  $\hat{T}$  the transformed Hamiltonian can be expressed in normal ordered, second quantized form using new matrix elements

$$\begin{aligned} \hat{H} = & \bar{h}_0 + \sum_{p,q} \bar{h}_{pq} \{\hat{p}^\dagger \hat{q}\} + \frac{1}{4} \sum_{p,q,r,s} \bar{h}_{pqrs} \{\hat{p}^\dagger \hat{r} \hat{q}^\dagger \hat{s}\} \\ & + \frac{1}{36} \sum_{p,q,r,s,t,u} \bar{h}_{pqrst} \{\hat{p}^\dagger \hat{s} \hat{q}^\dagger \hat{t} \hat{r}^\dagger \hat{u}\} + \dots \end{aligned} \quad (4)$$

The matrix elements of  $\hat{H}$  consist of products of amplitudes of the operator  $\hat{T}$  and matrix-elements of the original Hamiltonian  $\hat{H}$ . The so-called EOM Hamiltonian  $\hat{H}^{6,52}$  contains three- and higher-body operators (up to six-body components in the singles and doubles approximation), and the one- and two-particle components of  $\hat{H}$  are well documented in the literature.<sup>53,54</sup> The operator  $\hat{T}$  is determined by equating the

one- and two-body pure excitation operators in  $\hat{H}$  to zero, and this leads to the familiar CCSD equations

$$\bar{h}_{ai} = \langle \Phi_i^a | \hat{H} | \Phi_0 \rangle = \langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0, \quad (5)$$

$$\bar{h}_{abij} = \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0.$$

The constant term  $\bar{h}_0$  in the normal ordered representation of  $\hat{H}$  equals the coupled-cluster energy

$$\bar{h}_0 = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = E_{CC}. \quad (6)$$

In equation-of-motion coupled-cluster theory the transformed Hamiltonian is diagonalized over a suitable set of configurations to obtain ionized,<sup>55-58</sup> attached<sup>52</sup> or excited states.<sup>6</sup> The transformation serves two purposes. First the diagonalization space can be more compact than in a corresponding CI calculation: Only one excitation level beyond the states of interest needs to be included in the diagonalization space. Second the method yields size-intensive results for energy differences like excitation energies and ionization potentials. Both properties ultimately derive from the fact that

$$(\hat{H} - E_{CC}) \hat{q}^{\text{ex}} | 0 \rangle = [\hat{H}, \hat{q}^{\text{ex}}] | 0 \rangle, \quad (7)$$

which in turn can be attributed to the vanishing pure excitation parts in  $\hat{H}$ . The commutator form provides the relation with propagator and equation-of-motion formulations, and a possible representation of the theory in terms of connected diagrams.<sup>55,56</sup> This statement refers to the one- and two-particle Green's functions or propagators associated with EOM-CC, not to the perturbation series for the excitation energies themselves, which do contain disconnected diagrams.<sup>44,45</sup> The latter, unlinked, terms do not violate the extensivity of second-order properties for extended systems<sup>59</sup> within EOM-CC theory in the so-called quadratic model,<sup>60</sup> or CCLRT, but do violate charge-transfer superability for excited states.<sup>10</sup>

In similarity transformed equation-of-motion coupled-cluster theory (STEOM-CC) we perform a second similarity transform

$$\hat{G} = \{e^{\hat{S}}\}^{-1} \hat{H} \{e^{\hat{S}}\}, \quad (8)$$

where the transformation operator consists of two parts  $\hat{S} = \hat{S}^+ + \hat{S}^-$

$$\hat{S}^+ = \hat{S}_1^+ + \hat{S}_2^+ = \sum_{a',e} s_e^{a'} \{\hat{a}^\dagger \hat{e}\} + \frac{1}{2} \sum_{a,b,j,e} S_{ej}^{ab} \{\hat{a}^\dagger \hat{e} \hat{b}^\dagger \hat{j}\}, \quad (9)$$

and

$$\hat{S}^- = \hat{S}_1^- + \hat{S}_2^- = \sum_{i',m} S_{i',m}^m \{\hat{m}^\dagger \hat{i}'\} + \frac{1}{2} \sum_{i,m,b,j} S_{ij}^{mb} \{\hat{m}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\}. \quad (10)$$

As mentioned before the indices  $m$  and  $e$  denote active indices of the hole and particle type respectively, while a prime denotes a restriction to orbitals that are not active. The corresponding operators  $\hat{m}^\dagger$  and  $\hat{e}$  give zero when acting upon the reference determinant [they are called quasiparticle (or  $q$ -) annihilation operators]. The presence of  $q$ -annihilation operators in  $\hat{S}$  implies that different components of  $\hat{S}$  in gen-

	0	S	D	T	Q
0	X	X	X		
S	0	X	X	X	
D	0	-	X	X	X
T	-	-	-	X	X
Q	-	-	-	-	X

FIG. 1. STEOM-CC: Diagonalize doubly similarity transformed Hamiltonian  $\hat{G}$  over excited determinants. X's indicate matrix-elements of normal magnitude, while the blocks indicated by a  $\sim$  correspond to small three-particle interactions in  $\hat{G}$ , or "inactive" two-body operators.

eral do not commute, and for this reason we use a normal ordered exponential, in which all  $q$ -annihilation operators by definition are moved to the right. The basic bookkeeping mechanism in many-body theory amounts to writing products of operators in normal order and starting from normal ordered operators therefore generally simplifies equations. Once the amplitudes of the operator  $\hat{S}$  are determined one can obtain the transformed Hamiltonian  $\hat{G}$  in second quantization (and as always, normal order)

$$\hat{G} = g_0 + \sum_{p,q} g_{pq} \{\hat{p}^\dagger \hat{q}\} + \frac{1}{4} \sum_{p,q,r,s} g_{pqrs} \{\hat{p}^\dagger \hat{r} \hat{q}^\dagger \hat{s}\} + \dots, \quad (11)$$

where now the matrix-elements of  $\hat{G}$  are (connected) products of matrix elements of  $\hat{H}$  and amplitudes of  $\hat{S}$ . The transformation with the operator  $\{e^{\hat{S}}\}$  preserves the zeros for the pure excitation components  $g_{ai} = g_{abij} = 0$ , independent of the coefficients of  $\hat{S}$ .<sup>11</sup> In addition  $g_0 = \bar{h}_0 = E_{CC}$ .

The equations that determine the amplitudes of  $\hat{S}$  are obtained by equating the corresponding elements of  $\hat{G}$  to zero, hence

$$g_{mi'} = g_{a'e} = 0, \quad g_{abej} = g_{mbij} = 0. \quad (12)$$

Obviously, the number of coefficients to be determined equals the number of equations. The vanishing of the two-particle components of  $\hat{G}$ , having one (active)  $q$ -annihilation operator is very useful, as thereby the coupling of an excited determinant to more highly excited determinants is strongly reduced. The transformed Hamiltonian assumes a block form as indicated in Fig. 1.

The transformed Hamiltonian is evidently non-Hermitian, and simplifications only occur in the lower triangular block of the Hamiltonian matrix. Neglecting the matrix-elements in the lower triangle allows us to extract a subset of the eigenvalues of  $\hat{G}$  to good approximation by diagonalizing over a subspace corresponding to one particular excitation level.

The vanishing of the one-particle components in Eq. (12) is of no particular relevance, since they do not provide a coupling to more highly excited determinants anyway. The reason for the inclusion of the one-particle operator in  $\hat{S}$ , is that the nonlinear Eq. (12) can then be cast into an eigenvalue problem, which tends to be more stable numerically. We will show below that the amplitudes that define  $\hat{S}^+$  are

obtained by solving EA-EOM-CC<sup>52</sup> eigenvalue problems (corresponding to states with  $N+1$  electrons), while similarly, the amplitudes that define  $\hat{S}^-$  are obtained by solving for a number of eigenstates of the IP-EOM-CC Hamiltonian,<sup>56,61</sup> corresponding to states with  $N-1$  electrons.

Rather than using the inverse  $\{e^{\hat{S}}\}^{-1}$  the transformed Hamiltonian  $\hat{G}$  is solved from the linear equations

$$\{e^{\hat{S}}\} \hat{G} = \hat{H} \{e^{\hat{S}}\}, \quad (13)$$

which has been shown<sup>11</sup> to be equivalent to

$$(\{e^{\hat{S}}\} \hat{G})_C = (\hat{H} \{e^{\hat{S}}\})_C \quad (14)$$

or

$$\hat{G} = (\hat{H} \{e^{\hat{S}}\})_C - (\{e^{\hat{S}} - 1\} \hat{G})_C, \quad (15)$$

where the subscript  $C$  denotes a restriction to connected contributions. The components of  $\hat{G}$  that are required to vanish can be extracted by projecting against a suitable set of Slater determinants

$$\begin{aligned} g_{mi'} &= \langle \Phi_{i'} | \hat{G} | \Phi_m \rangle = 0, \\ g_{mbij} &= \langle \Phi_{ji}^b | \hat{G} | \Phi_m \rangle = 0, \\ g_{a'e} &= \langle \Phi^{a'} | \hat{G} | \Phi^e \rangle = 0, \\ g_{abej} &= \langle \Phi_j^{ba} | \hat{G} | \Phi^e \rangle = 0, \end{aligned} \quad (16)$$

where in defining the two-particle components we used that contributions from the pure creation parts of  $\hat{G}$  vanish, due to the solution of the CCSD equations. The first two equations involve projecting onto a space of inactive  $1h$  and  $2h1p$  configurations on the left and active  $1h$  determinants on the right. The third and fourth equation involve the  $1p$  and  $2p1h$  spaces. These equations can be summarized as

$$\langle Q^\pm | \hat{G} | P^\pm \rangle = 0, \quad (17)$$

where the projection manifolds are implicitly defined. Let us emphasize that due to the  $1h/1p$  character of the manifold  $P^\pm$  only (normal ordered) components of  $\hat{G}$  contribute that have precisely one  $q$ -annihilation operator of hole or particle type respectively. Substituting Eq. (15) for  $\hat{G}$ , the right-hand exponential  $(\hat{H} \{e^{\hat{S}}\})_C$  can immediately be linearized, and split according to components.

$$\langle Q^\pm | \hat{H} + (\hat{H} \hat{S}^\pm)_C - (\{e^{\hat{S}} - 1\} \hat{G})_C | P^\pm \rangle = 0. \quad (18)$$

The left-hand exponential  $(\{e^{\hat{S}} - 1\} \hat{G})_C | P^\pm \rangle$  requires some further manipulation. We know that only components of  $\hat{G}$  can contribute that have one active  $q$ -annihilation operator. But all of these operator components are equated to zero, except those that excite within the  $P$ -space. Hence we can write

$$\begin{aligned}
\langle \{e^{\hat{S}} - 1\} \hat{G} \rangle_C | P^\pm \rangle &= \langle e^{\hat{S}} - 1 \rangle | P^\pm \rangle \langle P^\pm | \hat{G} - g_0 | P^\pm \rangle \\
&= \hat{S}^\pm | P^\pm \rangle \langle P^\pm | \hat{G} - E_{\text{CC}} | P^\pm \rangle \\
&= \hat{S}^\pm | P^\pm \rangle \langle P^\pm | \hat{H} + (\hat{H} \hat{S}^\pm) - E_{\text{CC}} | P^\pm \rangle.
\end{aligned} \tag{19}$$

The constant  $g_0 = E_{\text{CC}}$  has to be subtracted to ensure the connectivity of the expression. In the final line we use that

$$\langle P^\pm | \{e^{\hat{S}} - 1\} \hat{G} \rangle_C | P^\pm \rangle = 0, \tag{20}$$

since  $\hat{S}$  always excites out of the active space. Collecting terms we find

$$\begin{aligned}
\langle Q^\pm | \hat{H} + (\hat{H} \hat{S}^\pm) \rangle_C | P^\pm \rangle - \langle Q^\pm | \hat{S}^\pm | P^\pm \rangle \\
\times \langle P^\pm | \hat{H} + (\hat{H} \hat{S}^\pm) \rangle_C - E_{\text{CC}} | P^\pm \rangle = 0.
\end{aligned} \tag{21}$$

The above equation is identical to the Fock Space coupled-cluster (FSCC) equations for the IP- and EA-sectors that have been derived by Mukherjee and Lindgren *et al.*<sup>12,14,15,19</sup> The relation between the many-body similarity transformations and FSCC theory has been addressed in general in a previous paper.<sup>11</sup> Sinha *et al.*<sup>37</sup> on the other hand, showed the relation between FSCC for the IP and EA sectors and coupled-cluster linear response theory (CCLRT) or equivalently equation-of-motion coupled-cluster (EOM-CC) for these sectors. This relation is most easily obtained by multiplying Eq. (21) on the right with a matrix  $U^\pm$  in the  $P$ -space that diagonalizes the effective Hamiltonian

$$\begin{aligned}
H_{\text{eff}} &= \langle P^\pm | \hat{G} - E_{\text{CC}} | P^\pm \rangle \\
&= \langle P^\pm | \hat{H} + (\hat{H} \hat{S}^\pm) \rangle_C - E_{\text{CC}} | P^\pm \rangle.
\end{aligned} \tag{22}$$

Hence

$$\begin{aligned}
\langle P^\pm | \hat{H} + (\hat{H} \hat{S}^\pm) \rangle_C - E_{\text{CC}} | P^\pm \rangle U^\pm \\
= U^\pm E^\pm \langle Q^\pm | \hat{H} + (\hat{H} \hat{S}^\pm) \rangle_C | P^\pm \rangle U^\pm \\
= \langle Q^\pm | \hat{S}^\pm | P^\pm \rangle U^\pm E^\pm.
\end{aligned} \tag{23}$$

Defining

$$|P^\pm\rangle U_\lambda^\pm + \hat{S}^\pm |P^\pm\rangle U_\lambda^\pm = \hat{R}_\lambda^\pm |\Phi_0\rangle. \tag{24}$$

We obtain the EOM-CC eigenvalue equations

$$\langle \Phi_\kappa^\pm | (\hat{H} \hat{R}_\lambda^\pm) \rangle_C | \Phi_0 \rangle = \langle \Phi_\kappa^\pm | \hat{R}_\lambda^\pm | \Phi_0 \rangle E_\lambda^\pm \tag{25}$$

or

$$\langle \Phi_\kappa^\pm | [\hat{H}, \hat{R}_\lambda^\pm] | \Phi_0 \rangle = \langle \Phi_\kappa^\pm | \hat{R}_\lambda^\pm | \Phi_0 \rangle E_\lambda^\pm. \tag{26}$$

The energy eigenvalues in these equations correspond directly to the energy differences, i.e., ionization potentials and electron affinities. The EOM-CC eigenvalue equations for the EA and IP sectors are well documented.<sup>52,55-57,61</sup> To obtain the amplitudes of the operator  $\hat{S}$  we solve for a number of principal ionization potentials and electron affinities and the corresponding eigenvectors  $R_\lambda^\pm$ . The matrices  $U^\pm$  are defined as the model components (corresponding to the active orbitals) of the vectors  $R_\lambda^\pm$ , hence

$$U_{p\lambda}^\pm = \langle \Phi_p^\pm | \hat{R}_\lambda^\pm | \Phi_0 \rangle = r_{p\lambda}^\pm. \tag{27}$$

The amplitudes of the operators  $\hat{S}^\pm$  are then obtained as

$$\langle \Phi_k^\pm | \hat{S}^\pm | \Phi_p^\pm \rangle = \sum_\lambda \langle \Phi_k^\pm | \hat{R}_\lambda^\pm | \Phi_0 \rangle U_{\lambda p}^{\pm-1}. \tag{28}$$

Writing explicit equations for the IP and EA amplitudes we find

$$s_{i'}^m = - \sum_\lambda r_{i'}(\lambda) r_{\lambda m}^{-1}, \quad s_{ji}^{bm} = - \sum_\lambda r_{ji}^b(\lambda) r_{\lambda m}^{-1}, \tag{29}$$

and

$$s_e^{a'} = \sum_\lambda r^{a'}(\lambda) r_{\lambda e}^{-1}, \quad s_{je}^{ba} = \sum_\lambda r_j^{ba}(\lambda) r_{\lambda e}^{-1}. \tag{30}$$

The extra minus sign for the IP-coefficients derives from the extra contraction over the hole line in evaluating the left-hand side of Eq. (28). The matrices  $r_{\lambda p}^{-1}$  are to be interpreted as the coefficients of the inverse of the matrix constructed from the principal, active components of the eigenvectors  $r_p(\lambda)$ .

The question arises to what extent the approach depends on the choice of active orbitals, and to what extent the approach is unique. In the above derivation we showed that the transformation operator  $\hat{S}$  that satisfies Eqs. (15) and (16) can be obtained by solving for a number of eigenvectors of the IP- and EA-EOM-CC problems and a normalization condition. Surprisingly, any selection of eigenvectors is possible. They do not need even correspond to principal IP's and EA's. This arbitrariness is directly related to the nonlinearity of the defining Eq. (16), which allows for multiple solutions. This issue has been discussed in detail by Meissner.<sup>62</sup> However, for the STEOM approach to be useful the three-particle components of  $\hat{G}$  should be small, and therefore so should the amplitudes  $\hat{S}_2$ . This implies that we will want to use eigenvectors of the EOM-CC eigenvalue problems that correspond to principal IP's and EA's. The notion of principal eigenvectors is related to the validity of Koopmans' theorem. If the MO picture of ionization or attachment breaks down, we expect also a breakdown of the STEOM concepts. In practice the selection of a definite set of principal EOM-CC eigenvectors is fairly straightforward, and we note that the EOM-CC results only (slightly) depend on the choice of reference state. They are invariant under a rotation of virtual (or occupied) orbitals among each other.

The second freedom in the definition of the transformation concerns the normalization condition and this depends on the selected active space. Let us emphasize that this choice is independent of the selection of EOM-CC eigenvectors. The choice of active orbitals is a delicate subject. They determine the matrix inverse in Eqs. (29) and (30) and in order to minimize the magnitude of  $\hat{S}_2$  it is advantageous to select a space of active orbitals that has maximum overlap with the selected EOM-CC eigenvectors. Canonical Hartree-Fock (HF) orbitals are an excellent choice in this respect. On the other hand the active orbitals, or better, the active space, determines precisely which transformed two-electron matrix

elements are transformed to zero. This determines (to some extent) the remaining coupling that is not taken into account when diagonalizing  $\hat{G}$  over a small subspace. In this context one would like to define an active space such that the final STEOM eigenvectors can be well represented within the active space and contain only a very small component outside the active space. In this sense canonical Hartree–Fock virtual orbitals are often a poor choice to describe excited states, as the Hartree–Fock virtual orbitals are often too diffuse.

It is clear that there is some tension between the two requirements, and we have not found a convenient solution for this potential problem yet. Presently, we usually define the active space as a selection of canonical Hartree–Fock orbitals. The computational expense of STEOM depends only slightly on the magnitude of the active space, and this allows us to use rather extensive active spaces, such that the active component of the STEOM eigenvectors usually exceeds 95%. In Sec. IV we will return to the issue of active orbitals and present numerical examples.

To summarize this section the  $s$ -amplitudes can be obtained from the EOM-CC eigenvectors for the IP and EA sectors corresponding to principal ionization potentials and electron affinities. The  $S^-$  components can be obtained by writing the IP-EOM-CC eigenvectors in anti-intermediate normalization w.r.t. to the active space, while the  $S^+$  amplitudes are obtained by writing the EA-EOM-CC eigenvectors in intermediate normalization.

## B. Matrix elements of the transformed Hamiltonian

We will show first that we will not need to consider the one-particle components of  $\hat{S}$ . To this end we note that

$$\{e^{\hat{S}_2}\}\{e^{\hat{S}_1}\} = \{e^{\hat{S}_1 + \hat{S}_2}\}. \quad (31)$$

This follows from Wick's theorem which states that the product of two normal ordered operators is the normal ordered product of the two operators plus all possible contractions. It is impossible to contract  $\hat{S}_2$  to  $\hat{S}_1$ , since the lines at the bottom of  $\hat{S}_2$  correspond to active orbitals, while the lines at the top of  $\hat{S}_1$  correspond to inactive labels. Therefore only the uncontracted term in Wick's theorem remains, which is the content of Eq. (31). It follows that the total similarity transform can be written as a sequence of two similarity transforms

$$\hat{G}_t = \{e^{\hat{S}_1}\}^{-1} \{e^{\hat{S}_2}\}^{-1} \hat{H} \{e^{\hat{S}_2}\} \{e^{\hat{S}_1}\} = \{e^{\hat{S}_1}\}^{-1} \hat{G}_2 \{e^{\hat{S}_1}\}. \quad (32)$$

Of course  $\hat{G}_t$  and  $\hat{G}_2$  have the same eigenvalue spectrum. Moreover the transformation with  $\{e^{\hat{S}_1}\}$  cannot change the particle-rank of an operator. This follows immediately because contracting  $\hat{S}_1$  to any operator does not change the particle rank. It does change the matrix elements, of course. The conclusion of the above is, however, that diagonalizing  $\hat{G}_t$  or  $\hat{G}_2$  over a subspace that contains all excitations (irrespective of active or inactive labels) up to a certain excitation level will lead to identical results. It is easier to calculate  $\hat{G}_2$ , and also subsequent manipulations are easier, and therefore

we will work with the transformation generated by  $\{e^{\hat{S}_2}\}$ . The transformed Hamiltonian will henceforth simply be called  $\hat{G}$ .

The matrix-elements that are needed in STEOM only require one and two-body components of  $\hat{G}$ , having at most two lines at the top. This further simplifies our equations since there are no contributions from the second, so-called renormalization term in Eq. (15). The equations (except the amplitude equations for  $\hat{S}$ , included below) are based upon  $\hat{G} \rightarrow (\bar{H}\{e^{\hat{S}_2}\})_C$ .

Below we give detailed expressions for the second quantized matrix-elements of  $\hat{G}$ . Because the reference determinant is assumed to be closed shell, the labels in these equations correspond to spatial orbitals, and the spin-integration is already carried out. All two-electron matrix-elements are given in '1212' notation. One and two-particle matrix elements of the EOM-Hamiltonian are denoted as  $w$ , and the expression for the matrix-element depends on the particle-hole character of the labels. The matrix elements in spin free format, precisely as they are used here, are documented in Ref. 54. Occasionally also the bare Hamiltonian matrix elements  $v$  are used. Matrix-elements of  $\hat{G}$ , denoted  $g$ , are defined over the complete set of orbitals. In addition we define intermediates  $u$  that will always contain one or more active labels. The matrix-elements of  $\hat{G}$  are most easily constructed in terms of these intermediates. In addition to the  $s$ -amplitudes defined before in terms of the EOM-CC eigenvectors we use symmetrized  $s$ -coefficients.

$$\tilde{s}_{ij}^{mb} = 2s_{ij}^{mb} - s_{ji}^{mb}, \quad \tilde{s}_{ej}^{ab} = 2s_{ej}^{ab} - s_{ej}^{ba}. \quad (33)$$

The equations below were obtained using diagrammatic techniques based on the Goldstone convention.

One-particle elements:

$hh$  elements

$$u_{mi} = \sum_{k,c} w_{kc} \tilde{s}_{ik}^{mc} - \sum_{k,l,d} w_{kld} \tilde{s}_{kl}^{md}, \quad (34)$$

$$g_{ki} = w_{ki} + \sum_m \delta_{km} u_{mi}, \quad (35)$$

$pp$  elements

$$u_{ae} = \sum_{k,c} w_{kc} \tilde{s}_{ek}^{ac} + \sum_{c,d,l} w_{alcd} \tilde{s}_{el}^{cd}, \quad (36)$$

$$g_{ac} = w_{ac} + \sum_e \delta_{ce} u_{ae}, \quad (37)$$

$hp$  elements

$$u_{ma} = - \sum_{k,l,d} w_{kld} \tilde{s}_{kl}^{md}, \quad (38)$$

$$u_{ie} = \sum_{c,d,l} w_{ilcd} \tilde{s}_{el}^{cd}, \quad (39)$$

$$g_{ia} = w_{ia} + \sum_m \delta_{im} u_{ma} + \sum_e u_{ie} \delta_{ea}, \quad (40)$$

*ph* elements

$$g_{ai} = w_{ai} = 0 \text{ (CCSD Eqs.)} \quad (41)$$

Two-particle matrix elements:

*hhhp* elements

$$u_{mlid} = \sum_{j,b} (v_{jlb} \tilde{s}_{ij}^{mb} - v_{ljbd} s_{ij}^{mb}), \quad (42)$$

$$u_{kmid} = - \sum_{j,b} v_{jkdb} s_{ji}^{mb}, \quad (43)$$

$$u_{klie} = \sum_{a,b} v_{klab} s_{ie}^{ab}, \quad (44)$$

$$g_{klid} = w_{klid} + \sum_m (\delta_{km} u_{mlid} + \delta_{lm} u_{kmid}) + \sum_e u_{klie} \delta_{ed}, \quad (45)$$

*phpp* elements

$$u_{aled} = \sum_{j,b} (w_{jlb} \tilde{s}_{ej}^{ab} - w_{jlbd} s_{ej}^{ab}), \quad (46)$$

$$u_{alce} = - \sum_{j,b} w_{jlc} s_{ej}^{ba}, \quad (47)$$

$$u_{amcd} = \sum_{i,j} w_{ijcd} s_{ji}^{ma}, \quad (48)$$

$$g_{alcd} = w_{alcd} + \sum_e (u_{alce} \delta_{ed} + u_{aled} \delta_{ec}) + \sum_m \delta_{lm} u_{amcd}, \quad (49)$$

*hhhh* elements

$$u_{mlij} = \sum_b s_{ij}^{mb} w_{lb} + \sum_{k,c} w_{klc} \tilde{s}_{ik}^{mc} - \sum_{k,c} (w_{klje} s_{ik}^{mc} + w_{klic} s_{kj}^{mc}), \quad (50)$$

$$u_{mnij} = \sum_b s_{ij}^{mb} u_{nb} + \sum_b s_{ji}^{nb} u_{mb} + \sum_{k,c} u_{knc} \tilde{s}_{ik}^{mc} - \sum_{k,c} (u_{knjc} s_{ik}^{mc} + u_{knic} s_{kj}^{mc}), \quad (51)$$

$$g_{klij} = w_{klij} + \sum_m (\delta_{km} u_{mlij} + \delta_{lm} u_{mkji}) + \sum_{m,n} \delta_{km} \delta_{ln} u_{mnij}, \quad (52)$$

*pppp* elements

$$u_{abcd} = - \sum_l w_{lb} s_{el}^{ab} + \sum_{k,c} w_{bkcd} \tilde{s}_{ek}^{ac} - \sum_{k,c} (w_{bkcd} s_{ek}^{ac} + w_{akcd} s_{ek}^{cb}), \quad (53)$$

$$u_{abef} = - \sum_l u_{lf} s_{el}^{ab} - \sum_l u_{le} s_{fl}^{ba} + \sum_{k,c} u_{bkfc} \tilde{s}_{ek}^{ac} - \sum_{k,c} (u_{bkcf} s_{ek}^{ac} + u_{akcf} s_{ek}^{cb}), \quad (54)$$

$$g_{abcd} = w_{abcd} + \sum_e (\delta_{ce} u_{abed} + \delta_{de} u_{baec}) + \sum_{e,f} \delta_{ec} \delta_{df} u_{abef}, \quad (55)$$

*phph* elements

$$u_{amci} = - \sum_k w_{kc} s_{ik}^{ma} + \sum_{l,d} w_{alcd} \tilde{s}_{il}^{md} - \sum_{l,d} w_{aldc} s_{il}^{md} + \sum_{k,l} w_{klci} s_{lk}^{ma}, \quad (56)$$

$$u_{akei} = - \sum_k w_{kc} s_{ei}^{ac} + \sum_{l,d} w_{lkdi} \tilde{s}_{el}^{ad} - \sum_{l,d} w_{lkid} s_{el}^{ad} + \sum_{c,d} w_{akcd} s_{ei}^{cd}, \quad (57)$$

$$u_{amei} = \sum_c u_{mc} s_{ei}^{ac} - \sum_k u_{ke} s_{ik}^{ma} + \sum_{l,d} u_{lmdi} \tilde{s}_{el}^{ad} - \sum_{l,d} u_{lmid} s_{el}^{ad} + \sum_{k,l} u_{klei} s_{lk}^{ma}, \quad (58)$$

$$g_{akci} = w_{akci} + \sum_e \delta_{ce} u_{akei} + \sum_m \delta_{mk} u_{amci} + \sum_{e,m} \delta_{ec} \delta_{km} u_{amei}, \quad (59)$$

*phhp* elements

$$u_{bmjc} = - \sum_k w_{kc} s_{kj}^{mb} + \sum_{k,l} w_{klc} s_{kl}^{mb} - \sum_{k,d} w_{kbcd} s_{kj}^{md}, \quad (60)$$

$$u_{bkje} = \sum_d w_{kd} s_{ej}^{db} + \sum_{c,d} w_{bkdc} s_{ej}^{cd} - \sum_{l,d} w_{lkjd} s_{el}^{db}, \quad (61)$$

$$u_{bmje} = \sum_d u_{md} s_{ej}^{db} - \sum_k u_{ke} s_{kj}^{mb} + \sum_{k,l} u_{klej} s_{kl}^{mb} - \sum_{ld} u_{lmjd} s_{el}^{db}, \quad (62)$$

$$g_{bkjc} = w_{bkjc} + \sum_e u_{bkje} \delta_{ce} + \sum_m \delta_{km} u_{bmjc} + \sum_{e,m} \delta_{km} \delta_{ce} u_{bmje}. \quad (63)$$

The following elements can be used to define the amplitude equations for  $\hat{S}$ . These equations are equivalent to the IP-EOM-CC and EA-EOM-CC equations, respectively.

*hhph* elements

$$\begin{aligned}
 g_{jidl} = & w_{jibm} + \sum_{l,d} w_{lbdj} \tilde{s}_{kl}^{md} - \sum_c t_{ij}^{cb} \sum_{k,l,d} w_{klcd} \tilde{s}_{kl}^{md} \\
 & - \sum_{ld} w_{lbdj} s_{il}^{md} - \sum_{kd} w_{kbid} s_{kj}^{md} + \sum_{k,l} w_{klij} s_{kl}^{mb} \\
 & - \sum_k w_{ki} s_{kj}^{mb} - \sum_l w_{lj} s_{il}^{mb} + \sum_d w_{bd} s_{ij}^{md} \\
 & - \sum_n g_{mn} s_{ij}^{nd}. \tag{64}
 \end{aligned}$$

In terms of the transformed matrix elements of  $g$ , the amplitude equations (which involve the transformation with  $\hat{S}_1$ ) read

$$g_{mi'} - \sum_{k'} w_{k'i'} s_{k'}^m + \sum_n \left( g_{mn} - \sum_{k'} w_{k'n} s_{k'}^m \right) s_{i'}^n = 0, \tag{65}$$

$$g_{jidl} - \sum_{k'} w_{jidl} s_{k'}^m - \sum_{n,k'} s_{ij}^{nd} w_{k'n} s_{k'}^m = 0,$$

*pphp* elements

$$\begin{aligned}
 g_{baje} = & w_{baje} + \sum_{ld} w_{lbdj} \tilde{s}_{el}^{ad} - \sum_k t_{kj}^{ab} \sum_{c,d,l} w_{klcd} \tilde{s}_{el}^{cd} \\
 & - \sum_{ld} w_{lbdj} s_{el}^{ad} - \sum_{kd} w_{alcj} s_{el}^{cb} + \sum_{c,d} w_{abcd} s_{el}^{cd} \\
 & + \sum_c w_{ac} s_{ej}^{cb} + \sum_d w_{bd} s_{ej}^{ad} - \sum_l w_{lj} s_{el}^{ab} \\
 & + \sum_f s_{fj}^{ab} g_{fe}. \tag{66}
 \end{aligned}$$

Amplitude equations that are equivalent to the EA-EOM-CC equations

$$g_{a'e} + \sum_{c'} w_{a'c'} s_{e'}^{c'} - \sum_f (g_{fe} + w_{fb'} s_{e'}^{b'}) s_{a'}^f = 0, \tag{67}$$

$$g_{baje} + \sum_{c'} w_{bajc'} s_{e'}^{c'} - \sum_{f,c'} s_{fj}^{ab} w_{fc'} s_{e'}^{c'} = 0.$$

Finally the *pphh* elements of  $\hat{G}$  vanish due to satisfaction of the CCSD equations

$$g_{aaii} = w_{aaii} = 0. \tag{68}$$

This concludes the list of transformed one- and two-particle matrix elements of  $\hat{G}$ .

### III. EXAMPLES OF DOUBLE IONIZATION AND DOUBLE ATTACHMENT CALCULATIONS

Calculations of double ionization potentials are immediately useful to interpret Auger spectra.<sup>63</sup> Currently we limit

TABLE I. Auger spectrum of the HF molecule.

Sym.	Char.	DIP		Excitation energy w.r.t. $^3\Sigma^-$		
		TDA	STEOM	TDA	STEOM	MRCI <sup>a</sup>
$^3\Sigma^-$	$1\pi^{-2}$	55.72	47.82	...	...	...
$^1\Delta$	$1\pi^{-2}$	58.07	51.00	2.35	3.18	3.0
$^3\Pi$	$3\sigma^{-1}\pi^{-1}$	57.67	51.27	1.95	3.46	3.4
$^1\Sigma^+$	$1\pi^{-2}$	59.30	52.44	3.58	4.62	4.6
$^1\Pi$	$3\sigma^{-1}\pi^{-1}$	59.92	54.30	4.20	6.48	6.3
$^1\Sigma^+$	$3\sigma^{-2}$	63.33	59.08	7.71	11.26	11.2
$^3\Pi$	$2\sigma^{-1}\pi^{-1}$	79.64	70.01	23.92	22.19	22.1
$^3\Sigma^+$	$2\sigma^{-1}3\sigma^{-1}$	81.55	73.38	25.83	25.56	25.5
$^1\Pi$	$2\sigma^{-1}\pi^{-1}$	88.55	79.72	32.84	31.90	31.4

<sup>a</sup>From Ref. 68.

ourselves to the calculation of energies of the doubly ionized states but we note that in assignments of Auger spectra the intensities of the transitions play a crucial rôle and depend on the particular site where the core-ionization takes place. This provides very useful information and Tarantelli *et al.*<sup>64,65</sup> introduced the concept of foreign imaging to explain these phenomena. To illustrate the DIP-STEOM-CC method we consider the HF molecule. In the calculations we used a TZ2P basis set<sup>66,67</sup> and the HF internuclear distance is taken to be 1.7329 a.u. To make the second transformation in STEOM-CC we first calculate the ionization potentials corresponding to the  $2\sigma$  (39.14 eV),  $3\sigma$  (19.82 eV), and  $1\pi$  (15.84 eV) states. In Table I we show the results of a DIP-TDA calculation using the bare Hamiltonian matrix elements and STEOM-CCSD results using the doubly transformed Hamiltonian. It is seen that STEOM and TDA results differ by 4–10 eV. In a recent paper<sup>68</sup> the Auger spectrum of HF was obtained at the MRCI level. The energies of the doubly ionized states were given with respect to the core-hole, as actually measured when taking the Auger spectrum. To make the comparison we report the excitation energies w.r.t. to the  $^3\Sigma^-$  ground state of the doubly ionized states. Our results compare nicely to the MRCI results. Let us note that the final diagonalization in STEOM is over the  $2h$  configurations in HF, and this leads to diagonalization problems of very small dimensions of the order of 1–10 determinants, for example.

Another possible application of DIP-STEOM-CC is the calculation of ionization spectra of doublet radicals. In this case we start from the closed-shell anion. The ground state of the radical corresponds to the first ionized state of the anion, of course, and from the double ionization potentials of the anion we can obtain the ionization potentials of the neutral radical. Doubly ionized states with at least one vacancy in the HOMO correspond to principal ionized states of the neutral, which can be either singlet or triplet states. As an example we consider the F atom, using again the TZ2P basis set. The  $2s$  and  $2p$  orbitals were taken to be active. Results are collected in Table II. The ionization potential of  $F^-$  (or electron affinity of F) is calculated to be 2.53 eV, compared to the experimental value of 3.40 eV. The electron affinity of the F atom is notoriously difficult to calculate,<sup>69</sup> but we do not expect that this influences very much the calculation of the ionization potentials of the F atom. As seen from Table II

TABLE II. Photo-electron spectrum of the fluorine atom.

Excitation	DIP-TDA	DIP-STEOM		Expt.
		PT	CC	
$2s^2 2p^4 \ ^3D$	23.41	17.62	17.55	17.4 <sup>a</sup>
$2s^2 2p^4 \ ^1D$	25.57	20.64	20.58	20.0 <sup>b</sup>
splitting	2.16	3.02	3.03	2.6 <sup>b</sup>
$2s^2 2p^4 \ ^1S$	27.61	23.34	23.27	23.0 <sup>b</sup>
$2s 2p^5 \ ^3P$	46.34	37.81	37.78	37.9 <sup>b</sup>
$2s 2p^5 \ ^1P$	55.25	47.95	47.92	47.1 <sup>b</sup>
splitting	8.91	10.14	10.14	9.2 <sup>b</sup>
$s^2 2p^5 \ ^2P$ (EA)	4.19	2.46	2.53	3.40 <sup>b</sup>

<sup>a</sup>Reference 74.<sup>b</sup>Extracted from data in Refs. 68 and 74.

STEOM-PT and STEOM-CC results are found to be in excellent agreement, while agreement with experiment appears better for the triplet states than the singlet states. The improvement of DIP-STEOM over DIP-TDA results, which are consistently too high is significant. Let us emphasize here that the ionized states of the F atom are described in the current scheme using orbitals for the closed-shell F<sup>-</sup> atom. This means that large relaxation effects will be present that have to be described by correlation. This in general is not a very efficient strategy. Taking into account the very small configuration space in the final diagonalization step we expect the results to be rather sensitive to the choice of reference state.

Double electron attachment calculations can be used to conveniently calculate excitation spectra of open-shell molecules like oxygen, or atomic excitation spectra of, for example, carbon or silicon which have two electrons out of a closed shell structure. Adding two electrons to the Be configuration of C<sup>2+</sup> yields all low-lying excited states of carbon as illustrated in Table III. Let us emphasize that incorporation of both spin and spatial symmetry is trivial in this scheme starting from a closed-shell parent state. In the STEOM calculations we used Sadlej's POL1 basis set,<sup>70</sup> and the 2*p*, 3*s*, 3*p*, 3*d*, 4*s*, and 4*p* orbitals were selected as active orbitals. From Table III we find a significant difference between STEOM-CC and STEOM-PT results. The

TABLE III. Carbon excitation spectrum.

Excitation	Double attachment schemes			Expt. <sup>a</sup>
	TDA	STEOM-PT	STEOM-CC	
$2p^2 \ ^3P$	0.0	0.0	0.0	0.0
$2p^2 \ ^1D$	1.35	1.35	1.34	1.26
$2p^2 \ ^1S$	2.81	3.36	2.77	2.68
$2p 3s \ ^3P^0$	6.32	7.77	7.55	7.48
$2p 3s \ ^1P^0$	6.45	7.92	7.70	7.68
$2p 3p \ ^1P$	7.57	8.60	8.40	8.54
$2p 3p \ ^3D$	7.69	8.86	8.66	8.64
$2p 3p \ ^3S$	7.88	9.08	8.86	8.77
$2p 3p \ ^3P$	8.18	9.12	8.88	8.85
$2p 3p \ ^1D$	8.46	9.46	9.23	9.00
$2p 3p \ ^1S$	8.88	9.86	9.55	9.17

<sup>a</sup>Reference 74.

TABLE IV. Vibrational frequencies for ozone.

Method	Basis	Geometry		Harmonic Vibrational frequencies (cm <sup>-1</sup> )		
		<i>r<sub>e</sub></i>	Θ <sub><i>e</i></sub>	ω <sub>1</sub> ( <i>a</i> <sub>1</sub> )	ω <sub>2</sub> ( <i>a</i> <sub>1</sub> )	ω <sub>3</sub> ( <i>b</i> <sub>2</sub> )
CCSD <sup>a</sup>	DZP	1.263	117.4	1256	748	1240
2R-MRCI <sup>b</sup>	DZP	1.261	116.5	1235	761	1338
2R-AQCC <sup>b</sup>	DZP	1.292	116.1	1070	694	1070
CCSDT <sup>a</sup>	DZP	1.286	116.7	1141	705	1077
DIP-STEOM	DZP	1.286	115.9	1108	718	932
CCSDT <sup>c</sup>	cc-PVTZ	1.274	116.8	1163	717	1117
DIP-STEOM	cc-PVTZ	1.274	116.0	1135	715	1013
Expt. <sup>d</sup>		1.272	116.8	1135	716	1089

<sup>a</sup>Reference 41.<sup>b</sup>Reference 42.<sup>c</sup>Reference 75.<sup>d</sup>References 76 and 77.

ground state of the doubly charged cation contains significant double excitation character. At the CCSD level we find a coefficient of  $-0.156$  for the  $2s^2 \rightarrow 2p^2$  excitation while at the MBPT<sup>2</sup> level this coefficient has the value  $-0.079$ . Relatedly, the CCSD correlation energy is  $-0.08639$  a.u. while the second-order correlation energy is  $-0.05374$ . This behavior seems to be typical of doubly charged cations. The empty valence orbitals are low in energy and quite compact. This leads to large correlation effects, and second-order perturbation theory is certainly not adequate to describe the doubly charged cation, while CCSD seems questionable. On the other hand in the low-lying excited states the *p*-orbitals will be doubly occupied and the troublesome excitation is absent from the neutral states. It seems, therefore, that our scheme introduces some artificial correlation in the treatment of the excited states, making the problem harder than it needs to be. In addition, as in the DIP scheme we use orbitals that are optimized for a state that differs by two electrons from the state we are interested in.

Both the DIP- and DEA-STEOM methods can be used to obtain very economical descriptions of traditional multi-reference situations. In the DIP scheme the parent state is a closed-shell determinant, but the actual states of interest contain two fewer electrons. This allows one to study cases that qualitatively require a linear combination of determinants in which in addition to a closed-shell "core" one has two electrons in two spatial orbitals, or four electrons in three orbitals, etc. At first, the partially occupied orbitals are filled completely, creating a di-anion(!) and the dynamical correlation contributions are evaluated. In the final step an effective Hamiltonian is diagonalized over the two-hole configurations with respect to the di-anion to obtain a qualitatively and quantitatively correct nondynamical correlated description of the neutral system. The DEA method can similarly be used for cases that require distributing two-electrons on top of a closed-shell, hence two electrons in two spatial orbitals, or two electrons in three orbitals, etc. This in principle allows the description of bi-radicals (singlets and triplets in a balanced way) and a surprising number of chemical systems and transition states.

In Table IV the results are presented of the calculation of vibrational frequencies of ozone, a notorious and well studied multireference problem.<sup>41,42</sup> The CCSD calculation is based on the di-anion, a nonexistent species. This illustrates the mathematical nature of the procedure. The essence is that one can access all important configurations by deleting two orbitals from the di-anion determinant, and one can base the definition of ‘‘excitations’’ and normal ordering on any state, physical or artificial.

The definition of the orbitals that define the di-anion determinant requires special attention since di-anion orbitals are too diffuse to be useful for the neutral. Here we used neutral Hartree–Fock orbitals, and defined the extra virtual orbital that defines the di-anion using a  $\bar{V}^{N-1}$  potential.<sup>71</sup> Results do not depend too critically on the precise scheme.

As seen from Table IV the DIP-STEOM frequencies and geometry compare very nicely to other highly correlated methods. The troublesome asymmetric stretch frequency  $\omega_3$  is very sensitive to the basis set and improvement of the basis set leads to higher frequencies. All quoted methods will eventually overshoot, but the highly efficient DIP-STEOM method is likely to be very close in the limit of a large basis set.

To summarize, relaxation effects will be important in DEA-STEOM and DIP-STEOM calculations, and it is probably better to use a set of orbitals that is optimized in some way for the states of interest. DEA-STEOM in addition appears to include some artificial correlation effects. We think that both methods can be improved by optimizing the parent state (or closed-shell) cluster coefficients explicitly for the state of interest. The theory behind such an open-shell CC scheme has been outlined in a previous paper.<sup>36</sup>

#### IV. THE RELATION BETWEEN STEOM-CC AND FSCC: THE ROLE OF THE ACTIVE SPACE

As shown in Sec. II the  $S$ -amplitudes in STEOM that define the second similarity transformation are identical to the FSCC amplitudes for the EA (or (1,0) sector), and the IP [or (0,1) sector]. Here we wish to establish the relation between STEOM and FSCC for the subsequent calculation of excitation energies, double ionization potentials or double electron affinities, corresponding to the (1,1), (0,2), and (2,0) sectors in Fock space, respectively. Let us focus on the excitation energy sector, to facilitate the discussion. In STEOM the procedure is straightforward. We simply diagonalize the transformed Hamiltonian  $\hat{G}$  over the space of mono-excited states (or  $1h1p$  configurations). To make the connection with FSCC we view this diagonalization process in two steps.<sup>72</sup> We partition the diagonalization space into an active space (determined by all excitations among active orbitals only), denoted  $P$ , and the orthogonal complement within the restricted diagonalization space  $Q$ . Define a transformation matrix  $U = e^X = 1 + X$ , where  $X = QXP$ . This defines a once more transformed Hamiltonian,  $F = U^{-1}GU$  say, and we require the  $QFP$  components to vanish, such that eigenvalues can be extracted by diagonalizing  $FPF = H_{\text{eff}}$ . Hence we have

$$UF = GU; \quad (69)$$

$$QFP = 0 \rightarrow U(Q + P)FP = UFPF = GUP.$$

The equations that determine the transformation  $U$  (or  $X$ ) are equivalent to the so-called Bloch equation

$$UH_{\text{eff}}P = GUP; \quad H_{\text{eff}} = PGUP. \quad (70)$$

In many-body language the transformation operator for the excitation energy sector can be defined as  $\hat{U} = \{e^{\hat{S}^{(1,1)}}\}$  (to be precise  $X = -\langle Q | \hat{S}^{(1,1)} | P \rangle$ ), because there is a contraction over a hole line, see Sec. II), where

$$\hat{S}^{(1,1)} = \sum_{a,i} \sum_{e,m} s_{ei}^{am} \{ \hat{a}^\dagger \hat{e} \hat{m}^\dagger \hat{i} \}. \quad (71)$$

The restriction in the summation excludes cases in which both  $a$  and  $i$  are active. In this alternative Bloch-equation strategy to STEOM the total transformation for the excitation sector can therefore be represented as a sequence of similarity transformations

$$e^{\hat{T}} \{ e^{\hat{S}^{(0,1)}} + \hat{S}^{(1,0)} \} \{ e^{\hat{S}^{(1,1)}} \}. \quad (72)$$

This presentation allows a direct comparison to FSCC. In FSCC the so-called wave operator is represented, not as a sequence of normal ordered exponentials, but as one single normal ordered operator

$$\{ e^{\hat{T}} + \hat{S}^{(0,1)} + \hat{S}^{(1,1)} \} = e^{\hat{T}} \{ e^{\hat{S}^{(0,1)}} + \hat{S}^{(1,0)} + \hat{S}^{(1,1)} \}, \quad (73)$$

and the amplitudes are determined from the Bloch equation as above, while eigenvalues are obtained by subsequent diagonalization of the effective Hamiltonian. If all orbitals are active results will be identical, since in both FSCC and STEOM one simply diagonalizes the full effective Hamiltonian. Likewise, if the active space is large enough STEOM and FSCC results will be virtually identical, since we might as well diagonalize over the active part of the transformed Hamiltonian. However, we note that in practice it may be difficult to solve the final Bloch equation in FSCC, since it requires a complete decoupling of the active and complementary spaces. Some of the higher lying (and noninteresting) states may well be near-degenerate with states in the complementary space, leading to the so-called intruder state problem. In STEOM we do not proceed via the Bloch equation but solve for the eigenvectors of interest directly. This is numerically a more stable procedure. Let us note here that recently Meissner<sup>62</sup> has shown that the intruder state problem in FSCC can be avoided by reformulating the final step as a similarity transformation in Hilbert space, and using the formalism of intermediate Hamiltonians. STEOM and FSCC can also be compared for higher sectors in Fock space. In this case these methods differ more significantly, and the STEOM procedure using a sequence of similarity transforms can be expected to converge more quickly.<sup>11</sup>

From the above discussion it is clear that FSCC and STEOM are very closely related methods, but we wish to emphasize that they are conceptually different. In the derivation of FSCC, one imposes the so-called subsystem embedding conditions. Hence to calculate an excited state, one has

TABLE V. Excitation spectrum of *s*-tetrazine: Comparison between FSCC and STEOM-CC.

State	FSCC <sup>a</sup>	STEOM-CC	% active	Expt. <sup>a</sup>
<sup>1</sup> B <sub>3u</sub>	2.28	2.35	98.9%	2.25
<sup>1</sup> A <sub>u</sub>	3.44	3.48	99.1%	
<sup>1</sup> B <sub>1g</sub>	4.98	5.02	96.0%	
<sup>1</sup> B <sub>2u</sub>	5.25	5.22	98.3%	4.43–5.40
<sup>1</sup> B <sub>2g</sub>	5.77	5.83	97.2%	3.88/4.06
<sup>1</sup> A <sub>u</sub>	5.83	5.90	97.9%	
<sup>3</sup> B <sub>3u</sub>	1.48	1.62	97.3%	1.69
<sup>3</sup> A <sub>u</sub>	3.14	3.22	97.9%	
<sup>3</sup> B <sub>1u</sub>	3.97	4.02	92.6%	
<sup>3</sup> B <sub>1g</sub>	3.99	4.10	91.5%	
<sup>3</sup> B <sub>2u</sub>	4.88	4.89	99.6%	
<sup>3</sup> B <sub>2g</sub>	5.01	5.13	95.1%	
<sup>3</sup> A <sub>u</sub>	5.30	5.41	96.4%	

<sup>a</sup>Reference 43.

to solve for the ground state and several ionized and attached states to determine all the amplitudes. This procedure is more or less imposed in order to have the same number of equations and parameters. However, the physics or the idea behind this approach has never been very clear in our opinion. In STEOM, second quantized matrix elements of the transformed Hamiltonian are equated to zero, and this very clearly reduces the coupling between determinants of different excitation level, and allows one to diagonalize over small subspaces. The idea behind STEOM is transparent and goes back to papers on Fock space coupled cluster theory by Stolarczyk and Monkhorst.<sup>21–24</sup>

As mentioned above the active space plays a rôle in the comparison of FSCC and STEOM-CC. In general, the magnitude of the active component in the final STEOM excited states is a good measure for the quality of the active space. In most calculations we would like an active component of over 98%. This indicates that enlargement of the active space is not significantly going to change the result. Let us emphasize that the transformations in STEOM account primarily for dynamical correlation. If the active component drops below threshold it means, therefore, that dynamical correlation is missing. The rôle of the active space in STEOM is different than in CASPT2 or MCSCF calculations where one often is satisfied with an active character that is constant over the states of interest, but which can be as low as 70% or even 50%.

To draw a numerical comparison between the STEOM and FSCC methods we consider the *s*-tetrazine molecule at the same geometry and using the same DZP basis set as in the earlier FSCC study.<sup>43</sup> The active space, consisting of the six highest occupied and two lowest virtual orbitals, is also chosen to be identical. The ionization spectrum and electron affinities of *s*-tetrazine is reproduced exactly in the current STEOM-CC calculation, as should be the case. In Table V we show the low-lying singlet and triplet states. The average deviation between the two methods over 14 states is 0.07 eV. The STEOM-CC results fairly consistently fall a little above the FSCC results (the <sup>1</sup>B<sub>2u</sub> state is the sole exception). The singlet states agree a little better (average deviation 0.04 eV)

than the triplet states (average deviation 0.09 eV), and this is roughly reflected by the magnitude of the active component, which tends to be less in the triplet states. However, we note there is no clear correlation between the magnitude of the active component and the deviation of the FSCC and STEOM-CC results.

To investigate further the rôle of the active orbitals in STEOM we consider the CO molecule using Sadlej's POL1 basis set<sup>70</sup> at an internuclear distance of 1.1282 Å. The choice of active occupied orbitals is usually pretty clear from the excitations under consideration. For CO the 5σ orbital (at 14.00 eV) and the 1π orbitals (at 16.84 eV) are obviously needed in the active space. However, also the 4σ orbital (at 19.63 eV) plays a part in the dynamical correlation for in particular the excited states of Π symmetry. The numbers in parentheses are ionization potentials at the IP-EOM-CC level. The choice of active virtual orbitals is less clear cut. Canonical Hartree–Fock orbitals make excellent approximations for electron-attached states, but they are often too diffuse for a compact description of excited states. This means that in terms of canonical Hartree–Fock orbitals often many determinants are required to describe excited states, and consequently a large active space is needed in the STEOM calculation. This can be seen in Table VI, where we gradually increase the active space from 0 to 1 to 2 to 3 virtual orbitals of both σ and π symmetry. In the final, almost saturated, calculation the active space consists of six orbitals of σ symmetry, four pairs of orbitals of π symmetry and one pair of orbitals of δ symmetry. The effect of correlation and choice of active space on valence excitations, in general, is larger than on Rydberg excited states. In addition, excitations into the valence π\* orbitals only slowly saturate with increase of the active space. It seems that an active component of over 95% is required in order to be converged within 0.05–0.1 eV, in particular for valence excited states.

An alternative to increasing the active space is a rotation of the virtual orbitals, such that they provide a more compact description of excited states. In the last two columns of Table VI we use so-called  $\bar{V}^{N-1}$  virtual orbitals.<sup>71</sup> They are defined by diagonalizing the virtual–virtual block of a Fock-matrix corresponding to the Hartree–Fock density matrix scaled by a factor  $(N_{\text{el}} - 1)/N_{\text{el}}$ .<sup>71</sup> This generates a more attractive potential and less diffuse virtual orbitals. The details of this potential do not seem very important, and we made the above simple choice because the new Fock matrix automatically has the same symmetry as the old one. Let us note that this definition of the virtual orbitals does not influence the CCSD, IP-EOM-CC, and EA-EOM-CC calculations, as long as the same final states are considered. The precise definition of the virtuals determines which transformed two-electron elements  $g_{abej}$  are transformed to zero, and hence it determines part of the remaining coupling to the doubly excited configurations, which is not included in STEOM. The other part stems from three-particle interactions in the transformed Hamiltonian which are neglected. Operationally the choice of orbitals only influences the normalization condition in the determination of  $\hat{S}$  (see Sec. II). From Table VI we find that

TABLE VI. Excitation energies (eV) for CO: Comparison of active spaces.

State	Exc.	Active space						
		0 <sup>a</sup>	1 <sup>b</sup>	2 <sup>c</sup>	3 <sup>d</sup>	Final <sup>e</sup>	1 <sup>f</sup>	2 <sup>g</sup>
A <sup>1</sup> Π(V)	5σ→2π	9.78	9.33	8.82	8.61	8.59	8.56	8.64
% active		0%	63%	92%	98.7%	99.1%	93.1%	95.0%
I <sup>1</sup> Σ <sup>-</sup> (V)	1π→2π	11.43	11.04	10.33	10.08	10.06	9.87	10.08
% active		0%	47%	86%	98.7%	99.1%	97.8%	98.2%
D <sup>1</sup> Δ(V)	1π→2π	11.57	11.19	10.47	10.24	10.21	10.00	10.22
% active		0%	48%	87%	98.8%	99.2%	97.3%	97.7%
B <sup>1</sup> Σ <sup>+</sup> (R)	5σ→6σ	11.41	11.20	11.10	11.08	11.06	11.01	11.06
% active		0%	89%	94%	97.2%	99.6%	83.3%	97.3%
C <sup>1</sup> Σ <sup>+</sup> (R)	5σ→7σ	11.79	11.77	11.61	11.62	11.56	11.71	11.60
% active		0%	1%	94%	97.4%	99.9%	21.4%	94.5%
E <sup>1</sup> Π(R)	5σ→3π	12.11	12.19	11.88	11.87	11.81	11.99	11.85
% active		0%	55%	94%	95.6%	99.2%	2.6%	96.6%
a <sup>3</sup> Π(V)	5σ→2π	7.32	7.06	6.57	6.37	6.36	6.34	6.41
% active		0%	35%	86%	97.5%	98.1%	96.4%	96.4%
a' <sup>3</sup> Σ <sup>+</sup> (V)	1π→2π	9.52	9.23	8.68	8.42	8.43	8.27	8.44
% active		0%	35%	78%	97.0%	97.6%	98.3%	98.9%
d <sup>3</sup> Δ(V)	1π→2π	10.50	10.18	9.58	9.34	9.33	9.18	9.35
% active		0%	40%	82%	97.7%	98.4%	98.1%	98.4%
e <sup>3</sup> Σ <sup>-</sup> (V)	1π→2π	11.23	10.86	10.22	9.97	9.96	9.80	9.98
% active		0%	45%	85%	98.6%	99.0%	97.8%	98.4%

<sup>a</sup>0: No active virtual space.

<sup>b</sup>1a: Active virtual space: 6σ, 2π; Canonical HF orbitals.

<sup>c</sup>2a: Active virtual space: 6 to 7σ, 2 to 3π; Canonical HF orbitals.

<sup>d</sup>3a: Active virtual space: 6–8σ, 2–4π; Canonical HF orbitals.

<sup>e</sup>Final a: Active virtual space: 6–11σ, 2–5π, 1δ; Canonical HF orbitals.

<sup>f</sup>1b: Active virtual space: 6σ, 2π;  $\bar{V}^{N-1}$  orbitals.

<sup>g</sup>2b: Active virtual space: 6 to 7σ, 2 to 3π;  $\bar{V}^{N-1}$  orbitals.

the active component using  $\bar{V}^{N-1}$  virtual orbitals is increased appreciably for small active spaces. With two active virtual orbitals of σ and π symmetry [column 2(b)] the valence excited states are close to convergence, and this is reflected by the active space component, which is well over 95%. Interestingly, the excitation energies in column 1(b) usually lie below the converged energies. This is a little peculiar because it implies that the total energy of the excited state is lower for the less accurate scheme (the ground state is unaffected). Evidently STEOM does not adhere even approximately to a variational principle. In addition the active space component in column 1(b) is usually only slightly smaller than in column 2(b), while the difference in excitation energy can be as large as 0.2 eV. Whereas the behavior using Hartree–Fock orbitals is very smooth, but rather slowly convergent, the behavior using  $\bar{V}^{N-1}$  appears more erratic, and the active space component appears not to be a good measure for convergence. Evidently, more work needs to be done to select the active space in STEOM. For now we recommend using Hartree–Fock orbitals and the active-space diagnostic.

## V. THE RELATION BETWEEN STEOM-CC AND EOM-CC: THE RÔLE OF IMPLICIT TRIPLE EXCITATIONS

The final wave function in STEOM can be written

$$|\Psi_\lambda\rangle = \sum_{i,a} e^{\hat{T}} \{e^{\hat{S}}\} |\Phi_i^a\rangle r_i^a(\lambda) + e^{\hat{T}} |\Phi_0\rangle r_0(\lambda). \quad (74)$$

If we substitute this parameterization into the Schrödinger equation, multiply by  $e^{-\hat{T}}$  and project on the space of singly and doubly excited determinants we find

$$\sum_{i,a} \langle \Phi_K | \hat{H} \{e^{\hat{S}}\} | \Phi_i^a \rangle r_i^a(\lambda) = \sum_{i,a} \langle \Phi_K | \{e^{\hat{S}}\} | \Phi_i^a \rangle r_i^a(\lambda) E_\lambda. \quad (75)$$

Due to the satisfaction of the CCSD equations  $r_0$  does not enter these equations. Expanding the normal ordered exponential

$$\begin{aligned} & \sum_{i,a} \langle \Phi_K | \hat{H} (1+S) | \Phi_i^a \rangle r_i^a(\lambda) \\ & + \sum_{i,a} \langle \Phi_K | \hat{H} \{ \frac{1}{2} \hat{S}^2 \} | \Phi_i^a \rangle r_i^a(\lambda) \\ & = \sum_{i,a} \langle \Phi_K | 1 + \hat{S} | \Phi_i^a \rangle r_i^a(\lambda) E_\lambda. \end{aligned} \quad (76)$$

If we define

$$\sum_{i,a} \langle \Phi_{kl}^{cd} | \hat{S} | \Phi_i^a \rangle r_i^a(\lambda) = r_{kl}^{cd}(\lambda), \quad (77)$$

and introduce a short-hand notation  $r_L(\lambda)$  for the combined expansion coefficients the equation reads

TABLE VII. Behavior of charge transfer excitation in  $\text{Be}\cdots\text{C}_2$  with increasing interunit distance.

$R$ (Å)	$-e^2/R$ (eV)	CIS	EE-(IP+EA) (in eV) STEOM-CCSD	EOM-CCSD	$\Delta$
5.0	-2.880	-2.868	-2.931	-2.937	-0.006
8.0	-1.800	-1.793	-1.797	-1.736	0.061
10.0	-1.440	-1.436	-1.438	-1.375	0.063
100.0	-0.144 0	-0.144 0	-0.144 0	-0.0799	0.064
1 000.0	-0.01 440	-0.014 40	-0.014 40	0.0496	0.064
10 000.0	-0.001 440	-0.001 440	-0.001 440	0.0626	0.064

$$\sum_L \langle \Phi_K | \hat{H} | \Phi_L \rangle r_L(\lambda) + \sum_{i,a} \langle \Phi_K | \hat{H} \{ \frac{1}{2} \hat{S}^2 \} | \Phi_i^a \rangle r_i^a(\lambda) = r_K(\lambda) E_\lambda. \quad (78)$$

If we now assume that the coefficients  $r_L(\lambda)$  are independent parameters, to be determined, this equation is equivalent to the EE-EOM-CCSD equations except for a triples correction given by the second term. This triples correction leads to a modification (or dressing) of the EOM-CCSD matrix-elements and was proposed by Meissner and Bartlett.<sup>44,45</sup> STEOM and EOM can both be related to the above dressed EOM equation. In EOM-CCSD the triple correction is absent, in STEOM the doubles part of the eigenvector is obtained from Eq. (77), where  $\hat{S}$  is obtained from the IP-EOM and EA-EOM equations, and the eigenvalue problem is restricted to the space of single excitations.

The relevance of the triple excitations becomes most evident if one considers a model charge transfer excitation between two separated fragments. In the limit that the fragments are at infinite separation the excitation energy reduces to the sum of the ionization potential ( $\text{IP} = E^{N-1} - E^N$ ) on one subsystem and the electron affinity ( $\text{EA} = E^{N+1} - E^N$ ) at the other. The wave function becomes the (antisymmetrized) product of the fragment wave functions. If the ionized state is described by  $1h$  and  $2h1p$  determinants and the attached state is described by  $1p$  and  $2p1h$  determinants it follows that the analogous description of the charge transfer excited state requires up to  $3h3p$  or triple excitations. We will refer to the above property as charge transfer separability. This property is assured by the fully linked nature of the diagrams representing the excitation energy. Operationally it requires that excited states, ionized states and electron attached states are all calculated by precisely the same method. The charge transfer excitation energy should satisfy

$$EE = \text{IP} + \text{EA} - \frac{e^2}{R}, \quad (79)$$

for large separation  $R$ . The correction term accounts for the long range Coulombic interaction between two charged fragments. In practice it may seem difficult to calculate all relevant quantities at precisely the same level of approximation. However for methods based on second quantization, IP's and EA's can be calculated using a program to calculate excitation energies. To calculate IP's using the  $EE$  code, one adds one "virtual molecular orbital"  $\chi_0$ , which is identically zero. So all transformed integrals involving this orbital are

zero. Excitations into  $\chi_0$  then correspond to ionizations, and separate off from the eigenvalue problem. Similarly, to calculate EA's using an excitation energy code one adds one occupied MO that is identically zero. Excitations from this MO into the virtual space amount to electron attachment. It is clear that this scheme can be used for most excitation energy methods. In case of the EE-EOM-CC method the above trick yields precisely the IP-EOM-CC and EA-EOM-CC results. EE-EOM-CCSD or CCSDLR (linear response) theory does not satisfy charge transfer separability however, due to the absence of triples. The dressing proposed by Meissner and Bartlett<sup>44,45</sup> restores charge transfer separability. The dressed EOM method reduces to the STEOM method for the charge transfer excitations in the case of large separation and STEOM is charge transfer separable. Interestingly CIS is also charge transfer separable. The relevant IP's and EA's in this case are the Koopmans' values, obtained by diagonalizing the Fock-matrix.

Let us consider an example of a charge transfer excitation for which the effect of triples can be expected to be important. We consider the  $\text{Be}\cdots\text{C}_2$  system in  $C_{2v}$  symmetry where the  $\text{C}_2$  unit is placed perpendicular to the axis connecting Be and the midpoint X of  $\text{C}_2$ . The  $\text{C}_2$  internuclear distance is kept fixed at 1.268 Å and we use a VDZP basis<sup>73</sup> on both C and Be. The ionization potential of Be is calculated as 9.279 413 97 eV at the IP-EOM-CC level, while the electron affinity of  $\text{C}_2$  is -2.752 260 97 eV at the EA-EOM-CC level. In Table VII we present the results from STEOM-CCSD and EE-EOM-CCSD calculations for a variety of distances  $R = \text{BeX}$ . The quantity of interest is the difference

TABLE VIII. Excitation energies (eV) for CO.

State	Exc.	STEOM			EOMCC	Expt. <sup>a</sup>
		PT	CC	CC no T		
$A \ ^1\Pi(V)$	$5\sigma \rightarrow 2\pi$	8.55	8.59	8.71	8.76	8.51
$I \ ^1\Sigma^-(V)$	$1\pi \rightarrow 2\pi$	9.91	10.06	10.24	10.19	9.88
$D \ ^1\Delta(V)$	$1\pi \rightarrow 2\pi$	10.05	10.21	10.34	10.31	10.23
$B \ ^1\Sigma^+(R)$	$5\sigma \rightarrow 6\sigma$	11.01	11.06	11.13	11.16	10.78
$C \ ^1\Sigma^+(R)$	$5\sigma \rightarrow 7\sigma$	11.55	11.56	11.58	11.64	11.40
$E \ ^1\Pi(R)$	$5\sigma \rightarrow 3\pi$	11.78	11.81	11.82	11.84	11.53
$a \ ^3\Pi(V)$	$5\sigma \rightarrow 2\pi$	6.27	6.36	6.55	6.41	6.32
$a' \ ^3\Sigma^+(V)$	$1\pi \rightarrow 2\pi$	8.45	8.43	8.61	8.47	8.51
$d \ ^3\Delta(V)$	$1\pi \rightarrow 2\pi$	9.25	9.33	9.52	9.46	9.36
$e \ ^3\Sigma^-(V)$	$1\pi \rightarrow 2\pi$	9.84	9.96	10.09		9.88

<sup>a</sup>As reported in Ref. 7.

TABLE IX. Excitation energies (in eV) for H<sub>2</sub>O. Comparison with full CI.

State Sym.	Char.	EOM CCSD	EOM-CCSDT-3	STEOM			CCSD no T	FCI <sup>a</sup>
				CC3 <sup>a</sup>	PT	CCSD		
2 <sup>1</sup> A <sub>1</sub>	2a <sup>1</sup> →3a <sup>1</sup>	9.806	9.855	9.855	9.645	9.772	9.821	9.874
1 <sup>1</sup> B <sub>1</sub>	1b <sub>1</sub> →3a <sup>1</sup>	7.375	7.426	7.427	7.243	7.343	7.391	7.447
1 <sup>1</sup> B <sub>2</sub>	2a <sup>1</sup> →2b <sup>2</sup>	11.525	11.587	11.591	11.400	11.520	11.546	11.612
1 <sup>1</sup> A <sub>2</sub>	1b <sub>1</sub> →2b <sup>2</sup>	9.122	9.185	9.187	9.036	9.132	9.164	9.211
	Average error	0.081	0.023	0.021	0.179	0.097	0.056	

<sup>a</sup>From Ref. 51.

between the excitation energy and the sum of the IP and the EA. It is seen that the STEOM-CCSD result attains the limiting  $-1/R$  behavior very quickly. The same is true for EOM-CCSD, except that the asymptotic EOM-CCSD excitation energy lies about 0.064 eV above the STEOM-CCSD=IP+EA limit. This is the charge transfer separability error of EOM-CCSD in this particular case. We also included the CIS results, which show similar behavior as STEOM-CC.

In order to obtain a further estimate on the effect of implicit triple excitations in STEOM for “normal” excitations we can discard the relevant terms (quadratic in  $\hat{S}$ ) from the matrix elements of  $\hat{G}$ . We label these results “STEOM-CC-no-T”. One would expect the results from this approximate STEOM treatment to be closer to EOM-CC results than STEOM results themselves. (Let us note that discarding the triples does not have an effect on charge transfer separability, because in STEOM-CC-no-T we are still diagonalizing a connected Hamiltonian  $\hat{G}$  over the space of single excitations. Only the one-particle operators in  $\hat{G}$  contribute to the asymptotic limit, and these are not affected by the approximation.)

As an example we consider again the CO molecule using Sadlej’s polarized basis set<sup>70</sup> at an internuclear distance of 1.1282 Å. In Table VIII we compare STEOM-CC, STEOM-CC-no-T, and EOM-CC results. It is seen that for the valence excited states the inclusion of triples reduces the excitation energy by 0.1 to 0.2 eV. For the singlet states the STEOM-CC-no-T results are consistently closer to EOM-CC, and we think this very clearly shows the effect of implicit triples in the STEOM-CC method. For comparison we have also included STEOM-PT results, and it is seen that the effect of

triples is of the same order of magnitude as the replacement of CCSD coefficients with their first-order analogs. For Rydberg states the effect of triples is much less, and this can be attributed to the fact that the EA-EOM-CC amplitudes for the corresponding attached orbitals have very little  $2p1h$  character. This immediately reduces the effect of triple excitations for Rydberg states.

Above we addressed the rôle of implicit triple excitations in STEOM-CC and this appears to be a nice feature that is important for the description of, in particular, valence excited states.<sup>33,48</sup> Let us note that in comparison to EOM-CC or dressed EOM-CC other important effects are not considered in STEOM-CC. As mentioned before we neglect the three-body terms in the transformed Hamiltonian  $\hat{G}$  that is responsible for a remaining coupling between the singly excited determinants and double excitations. In the EOM-picture this means that certain interactions in the doubles-doubles block that “couple the hole and particle” are absent. In STEOM one might say the hole is correlated separately, and the particle is correlated separately. Interactions between the two are absent in the doubles-doubles block of the matrix. Full coupling is present in the other blocks. This will of course have an effect on the accuracy of STEOM-CC results. An estimate of the importance of full particle-hole coupling can be obtained from results from the dressed EOM scheme as proposed by Meissner and Bartlett, but is not considered here.

It is interesting to compare the relative accuracy of the EOM-CC and STEOM-CC methods. At first glance EOM-CCSD appears to be the more complete treatment, but the implicit inclusion of triples favors the STEOM approach. In order to eliminate basis set effects, experimental uncertain-

TABLE X. Excitation energies (in eV) for N<sub>2</sub>. Comparison with full CI.

State Sym.	Char.	EOM CCSD	EOM-CCSDT-3	STEOM			CCSD no T	FCI <sup>a</sup>
				CC3 <sup>a</sup>	PT	CCSD		
<sup>1</sup> Π <sub>g</sub>	3σ <sub>g</sub> →1π <sub>g</sub>	9.665	9.624	9.618	9.544	9.446	9.596	9.584
<sup>1</sup> Σ <sub>u</sub> <sup>-</sup>	1π <sub>u</sub> →1π <sub>g</sub>	10.465	10.345	10.336	10.373	10.368	10.581	10.329
<sup>1</sup> Δ <sub>u</sub>	1π <sub>u</sub> →1π <sub>g</sub>	10.898	10.752	10.727	10.839	10.833	11.008	10.718
<sup>1</sup> Π <sub>u</sub>	2σ <sub>u</sub> →1π <sub>g</sub>	14.009	13.826	13.786	14.026	13.981	14.083	13.608
	Average error	0.200	0.077	0.057	0.156	0.166	0.232	

<sup>a</sup>From Ref. 51.

ties and the issue of nuclear vibrations it is best to compare with full CI calculations. We consider the H<sub>2</sub>O, N<sub>2</sub>, and C<sub>2</sub> molecules for which full CI results for the excited states have recently been reported.<sup>51</sup> In this paper Christiansen *et al.*<sup>51</sup> compared the CC3 method that includes a triple correction to CCLR (or EOM-CCSD) excitation energies to FCI results and these provide very useful benchmark results for our present purpose. Here we include EOM-CCSDT-3<sup>49</sup> results as well. Of course, precisely the same geometry and basis set is used and results for the excitation energies are reported in Tables IX–XI. The excited states for the water molecule are all Rydberg like, and as before there is relatively little difference between EOM-CCSD and STEOM-CC while also the effect of triples is moderate (compare CC3 or EOM-CCSDT-3 results and STEOM-CC-no-T). Replacing the CCSD coefficients with their first-order MBPT analogs tends to lower the excitation energy by  $\sim 0.1$  eV.

The excited states in N<sub>2</sub> are all valence like and consequently inclusion of triples lowers the STEOM excitation energies considerably. This is also true for CC3 or EOM-CCSDT-3 compared to EOM-CCSD. The description of the ground state has only a minor effect on the excitation energies. The <sup>1</sup>Π<sub>u</sub> state of N<sub>2</sub> has substantial double excitation character<sup>51</sup> and is not very well described by either method. Even CC3 has an error of 0.18 eV. A little surprisingly, STEOM-CC and EOM-CC are in close agreement, implying some kind of cancellation between the extra terms included in EOM-CCSD and the missing triples correction.

The ground state of the C<sub>2</sub> molecule suffers from near degeneracy problems and is difficult to describe. Nevertheless excitation energies for both EOM-CCSD and STEOM-CCSD are in fair agreement with the full CI results. STEOM-PT fails completely due to its erroneous description of the ground state. Again triple excitation effects are considerable. Let us note that in Ref. 51 in addition two doubly excited states are described which cannot be obtained in STEOM which is restricted to predominantly singly excited states. Triple excitation EOM-methods were developed initially to describe precisely such doubly excited states,<sup>46</sup> and provide dramatically improved results.

The overall error in comparison to the full CI results is 0.14 eV for EOM-CCSD, 0.19 eV for STEOM-PT, 0.12 eV for STEOM-CC, and 0.40 eV for STEOM-CC-no-T. Inclusion of triples on top of EOM-CCSD as in the EOM-CCSDT-3 method reduces the average error substantially to 0.049 eV, while the average error for CC3 is 0.043 eV. From these comparisons a coherent picture emerges. The implicit triple correction in STEOM-CC is quite important for valence excited states. Compared to our model STEOM-CC-no-T approach excitation energies are often lowered by 0.1–0.2 eV. Relatedly, for valence states EOM-CCSD excitation energies are often a little higher than STEOM-CCSD energies. In fact they are often quite close to the STEOM-CC-no-T results which tend to lie a little higher still. Compared to experiment, excitation energies in EOM-CCSD (and even full CI) are often a little high, and this is partly due to basis sets that are usually optimized for the ground state. STEOM-CCSD excitation energies for valence states therefore tend to

agree a little better with experiment. For Rydberg states the STEOM-CCSD and EOM-CCSD methods are usually very close and triple excitation effects are less important. These conclusions are in agreement with work that has been done to include triple excitation effects in EOM-CC and CCLR methods, e.g., EOM-CCSD ( $\hat{T}$ ) studies<sup>49</sup> and CC3.<sup>50,51</sup>

## VI. THE CALCULATION OF PROPERTIES AND TRANSITION MOMENTS IN STEOM

The transformed Hamiltonian in STEOM is nonsymmetric, as in EOM-CC, and therefore properties and transition moments require both the left- and right-hand eigenstates<sup>6,55,56</sup> Alternatively properties may be calculated as energy derivatives. The latter is more complicated computationally, however, and demanding, if a large set of excited states is considered. Here we will limit ourselves to a biorthogonal expectation value approach. Due to the (approximate) blockform of  $\hat{G}$  the right-hand eigenstates and energies can be extracted easily. However, this is not true for the left-hand eigenstates. These states can be obtained approximately as follows. If we neglect three-body operators in  $\hat{G}$ , the matrix representation of  $\hat{G}$  over the space containing the reference determinant and single and double excitations takes the block form

$$\mathbf{G} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{0} & \mathbf{D} \end{pmatrix}. \quad (80)$$

The partitioning is assumed to be into a primary space (=reference determinant plus single excitations) and a secondary space that consists of doubly excited determinants. It is easily seen that the right-hand vectors corresponding to the primary space can be obtained as the right hand vectors of  $\mathbf{A}$  (this is the reason to do the transformation). The left-hand eigenvectors satisfy

$$\mathbf{l}_1 \mathbf{A} = \mathbf{E} \mathbf{l}_1, \quad (81)$$

$$\mathbf{l}_1 \mathbf{B} + \mathbf{l}_2 \mathbf{D} = \mathbf{E} \mathbf{l}_2 \rightarrow \mathbf{l}_2 = (\mathbf{E} - \mathbf{D})^{-1} (\mathbf{l}_1 \mathbf{B}).$$

We make the additional approximation that the doubles–doubles block is diagonal, where the diagonal consists of Hartree–Fock orbital energies, as in second-order perturbation theory. In this way we obtain an approximation for the left hand STEOM states. Explicitly the left-hand doubles coefficients for state  $\lambda$  are given by

$$l_{ij}^{ab}(\lambda) = \frac{1 + P(a, i \leftrightarrow b, j)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \left( \sum_c l_i^c(\lambda) g_{cjab} - \sum_k l_k^a(\lambda) g_{ijkb} + l_i^a(\lambda) g_{jib} \right). \quad (82)$$

Let us mention here that due to the last term in Eq. (82) the left-hand STEOM vectors are not explicitly connected. As a consequence STEOM properties calculated as biorthogonal expectation values are not fully connected either.

The matrix  $\mathbf{A}$  has a further blockform  $\mathbf{A} = \begin{pmatrix} \mathbf{0} & \mathbf{b} \\ \mathbf{0} & \mathbf{d} \end{pmatrix}$ . The single excitation component of the left-hand excited-state eigenvectors therefore can be written as

TABLE XI. Excitation energies (in eV) for C<sub>2</sub>. Comparison with full CI.

State Sym.	Char.	EOM CCSD	EOM-CCSDT-3	STEOM			CCSD no T	FCI <sup>a</sup>
				CC3 <sup>a</sup>	PT	CCSD		
<sup>1</sup> Π <sub>u</sub>	1 π <sub>u</sub> → 3 σ <sub>g</sub>	1.474	1.338	1.316	1.079	1.422	1.596	1.385
<sup>1</sup> Σ <sub>u</sub> <sup>+</sup>	2 σ <sub>u</sub> → 3 σ <sub>g</sub>	5.799	5.650	5.555	5.312	5.726	5.817	5.602
	Average error	0.143	.048	0.058	0.298	0.081	0.213	

<sup>a</sup>From Ref. 51.

$$(\mathbf{0} \mathbf{1}_1) \begin{pmatrix} \mathbf{0} & \mathbf{b} \\ \mathbf{0} & \mathbf{d} \end{pmatrix} = (\mathbf{0} \mathbf{1}_1 \mathbf{d}) = (\mathbf{0} \mathbf{E} \mathbf{1}_1), \quad (83)$$

and contain no component along the reference determinant. The left-hand STEOM ground state is obtained from

$$(\mathbf{1}, \mathbf{1}_1) \begin{pmatrix} \mathbf{0} & \mathbf{b} \\ \mathbf{0} & \mathbf{d} \end{pmatrix} = (\mathbf{0}, \mathbf{b} + \mathbf{1}_1 \mathbf{d}) = (\mathbf{0}, \mathbf{0}) \rightarrow \mathbf{1}_1 = -\mathbf{b} \mathbf{d}^{-1}, \quad (84)$$

while the doubles component of the left-hand ground state is given by Eq. (82) in addition to the standard first-order contribution

$$l_{ij}^{ab}(0) = \frac{1 + P(a, i \leftrightarrow b, j)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \left( \frac{1}{2} v_{abij} + \sum_c l_i^c(0) g_{cjab} - \sum_k l_k^a(0) g_{ijkb} + l_i^a(0) g_{jb} \right). \quad (85)$$

The right-hand vectors satisfy

$$\begin{pmatrix} \mathbf{0} & \mathbf{b} \\ \mathbf{0} & \mathbf{d} \end{pmatrix} \begin{pmatrix} \mathbf{r}_0 \\ \mathbf{r}_1 \end{pmatrix} = \begin{pmatrix} \mathbf{b} \mathbf{r}_1 \\ \mathbf{d} \mathbf{r}_1 \end{pmatrix} = \begin{pmatrix} \mathbf{r}_0 \\ \mathbf{r}_1 \end{pmatrix} \mathbf{E}. \quad (86)$$

The singles component and the excitation energy are determined from the eigenvalue problem in the singles space, while the right-hand reference component is subsequently determined as  $r_0 = \mathbf{b} \mathbf{r}_1 / E$ , or explicitly (for singlet states)

$$r_0 = 2 \sum_{i,a} g_{ia} r_{ai} / E. \quad (87)$$

Expectation values  $\langle \hat{O} \rangle$  are determined in the STEOM picture as

$$\langle L | \{e^{\hat{S}_2}\}^{-1} e^{-\hat{T}} \hat{O} e^{\hat{T}} \{e^{\hat{S}_2}\} | R \rangle = \langle L | \{e^{\hat{S}_2}\}^{-1} \hat{O} \{e^{\hat{S}_2}\} | R \rangle. \quad (88)$$

In Ref. 11 a general prescription was given to calculate the similarity transform of an arbitrary operator. Here we will make a connection with biorthogonal expectation values in the EOM picture. To this end we define

$$\hat{Q} = \{e^{\hat{S}_2}\}^{-1} \hat{O} \{e^{\hat{S}_2}\} \quad (89)$$

or

$$\{e^{\hat{S}_2}\} \hat{Q} = \hat{O} \{e^{\hat{S}_2}\},$$

$$\hat{Q} = \hat{O} \{e^{\hat{S}_2}\} - \hat{S}_2 \hat{Q} - \dots = \hat{O} + \hat{O} \hat{S}_2 + \hat{O} \left\{ \frac{1}{2} \hat{S}_2^2 \right\} + \dots - \hat{S}_2 (\hat{O} + \hat{O} \hat{S}_2) - \dots. \quad (90)$$

Here we restricted ourselves explicitly to those contributions to  $\hat{Q}$  that enter the matrix element  $\langle L | \hat{Q} | R \rangle$ . Let us note that although  $\hat{Q}$  as expressed above is not explicitly a connected operator, all disconnected contributions cancel precisely. If we write

$$\langle \tilde{L} | = \langle L | (1 - \hat{S}_2), \quad (91)$$

$$| \tilde{R} \rangle = (1 + \hat{S}_2 + \left\{ \frac{1}{2} \hat{S}_2^2 \right\}) | R \rangle.$$

The property can be evaluated as

$$\langle \tilde{L} | \hat{O} | \tilde{R} \rangle. \quad (92)$$

This formulation allows us to obtain properties as in the CI-like approximation to EE-EOM-CCSD,<sup>6</sup> except for a triples correction given by

$$\langle L_2 | \hat{O} \left\{ \frac{1}{2} \hat{S}_2^2 \right\} | R_1 \rangle. \quad (93)$$

Let us note that the above analysis is strictly valid for one-particle operators only. Explicitly the equations for the singles and doubles amplitudes in the EOM picture read

$$\begin{aligned} \tilde{r}_i^a &= r_i^a, \\ \tilde{r}_{ij}^{ab} &= (1 + P(ai \leftrightarrow bj)) \left[ \sum_e r_i^e s_{ej}^{ab} - \sum_m r_m^a s_{ij}^{mb} \right], \end{aligned} \quad (94)$$

$$\tilde{l}_i^a = l_i^a - \sum_{c,j,b} l_{ij}^{cb} \tilde{s}_{aj}^{cb} + \sum_{k,j,b} l_{kj}^{ab} \tilde{s}_{kj}^{ib}, \quad \tilde{l}_{ij}^{ab} = l_{ij}^{ab}. \quad (95)$$

The triple correction may be evaluated through similar intermediates that are used to calculate the effective interactions (see Sec. II B). Hence in the equations that determine the contributions to the *phph* and *phhp* integrals with two active indices ( $u_{amei}$  and  $u_{bmje}$ ) and the intermediates therein we replace  $w_{ijab}$  with  $l_{ij}^{ab}$  to define two-particle quantities  $d_{amei}$  and  $d_{bmje}$  and evaluate the triples contribution to the property as

$$\langle o \rangle_t = \sum_{e,m,a,i} r_m^e \bar{o}_{ia} (4d_{amie} - 2d_{amei}). \quad (96)$$

TABLE XII. Transition moments (in a.u.) of allowed singlet excited states of CO.

State	STEOM					EOMCC
	PT	CC <sup>a</sup>	CC <sup>b</sup>	CC no T <sup>c</sup>	CC no T <sup>d</sup>	
A <sup>1</sup> Π	0.0867	0.0863	0.0898	0.0861	0.0886	0.0867
B <sup>1</sup> Σ <sup>+</sup>	0.0761	0.0436	0.0381	0.0436	0.0124	0.0059
C <sup>1</sup> Σ <sup>+</sup>	0.1928	0.2230	0.2483	0.2237	0.2404	0.2069
E <sup>1</sup> Π	0.0458	0.0532	0.0623	0.0534	0.0504	0.0494

<sup>a</sup>Standard approximation: The right-hand ground state is obtained from CCSD. The left-hand ground state is obtained from EOM (Lambda equations). STEOM left- and right-hand vectors. Triples correction included in evaluation of transition moment.

<sup>b</sup>As <sup>a</sup> except left hand ground state is obtained from STEOM.

<sup>c</sup>As <sup>a</sup> triplets correction to transition moment is not included.

<sup>d</sup>As <sup>c</sup> but triples contribution to  $G$  is not included  $\rightarrow$  different STEOM eigenstates.

Unless explicitly stated we do not include the triples correction to excited state expectation values, since it is rather costly, while it cannot be expected to add much to the accuracy considering our rather crude treatment of the left-hand eigenstates.

The evaluation of transition moments follows similar lines. We can define a STEOM left- and right-hand ground state. The right-hand ground state is simply the reference determinant, while the STEOM left-hand ground state is discussed above. These states can be transformed to the EOM-picture and transition moments are calculated as in EOM-CC. Preferably, however, we describe the left-hand ground state at the full EOM-CCSD level, and in our standard approximation we solve for the so-called Lambda state.<sup>6</sup> In addition we add the triples correction to the transition moments, since the intermediates only have to be calculated once.

The CO molecule discussed before is taken as an illustration of the calculation of properties and transition moments in the STEOM framework. To estimate the effect of the various approximations we consider the following schemes for transition moments. The ground-state amplitudes that enter the transformation can be obtained by first-order perturbation theory or by solving the CCSD equations. The excited states are obtained by solving the respective STEOM equations for the left- and right-hand side. The left hand ground state is either the EOM ground state (Lambda) (a) or it is the approximated STEOM ground state (b). Finally we estimate the effect of triples. In CC no T (c) we exclude the triples contribution to the transition moment. This is the direct effect from triples. In CC no T (d) we in addition discard the triple contributions from the transformation (as in Sec. V). This changes the STEOM eigenvectors and has an indirect effect on the transition moment. The results are collected in Table XII and a comparison is made with the EOM-CC transition moments. From Table XII we conclude that STEOM-PT and STEOM-CC are in fair agreement. The direct contribution of triples to the transition moment is negligible [compare (c) and (a)]. There may be an appreciable indirect effect from triples (d) if the STEOM eigenvectors change appreciably if triples contributions are discarded from the similarity transformation. This is most noticeable for the Rydberg states of  $\Sigma^+$  symmetry. Replac-

ing the EOM ground state with the more approximate STEOM ground state has some effect, but overall the results are fairly close. Comparing the results with EOM-CC transition moments we find fair agreement except for the first Rydberg state of  $\Sigma^+$  symmetry. The precise nature of the single excitation components depends strongly on the approximations used and this has a large influence on the transition moment.

In Table XIII we present the dipole moments along the molecular axis for the excited states of CO. In general, dipole moments are very sensitive to the degree of correlation and this is reflected in Table XIII. The column labeled CC+T includes the triples correction to the dipole moment. As expected this contribution is negligible, and therefore, we do not consider this computationally expensive contribution in our standard approximation. Excluding the triples correction from the similarity transformation modifies the STEOM eigenvectors and the dipole moments of the Rydberg states appear to be very sensitive to this inclusion of triples. Interestingly, the dipole moments in the CC-no-T approximation agree very well with the EOM-CCSD dipole moments. STEOM-PT dipole moments are in good agreement with STEOM-CC results except for the Rydberg states of  $\Sigma^+$  symmetry.

In order to gain a better insight in the validity of the approximations made, we compare the dipole moments ob-

TABLE XIII. Dipole moments of singlet excited states of CO.

State	Exc.	STEOM				EOMCC
		PT	CC <sup>a</sup>	CC+T <sup>b</sup>	CC no T <sup>c</sup>	
X <sup>1</sup> Σ <sup>+</sup>		0.048	-0.071			
A <sup>1</sup> Π(V)	5σ→2π	0.155	0.079	0.078	0.070	0.059
I <sup>1</sup> Σ <sup>-</sup> (V)	1π→2π	-0.793	-0.810	-0.805	-0.821	-0.727
D <sup>1</sup> Δ(V)	1π→2π	-0.731	-0.745	-0.739	-0.754	-0.658
B <sup>1</sup> Σ <sup>+</sup> (R)	5σ→6σ	0.026	0.451	0.451	1.221	1.226
C <sup>1</sup> Σ <sup>+</sup> (R)	5σ→7σ	-0.799	-1.302	-1.301	-1.900	-1.938
E <sup>1</sup> Π(R)	5σ→3π	0.269	0.271	0.270	0.379	0.398

<sup>a</sup>Standard approximation: STEOM left- and right-hand vectors. Triples correction not included in evaluation of transition moment.

<sup>b</sup>As footnote a triples correction to expectation value is included.

<sup>c</sup>As footnote a but triples contribution to  $G$  is not included  $\rightarrow$  different STEOM eigenstates.

TABLE XIV. Dipole moments (in a.u.) of singlet excited states of CO: Comparison of biorthogonal expectation values with finite field derivatives.

State	Exc.	STEOM		EOMCC	
		Expectation	Derivative	Expectation	Derivative
A $^1\Pi$	$5\sigma \rightarrow 2\pi$	0.079	0.036	0.059	0.038
I $^1\Sigma^-$	$1\pi \rightarrow 2\pi$	-0.810	-0.670	-0.727	-0.679
D $^1\Delta$	$1\pi \rightarrow 2\pi$	-0.745	-0.586	-0.658	-0.607
B $^1\Sigma^+$	$5\sigma \rightarrow 6\sigma$	0.451	0.385	1.226	1.165
C $^1\Sigma^+$	$5\sigma \rightarrow 7\sigma$	-1.302	-1.286	-1.938	-1.996
E $^1\Pi$	$5\sigma \rightarrow 3\pi$	0.271	0.165	0.398	0.341

tained in the biorthogonal expectation value framework with finite field derivatives. The field in these calculations was added after the SCF calculations, so the orbital response to the field is not included. From Table XIV we find that EOM-CC dipole moments in the derivative and expectation forms agree somewhat better (average absolute deviation is 0.05 a.u.) than in the STEOM-CC approximation (average absolute deviation is 0.09 a.u.). This is presumably due to the perturbative approximation made for the doubles component of the STEOM left-hand eigenvector. The significant difference for the dipole moments of the Rydberg states in STEOM and EOM persists also at the derivative level, however. From the previous table it is clear that effects from triple excitations must be held responsible, indicating the sensitivity of dipole moments, especially in view of the relative insensitivity of the excitation energies of the Rydberg states to the inclusion of triple excitation effects (see Table VIII).

Second moments are much less sensitive. In Table XV we report the average extension  $\frac{1}{3}(\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle)$  for the excited states of CO. The results are almost independent of the approximations made. In fact neglecting the doubles component of the STEOM left-hand eigenvectors leaves these results largely unchanged. The spatial extent is an important characteristic of the Rydberg character of the excited state, and it is useful that this is not sensitive to the details of the calculation.

Let us summarize here, for future reference, the standard approach to STEOM transition moments and properties in excited states. In STEOM-CCSD the ground state is evaluated as in EOM-CCSD, requiring the solution of the CCSD and so-called Lambda equations. The doubles components of

TABLE XV.  $1/3(\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle)$  in a.u. for ground and excited states of CO.

State	Exc.	STEOM			EOMCC
		PT	CC	CC no T	
Ground state		13.4			13.4
A $^1\Pi$	$5\sigma \rightarrow 2\pi$	14.1	14.1	14.2	14.0
I $^1\Sigma^-$	$1\pi \rightarrow 2\pi$	14.4	14.4	14.4	14.2
D $^1\Delta$	$1\pi \rightarrow 2\pi$	14.3	14.4	14.4	14.2
B $^1\Sigma^+$	$5\sigma \rightarrow 6\sigma$	20.5	20.4	20.1	20.2
C $^1\Sigma^+$	$5\sigma \rightarrow 7\sigma$	24.2	24.5	24.9	24.9
E $^1\Pi$	$5\sigma \rightarrow 3\pi$	23.4	23.4	23.3	23.1

the left-hand excited states are evaluated perturbatively. To calculate transition moments we include the triples component of the right-hand states (in the EOM picture), however in evaluating diagonal properties this triples correction is neglected. In STEOM-PT the ground-state amplitudes (right and left) are defined by first-order Møller–Plesset perturbation theory. All else is the same as in STEOM-CCSD.

## VII. SUMMARY

We have presented a detailed exposition of the similarity transformed equation-of-motion coupled-cluster method for excited, doubly ionized, and doubly attached electronic states, relative to a closed-shell parent state. In STEOM-CC we achieve an approximate decoupling of the relevant eigenvalue problems by performing many-body similarity transformations of the Hamiltonian. The first transformation requires the solution of the CCSD equations and results in vanishing pure excitation ( $ph$  and  $2p2h$ ) operators of the so-called EOM Hamiltonian. The second transformation requires selected solutions of the IP-EOM-CC and EA-EOM-CC eigenvalue problems, and results in selected vanishing  $hhhp$  and  $hppp$  components in the final transformed STEOM Hamiltonian  $\hat{G}$ . Due to the vanishing of the most relevant net excitation operators the transformed Hamiltonian can subsequently be diagonalized over very small subspaces.

STEOM is closely related to Fock space coupled-cluster theory. From a practical point of view the most important difference is that in the final step in STEOM we solve an eigenvalue problem, which is stable numerically, while in FSCC one needs to solve a set of nonlinear equations which is prone to the infamous intruder state problem. In addition STEOM is conceptually straightforward and this is a major advantage over the FSCC framework. We view STEOM as a starting point for further developments in open-shell coupled-cluster theory.

We also compared the STEOM approach with EOM-CC. Due to the implicit inclusion of triple excitation effects in STEOM the method is fully linked and charge transfer separable, contrary to EOM-CC/CCLR. Discarding the triples contribution from STEOM was shown to have a large effect for valence excited states, and often brings the results closer to results from EOM-CC calculations. Comparison of STEOM and EOM-CC results with FCI slightly favored the more economical STEOM method.

The calculation of properties and transition moments in STEOM requires some additional approximations, but results agree fairly well with results from EOM-CC calculations and also with finite difference derivative results, which are formally more satisfactory.

We have also established some limitations of the STEOM method.

(1) Not all states can be obtained in the STEOM scheme. For example we are only able to obtain excited states that are predominantly described as single excitations from a closed shell reference determinant.

(2) The scheme is built upon a closed shell reference determinant, that needs to be reasonably described at the Hartree–Fock level. Let us note, however, that coupled-cluster theory is quite capable of stretching the notion of “reasonable” as demonstrated on a calculation on the excited states of  $C_2$ .

(3) STEOM results are sensitive to the selection of active orbitals. The magnitude of the active component of the final STEOM eigenvector appears to be a reliable criterium that allows us to judge the quality of the active space. However, particularly if the basis set contains many diffuse orbitals, it may be hard to improve the active space for the description of valence excited states. For the sake of convergence of the attached states described by the EA-EOM-CC equations one would like to use canonical Hartree–Fock orbitals, while a compact description of the excited state requires a different type of orbital, e.g., natural orbitals averaged over a number of excited states or  $\bar{V}^{N-1}$  orbitals. In this latter case the active-space diagnostic appears less reliable. The dependence on active orbitals may also lead to complications when investigating potential energy surfaces for excited states.

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