



High-order determinantal equation-of-motion coupled-cluster calculations for electronic excited states

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Abstract

A general-order equation-of-motion coupled-cluster (EOM-CC) method, which is capable of computing the excitation energies of molecules at any given pair of orders (m and n) of the cluster operator and the linear excitation operator, is developed by employing a determinantal algorithm. The EOM-CC(m,n) results of the vertical excitation energies are presented for CH^+ with m and n varied independently in the range of $1 \leq m, n \leq 4$ and for CH_2 with $1 \leq m = n \leq 6$. EOM-CCSDT [EOM-CC(3,3)] provides the excitation energies that are within 0.1 eV of the full configuration interaction results for dominant double replacement transitions. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

We have recently demonstrated [1] that the wavefunction and energy of a molecule can be calculated at any arbitrary order of coupled-cluster (CC) theory [2] by using a determinantal algorithm. The calculation proceeds by generating an exponential wavefunction as an explicit linear combination of determinants and substituting it into the Schrödinger equation, which is subsequently projected onto the basis of a certain class of determinants. The procedure is well defined in terms of determinants in that each step of the procedure can be described by a finite number of the second quantized creation and annihilation operators acting on the determinants. The exponential wave operator and the Hamiltonian

operator, for example, are expressed as combinations of a finite number of such operators by virtue of the finite number of electrons and one-particle basis functions. The determinantal CC method can be implemented in a simple and general manner by employing the determinantal full configuration interaction (FCI) algorithms [3–6] at the sacrifice of the applicability to large molecules or basis sets. The method is, therefore, intended to provide benchmark results and to help analyze and develop the hierarchy of existing or new CC methods.

It is of interest to extend the determinantal method to analyze CC-based methods for electronic excited states. One CC-based approach to the excited-state problems is the multi-reference coupled-cluster (MR-CC) scheme within Fock or Hilbert space [2,7], but perhaps the simplest and widely applicable approach is the equation-of-motion coupled-cluster (EOM-CC) method [2]. This method was originally derived from

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a time-dependent linear response framework by Monkhorst [8,9] and was considered by others [10–23] with different approximations. These initial efforts were greatly enhanced when the biorthogonal nature of CC theory was fully developed with its left and right eigenvectors ($1 + \Lambda$ operator of CC gradient theory [24] is the left-hand eigenvector for the ground state) leading to the fully developed, time-independent, EOM-CC theory. This theory, without further approximation, was presented by Comeau, Stanton, and Bartlett [21,22]. So far the EOM-CC method that includes the connected single and double excitations (EOM-CCSD) has been implemented and shown to yield accurate excitation energies for the excited states with dominant single excitation character [2]. It is well documented [25], however, that EOM-CCSD cannot generally provide the equally accurate excitation energies when the associated excited-state wavefunctions have substantial double excitation character, and the inclusion of higher orders of the excitation operators, particularly the triple excitation operator [26–29], is warranted when handling these excited states.

In this Letter, we explore the effects of triple and higher-order excitation operators in EOM-CC with the aid of the determinantal CC method. We develop a general-order EOM-CC method capable of computing the excitation energies of molecules at any given pair of orders (m and n) of the cluster operator and the linear excitation operator. This is possible since EOM-CC is a well-defined procedure in terms of determinants. We present the results of the EOM-CC(m,n) calculations, which include the initial results of the complete EOM-CCSDT [EOM-CC(3,3)] through EOM-CCSDTQPH [EOM-CC(6,6)] calculations, for the vertical excitation energies of CH^+ and CH_2 , some of whose low-lying excited states are known to have substantial double excitation character. We demonstrate that EOM-CCSDT [EOM-CC(3,3)] provides the excitation energies that are within 0.1 eV of the FCI results for dominant single, dominant double, and mixed single and double replacement transitions, whereas the comparable accuracy can be achieved only for dominant single replacement transitions by EOM-CCSD [EOM-CC(2,2)]. This observation supports the conclusion drawn earlier by Watts and Bartlett [26,27,29], with the aid of approximate but efficient variants of

EOM-CCSDT, that the triple excitation operators appropriately capture the differential electron correlation effects associated with the double replacement transitions. EOM-CC(m,n) also allows us to use different orders of the cluster operators and the linear excitation operators and to examine the effects of these two operators independently of each other on the performance of the method. Including the same orders of the exponential operators and the linear excitation operators, we arrive the usual balanced EOM-CC models which also correspond to CC linear response theory.

2. Theory

The CC method [2] uses an exponential ground-state wavefunction $|\Psi_0\rangle$ written as

$$|\Psi_0\rangle = \exp(T)|\Phi_0\rangle = \sum_{h=0}^N \frac{T^h}{h!} |\Phi_0\rangle, \quad (1)$$

where $|\Phi_0\rangle$ is some independent particle model ground state, in this case, a restricted Hartree–Fock (HF) determinant. The summation terminates at $h = N$ (the maximum allowed number of excitations from $|\Phi_0\rangle$) by virtue of the finite number of electrons and one-particle basis functions. The cluster operator T is a sum of the excitation operators of different types such as single excitations T_1 and double excitations T_2 . We may truncate the summation at m -tuple excitations T_m ,

$$T = T_1 + T_2 + T_3 + \dots + T_m, \quad (2)$$

defining the m -tuple excitation CC method as CC(m). The excitation operators are defined by the respective t -amplitudes ($t_i^a, t_{ij}^{ab}, \dots$) and creation p^\dagger and annihilation p operators of electrons, e.g.,

$$T_1 = \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} t_i^a a^\dagger i, \quad (3a)$$

$$T_2 = \sum_{i>j}^{\text{occ.}} \sum_{a>b}^{\text{virt.}} t_{ij}^{ab} a^\dagger i b^\dagger j, \quad (3b)$$

where we adhere to the convention that i, j, \dots represent orbitals that are occupied in $|\Phi_0\rangle$, a, b, \dots refer to unoccupied orbitals, and p, q, \dots refer to

general orbitals. The t -amplitudes and the total ground-state electronic energy E_0 are determined uniquely by substituting the exponential wavefunction into the Schrödinger equation and projecting the equation onto the basis of determinants obtained by applying $(1 + T)$ to $|\Phi_0\rangle$, i.e.,

$$\langle \Phi_0 | H | \Psi_0 \rangle = E_0, \quad (4a)$$

$$\langle \Phi_i^a | H | \Psi_0 \rangle = E_0 \langle \Phi_i^a | \Psi_0 \rangle, \quad (4b)$$

$$\langle \Phi_{ij}^{ab} | H | \Psi_0 \rangle = E_0 \langle \Phi_{ij}^{ab} | \Psi_0 \rangle, \quad (4c)$$

etc., where Φ_i^a and Φ_{ij}^{ab} represent a singly and a doubly substituted determinant, respectively. The Hamiltonian H can be written as

$$H = \sum_{p,q} h_{pq} p^\dagger q + \frac{1}{2} \sum_{p,q,r,s} \langle pq | rs \rangle p^\dagger q^\dagger sr, \quad (5)$$

where h_{pq} is an element of the one-electron part of the Fock matrix and $\langle pq | rs \rangle$ is a two-electron integral.

In EOM-CC [2,8–23], the k th excited-state wavefunction $|\Psi_k\rangle$ is created by operating on the exponential ground-state wavefunction $|\Psi_0\rangle$ with a linear excitation operator $R(k)$,

$$|\Psi_k\rangle = R(k)|\Psi_0\rangle = R(k)\exp(T)|\Phi_0\rangle, \quad (6)$$

with $R(k)$ being a sum of single, double, etc. excitation operators,

$$R(k) = R_0(k) + R_1(k) + \dots + R_n(k), \quad (7)$$

and

$$R_0(k) = r_0(k), \quad (8a)$$

$$R_1(k) = \sum_i^{\text{occ. virt.}} \sum_a r_i^a(k) a^\dagger i, \quad (8b)$$

$$R_2(k) = \sum_{i>j}^{\text{occ. virt.}} \sum_{a>b} r_{ij}^{ab}(k) a^\dagger i b^\dagger j, \quad (8c)$$

etc. In this way, we can conveniently take into account the correlation effects that are common to the ground and excited states by the exponential wave operator, allowing the linear excitation operator to describe the essential differential correlation effects. The summation of Eq. (7) may be truncated at a certain tractable order, and accordingly, EOM-CC can be characterized by two parameters, m and n , the orders of T and $R(k)$ operators, respectively,

and each model is denoted by EOM-CC(m,n). Substituting the excited-state wavefunction $|\Psi_k\rangle$ into the Schrödinger equation, we obtain

$$H|\Psi_k\rangle = E_k|\Psi_k\rangle, \quad (9)$$

which can then be written as

$$HR(k)\exp(T)|\Phi_0\rangle = E_k R(k)\exp(T)|\Phi_0\rangle. \quad (10)$$

Operating on both sides of Eq. (10) with $\exp(-T)$ from the left and using the fact that $R(k)$ and T commute, we find

$$\bar{H}R(k)|\Phi_0\rangle = E_k R(k)|\Phi_0\rangle, \quad (11)$$

with the non-Hermitian effective Hamiltonian \bar{H} being defined by the similarity transformation

$$\bar{H} \equiv \exp(-T)H\exp(T). \quad (12)$$

The amplitudes of the linear excitation operator $R(k)$ and the electronic energy E_k of the k th excited state are determined by projecting Eq. (11) onto the basis of determinants obtained by applying $\{1 + R(k)\}$ to $|\Phi_0\rangle$, i.e.,

$$\langle \Phi_0 | \bar{H}R(k) | \Phi_0 \rangle = E_k \langle \Phi_0 | R(k) | \Phi_0 \rangle, \quad (13a)$$

$$\langle \Phi_i^a | \bar{H}R(k) | \Phi_0 \rangle = E_k \langle \Phi_i^a | R(k) | \Phi_0 \rangle, \quad (13b)$$

$$\langle \Phi_{ij}^{ab} | \bar{H}R(k) | \Phi_0 \rangle = E_k \langle \Phi_{ij}^{ab} | R(k) | \Phi_0 \rangle, \quad (13c)$$

etc. Unlike Eqs. (4), which constitute a set of non-linear algebraic equations for the t -amplitudes owing to the non-linear nature of the exponential wave operator, Eqs. (13) lead to a (non-Hermitian) CI-like eigenvalue problem for the amplitudes of $R(k)$. When $m \geq n$, the ground-state wavefunction $|\Phi_0\rangle$ and energy E_0 obtained from CC(m) is a solution [$R(k) = 1$] to the EOM-CC Eqs. (13); the excited-state solutions of EOM-CC do not interact with the ground-state solution in this case, since $\langle \Phi_l | \bar{H} | \Phi_0 \rangle = 0$ with Φ_l being a singly, doubly, ..., or m -tuply substituted determinant. When $m < n$, on the other hand, the effective Hamiltonian matrix elements associated with the $(m+1)$ -, $(m+2)$ -, ..., and n -tuply substituted determinants would be non-vanishing, and the ground-state CC wavefunction is not a solution to the EOM-CC equations anymore. It may be appreciated that EOM-CC is a formally exact procedure unless an approximation is made to $R(k)$ by truncating the summation of Eq. (7) at $n < N$, as

the similarity transformation of Eq. (12) does not change the eigenvalues of the original full Hamiltonian H even when the T operator is truncated at $m < N$. Therefore, EOM-CC(m, N) is equivalent to FCI, regardless of the choice of m . As the HF determinant is a solution to CC(1) for the ground state, EOM-CC(1, n) reduces to n -tuple substitution CI or CI(n); the EOM-CC formalism encompasses that of CI as a particular case when the HF determinant is used as a reference.

3. Implementation

The general-order determinantal EOM-CC method was implemented in the POLYMER program [30] by using the algorithm that literally follows the procedure described in the previous section. We first generate all possible determinants for α and β electrons. These α and β determinants may be compactly stored in memory as strings of bits with each bit representing the occupancy of an orbital [3]. Any determinant can be specified by a pair of α - and β -strings, each of which is associated with an address in a consecutive lexical order. Accordingly, any wavefunction can be represented by an array of α - and β -strings, whose elements store the CI coefficients of the corresponding determinants. Likewise a set of all the t -amplitudes and a set of all the amplitudes of $R(k)$ can be conveniently packed into arrays having the same structure [1].

Eigenvalues and eigenvectors of the effective Hamiltonian \bar{H} can be determined by using a non-Hermitian modification [31] of Davidson's iterative subspace method [32]. In this method, we project the full matrix of \bar{H} onto a subspace of greatly reduced dimension spanned by a set of orthonormal trial vectors $\{\mathbf{w}^{(1)}, \mathbf{w}^{(2)}, \dots, \mathbf{w}^{(u)}\}$. Each iteration involves the formation of the matrix–vector products

$$z_j^{(p)} = \sum_I \langle \Phi_j | \bar{H} | \Phi_I \rangle w_I^{(p)}, \quad (14)$$

where Φ_I and Φ_j are determinants. The subspace representation of \bar{H} , denoted as \bar{H}^R , is obtained by forming the inner product of the trial vectors and the product vectors

$$\bar{H}_{pq}^R = \sum_I w_I^{(p)} z_I^{(q)}. \quad (15)$$

In Eqs. (14) and (15), the summation may be confined to the determinants which are considered in Eqs. (13) (up to n -tuply substituted determinants). The approximate eigenvalues E_k^R and right-hand eigenvectors $r^R(k)$ are obtained by solving the non-Hermitian eigenvalue equation of the reduced dimension

$$\sum_q \bar{H}_{pq}^R r_q^R(k) = E_k^R r_q^R(k). \quad (16)$$

Subspace size is increased iteratively until the approximate eigenvectors

$$R(k) |\Phi_0\rangle = \sum_q \sum_I r_q^R(k) w_I^{(q)} |\Phi_I\rangle \quad (17)$$

satisfy Eqs. (13) within a preset tolerance. We consider that the convergence is achieved when the norm of the largest residual vector becomes less than 10^{-5} .

The formation of the matrix–vector products of Eq. (14) can be carried out in three separate steps, i.e.,

$$x_K^{(p)} = \sum_I \langle \Phi_K | \exp(T) | \Phi_I \rangle w_I^{(p)}, \quad (18a)$$

$$y_L^{(p)} = \sum_K \langle \Phi_L | H | \Phi_K \rangle x_K^{(p)}, \quad (18b)$$

$$z_J^{(p)} = \sum_L \langle \Phi_J | \exp(-T) | \Phi_L \rangle y_L^{(p)}, \quad (18c)$$

where the t -amplitudes that define $\exp(T)$ and $\exp(-T)$ operators must be determined in the preceding CC(m) calculations [1]. The second step [Eq. (18b)] is common to the implementation of determinantal FCI methods, and efficient algorithms for this procedure are available [3–6]. The first and third steps [Eqs. (18a) and (18c)] can be accomplished by operating with $\pm T$ on a trial wavefunction $|\Psi\rangle$ (which in this case is either $\sum_I |\Phi_I\rangle w_I^{(p)}$ or $\sum_L |\Phi_L\rangle y_L^{(p)}$) recursively and by accumulating $(\pm T)^h |\Psi\rangle / h!$. The schematic representation of the algorithm (loop structures) of this process can be found in Ref. [1]. We note that the summation over the intermediate determinants $|K\rangle$ in Eq. (18b) must span the full spin space, even when the T and/or $R(k)$ operators are truncated.

4. Demonstrative calculations

The EOM-CC calculations of the vertical excitation energies are performed for CH^+ with the 6-31G** basis set and for CH_2 with the 6-31G* basis set. The lowest occupied and highest unoccupied

orbitals are kept frozen in the correlation treatment. Our objective is to obtain a preliminary comparative assessment of the EOM-CC methods with different orders of truncation for the T and $R(k)$ operators. The basis sets employed are not of sufficient size to make comparison to experimental results meaning-

Table 1

The ground-state total energies (in parentheses; in hartree) and vertical excitation energies (in eV) of CH^+ ($r_{\text{CH}} = 1.131 \text{ \AA}$) calculated by EOM-CC(m,n) (m and n being the orders of the cluster operator and the linear excitation operator, respectively) with the 6-31G** basis set. The lowest and highest orbitals are kept frozen in the correlation treatment. The HF total energy for the ground state is -37.897259 hartree. The percentage contributions of the singly and doubly substituted determinants in the FCI wavefunctions are also given

		EOM-CC($m,1$)	EOM-CC($m,2$)	EOM-CC($m,3$)	EOM-CC($m,4$) ^a	%singles	%doubles
EOM-CC(1, n) ^b	$^1\Sigma^+$	(-37.897259)	(-37.994312)	(-37.996119)	(-37.998811)	0.11	7.66
	$^1\Sigma^+$...	9.5352	9.0453	8.5304	0.23	95.59
	$^1\Sigma^+$	14.8522	15.2851	14.3194	14.3042	87.47	9.53
	$^1\Sigma^+$...	19.8751	18.0189	18.0224	0.00	95.95
	$^1\Pi$	2.9262	4.0576	3.1732	3.2087	94.70	3.09
	$^1\Pi$	15.3216	15.2574	14.3126	14.1595	59.60	34.18
	$^1\Pi$...	18.2686	17.3000	17.0573	32.47	64.48
	$^1\Delta$	7.1686	6.9335	0.22	97.92
	$^1\Delta$	17.2461	16.8460	1.04	96.57
EOM-CC(2, n)	$^1\Sigma^+$	(-37.996871)	(-37.996871)	(-37.998714)	(-37.998811)	0.11	7.66
	$^1\Sigma^+$...	9.0742	8.6141	8.5304	0.23	95.59
	$^1\Sigma^+$	16.4858	14.3658	14.3052	14.3042	87.47	9.53
	$^1\Sigma^+$...	19.8063	18.0557	18.0224	0.00	95.95
	$^1\Pi$	4.7292	3.2366	3.2127	3.2087	94.70	3.09
	$^1\Pi$	16.8296	14.5036	14.2279	14.1595	59.60	34.18
	$^1\Pi$...	17.6963	17.1266	17.0573	32.47	64.48
	$^1\Delta$...	7.8325	6.9725	6.9335	0.22	97.92
	$^1\Delta$...	17.6687	16.8063	16.8460	1.04	96.57
EOM-CC(3, n)	$^1\Sigma^+$	(-37.998714)	(-37.998714)	(-37.998714)	(-37.998811)	0.11	7.66
	$^1\Sigma^+$...	9.1160	8.6030	8.5304	0.23	95.59
	$^1\Sigma^+$	16.5199	14.4078	14.3070	14.3042	87.47	9.53
	$^1\Sigma^+$...	19.8629	18.0541	18.0224	0.00	95.95
	$^1\Pi$	4.7619	3.2732	3.2066	3.2087	94.70	3.09
	$^1\Pi$	16.8604	14.5417	14.2220	14.1595	59.60	34.18
	$^1\Pi$...	17.7375	17.1199	17.0573	32.47	64.48
	$^1\Delta$...	7.8799	6.9707	6.9335	0.22	97.92
	$^1\Delta$...	17.7150	16.8020	16.8460	1.04	96.57
EOM-CC(4, n)	$^1\Sigma^+$	(-37.998811)	(-37.998811)	(-37.998811)	(-37.998811)	0.11	7.66
	$^1\Sigma^+$...	9.1200	8.6070	8.5304	0.23	95.59
	$^1\Sigma^+$	16.5224	14.4104	14.3100	14.3042	87.47	9.53
	$^1\Sigma^+$...	19.8657	18.0567	18.0224	0.00	95.95
	$^1\Pi$	4.7642	3.2755	3.2091	3.2087	94.70	3.09
	$^1\Pi$	16.8618	14.5434	14.2245	14.1595	59.60	34.18
	$^1\Pi$...	17.7401	17.1226	17.0573	32.47	64.48
	$^1\Delta$...	7.8825	6.9733	6.9335	0.22	97.92
	$^1\Delta$...	17.7174	16.8043	16.8460	1.04	96.57

^a Equivalent to FCI.

^b Equivalent to CI(n).

ful. However, EOM-CC systematically approaches FCI as the expansion of T and $R(k)$ operators becomes closer to complete, and we consider that the comparison against themselves is instructive.

The EOM-CC(m,n) excitation energies of the singlet excited states of CH^+ are given in Table 1 with m and n varied independently in the range of $1 \leq m, n \leq 4$. Within the frozen core approximation, EOM-CC($m,4$) corresponds to FCI and gives the same results (that are exact within the one-particle basis set) regardless of the CC order m . The contributions from singly and doubly substituted determinants in the FCI wavefunctions are also given in the table, and they indicate that there are several excited states with substantial double excitation character. EOM-CC(m,m) covers the standard models based on CC(m), such as EOM-CCSD and EOM-CCSDT, and are of particular interest. EOM-CC(2,2) or EOM-CCSD provides the transition energies for dominant single excitations with accuracy of 0.1 eV. As previously reported for CH^+ (Refs. [19,22,23,26–29]), EOM-CC(2,2) performs less well for dominant double replacement transitions. The EOM-CC(2,2) excitation energies are too high by 0.5–1.9 eV relative to the FCI results, indicating that this method does not

adequately recover electron correlation in the excited states with double excitation character. The next higher level of the EOM-CC(m,m) model, i.e., EOM-CC(3,3) or EOM-CCSDT, remedies this situation remarkably well, reproducing the excitation energies for dominant single, dominant double, and mixed single and double replacement transitions within 0.1 eV of the FCI results. The readers might question the generality of this observation, considering that EOM-CC(4,4) is already FCI in this case. However, the same trend can be seen in the EOM-CC results of CH_2 with six active electrons (see below). Thus, it may be said that the triple excitation operator must be included in the $R(k)$ operator to describe the dominant double replacement transitions well [25–29].

Comparing the calculated excitation energies within each column, we can assess the effects of the similarity transformation of the Hamiltonian with different orders of the T operator. We can identify the trend that either increase or decrease in the order of the T operator deteriorates the calculated excitation energies, relative to the EOM-CC(m,m) results. In particular, EOM-CC(l,m) with $l < m$ are inferior to EOM-CC(m,m), until $l = 2$ and $m = 3$ when the

Table 2

The vertical excitation energies (in eV) of CH_2 ($r_{\text{CH}} = 1.102 \text{ \AA}$, $a_{\text{HCH}} = 104.7^\circ$) calculated by the EOM-CC(m,m) method (the orders of the cluster operator and linear excitation operator are m) with the 6-31G* basis set. The lowest and highest orbitals are kept frozen in the correlation treatment. The percentage contributions of the singly and doubly substituted determinants in the FCI wavefunctions are also given

	CC(1,1) ^a	CC(2,2) ^b	CC(3,3) ^c	CC(4,4) ^d	CC(5,5) ^e	CC(6,6) ^f	CCSD(\tilde{T}) ^g	CCSDT-3 ^h	%singles	%doubles
¹ B ₁	1.5490	1.6677	1.6776	1.6787	1.6787	1.6787	1.6252	1.6730	94.61	2.66
¹ A ₁	...	5.8437	4.5629	4.5178	4.5168	4.5168	4.9046	4.9749	0.17	92.58
¹ A ₂	6.4549	6.1006	6.0920	6.0926	6.0926	6.0926	6.0494	6.1006	92.15	5.06
¹ B ₂	...	9.6915	8.2780	8.2540	8.2536	8.2536	8.7292	8.7500	2.81	92.64
¹ A ₁	9.6873	9.1202	9.0559	9.0531	9.0529	9.0529	9.0240	9.0762	89.32	7.58
³ B ₁	-0.7589	-0.3443	-0.3120	-0.3101	-0.3101	-0.3101	-0.3675	-0.3224	94.88	2.30
³ A ₂	5.2811	5.3001	5.3143	5.3150	5.3150	5.3150	5.2648	5.3147	92.94	4.28
³ B ₂	...	8.3816	6.9525	6.9054	6.9041	6.9041	7.5111	7.4750	2.53	93.03
³ A ₁	8.5920	8.3891	8.3291	8.3267	8.3265	8.3265	8.3079	8.3520	90.07	6.64
³ B ₂	8.7944	9.3035	9.1548	9.1504	9.1502	9.1502	9.0482	9.1896	91.18	5.48

^a EOM-CC(1,1) = EOM-CCS = CI(1). The CC(1) = HF energy of the lowest-lying singlet (¹A₁) state is -38.872249 hartree.

^b EOM-CC(2,2) = EOM-CCSD. The CC(2) energy of the lowest-lying singlet (¹A₁) state is -38.993284 hartree.

^c EOM-CC(3,3) = EOM-CCSDT. The CC(3) energy of the lowest-lying singlet (¹A₁) state is -38.996513 hartree.

^d EOM-CC(4,4) = EOM-CCSDTQ. The CC(4) energy of the lowest-lying singlet (¹A₁) state is -38.996643 hartree.

^e EOM-CC(5,5) = EOM-CCSDTQP. The CC(5) energy of the lowest-lying singlet (¹A₁) state is -38.996647 hartree.

^f EOM-CC(6,6) = EOM-CCSDTQPH = FCI. The CC(6) = FCI energy of the lowest-lying singlet (¹A₁) state is -38.996647 hartree.

^g EOM-CCSD(\tilde{T}). The CCSD(\tilde{T}) energy of the lowest-lying singlet (¹A₁) state is -38.995578 hartree.

^h EOM-CCSDT-3. The CCSDT-3 energy of the lowest-lying singlet (¹A₁) state is -38.995744 hartree.

difference from full CI are modest. For such a case where $l \neq m$, the interaction between the $CC(l)$ ground-state wavefunction and the EOM- $CC(l,m)$ excited-state wavefunctions is no longer null, and must be taken into account. However, this does suggest that the excited states are less sensitive to T_3 in the ground state than in the excited states.

Another consequence of this trend is the well-known fact [2] that EOM- $CC(m,m)$ constitutes a uniform and significant improvement over EOM- $CC(1,m)$ or CI(m) for the excited states. We consider that the slight deterioration of the calculated excitation energies on going from EOM- $CC(m,m)$ to EOM- $CC(l,m)$ with $l > m$ is caused by the fact that the $CC(l)$ treatment selectively improves the ground-state wavefunction and energy, while the m -tuple excitation $R(k)$ operator leaves the description of the excited states essentially unimproved. Overall, consistently including the same orders of excitations in the T and $R(k)$ operators leads to physically (in that it amounts to the proper linear response to the underlying CC model) and numerically well-balanced EOM-CC models.

The EOM- $CC(m,m)$ excitation energies of the singlet and triplet excited states of CH_2 are compiled in Table 2. CH_2 is another example some of whose low-lying excited states have dominant double excitation character [23,26,28]. There are six correlated electrons in CH_2 (within the frozen core approximation) and hence EOM- $CC(6,6)$ corresponds to FCI. The lowest triplet (3B_1) state has a lower total energy by 0.31 eV than that of the lowest singlet state which we choose as the basis of the EOM-CC calculations. The negative excitation energy associated with this triplet state does not cause any technical problem in any of the EOM-CC models employed here. For the dominant single replacement transitions, EOM- $CC(2,2)$ provides accurate excitation energies that are within 0.2 eV of the FCI results, in contrast to 0.03–0.64 eV deviations in the EOM- $CC(1,1)$ results for these transitions. For the dominant double replacement transitions, EOM- $CC(2,2)$ is not capable of achieving equally accurate results, and one must go to the EOM- $CC(3,3)$ model, which in turn yields the excitation energies for these transitions accurate to within 0.1 eV. EOM- $CC(3,3)$ also improves appreciably the excitation energies for the dominant single replacement transitions relative to the EOM-

$CC(2,2)$ results. This observation substantiates the previous conclusion that EOM- $CC(3,3)$ would appear to be the minimal level of the EOM-CC model that can handle the excited states with single, double, and mixed single and double excitation characters with uniform and high accuracy. Table 2 also includes the results of approximate variants of EOM- $CC(3,3)$, i.e., EOM- $CCSD(\tilde{T})$ and EOM- $CCSDT-3$ [29]. These models systematically reduce the errors in the EOM- $CC(2,2)$ results for both the dominant single and dominant double replacement transitions, with the exception that EOM- $CCSD(\tilde{T})$ corrects the excitation energies to the lowest-lying 3B_1 state in a wrong direction. However, the magnitude of the corrections predicted by these models appears to be too small for dominant double replacement transitions; the excitation energies calculated by these models are sometimes too large by 0.5 eV relative to the FCI results.

Note added in proof

Very recently, a related method was reported by Kállay and Surján [33].

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