High-order determinantal equation-of-motion coupled-cluster calculations for ionized and electron-attached states

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Abstract

General-order equation-of-motion coupled-cluster methods for ionization potentials and electron affinities (IP-EOM-CC and EA-EOM-CC) are developed by employing a determinantal algorithm. With these, principal ionization potentials or electron affinities of diatomic molecules and the excitation energies of their ionized or electron-attached counterparts are computed across different approximations of the cluster operator and the ionization (electron-attachment) operator. IP-EOM-CC(2,2h-1p) = IP-EOM-CCSD and EA-EOM-CC(2,1h-2p) = EA-EOM-CCSD or EA-EOM-CC(2,2h-3p) prove to be well-balanced models for principal ionization potentials and electron affinities, whereas for the quantitative descriptions of non-Koopmans ionization or electron-attachment processes IP-EOM-CC(3, 3h-2p) = IP-EOM-CCSDT and EA-EOM-CC(2,2h-3p) appear to be the minimal levels. © 2000 Elsevier Science B.V.

1. Introduction

The coupled-cluster (CC) method for energy differences (EOM-CC) [1–4] uses the equation-of-motion (EOM) concept of Rowe [5] for the simultaneous treatment of two states, which in that work leads to the random-phase approximation (RPA). McCurdy Jr. et al. [6] and Simons [7] also employed this concept using both excitation and deexcitation operators, sometimes applying a 'killer' condition self-consistently, to develop higher RPA techniques for excitation energies and ionized and electron-attached states, respectively.

EOM-CC differs substantially from these efforts in that it employs the highly correlated CC reference function with only excitation operators in its development [4], leading to one correlated Hamiltonian $\exp(-T)H \exp(T)$ for all processes. This has been implemented [1–4,8] and related variants such as CC linear response [9–14] into a computationally efficient and widely applicable approach for the description of excited [1–4,8–14], ionized [15–18], and electron-attached [19] states (see also Ref. [20] for symmetry-adapted-cluster configuration interaction, Ref. [21] for Fock-space multi-reference CC theory, and Ref. [22] for CC Green's-function theory, all of which are intimately related to EOM-CC). In this approach, the wavefunction $|\Psi_k\rangle$ of the kth target state (excited, ionized or electron-attached state) is created by operating on a reference wavefunction $|\Psi_0\rangle$ (typically but not

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necessarily the ground-state wavefunction) with a linear operator $\Omega(k)$,

$$|\Psi_k\rangle = \Omega(k)|\Psi_0\rangle. \tag{1}$$

The reference wavefunction $|\Psi_0\rangle$ is given by the CC approximation (see Ref. [23] for a review and references therein)

$$|\Psi_0\rangle = \exp(T)|\Phi_0\rangle, \tag{2}$$

where $|\Phi_0\rangle$ represents an independent particle reference [in our case a Hartree–Fock (HF) determinant] and T is the cluster operator of the form

$$T = \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} t_i^a a^\dagger i + \sum_{i>j}^{\text{occ.}} \sum_{a>b}^{\text{virt.}} t_{ij}^{ab} a^\dagger i b^\dagger j + \cdots. \tag{3}$$

The linear operator $\Omega(k)$ can be chosen with considerable flexibility according to the nature of target states. For the excited states having the same number of electrons as the reference state, we may choose the excitation operator $R(k)$ as $\Omega(k)$ given by

$$R(k) = R_0(k) + \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} R_i^a(k) a^\dagger i$$
$$+ \sum_{i>j}^{\text{occ.}} \sum_{a>b}^{\text{virt.}} R_{ij}^{ab}(k) a^\dagger i b^\dagger j + \cdots. \tag{4}$$

For ionized or electron-attached states, we simply allow excitation into the continuum to give the ionization operator $I(k)$ as $\Omega(k)$ or deexcitation from the continuum to give the electron-attachment operator $A(k)$,

$$I(k) = \sum_i^{\text{occ.}} I_i(k) i + \sum_{i>j}^{\text{occ.}} \sum_a^{\text{virt.}} I_{ij}^a(k) i a^\dagger j + \cdots \tag{5}$$

and

$$A(k) = \sum_a^{\text{virt.}} A^a(k) a^\dagger + \sum_i^{\text{occ.}} \sum_{a>b}^{\text{virt.}} A_i^{ab}(k) a^\dagger i b^\dagger + \cdots. \tag{6}$$

These particular EOM-CC methods are referred to as EE-EOM-CC, IP-EOM-CC, and EA-EOM-CC, respectively. Approximating the target-state wavefunctions by Eq. (1), we can conveniently take into account the correlation effects that are common to the reference and target states by the

exponential wave operator $\exp(T)$ and allow the linear operator $\Omega(k)$ to describe the essential differential correlation effects. The action of $\exp(T)$ and $\Omega(k)$ on a closed-shell reference determinant creates properly spin-adapted wavefunctions for open-shell systems, rendering IP-EOM-CC and EA-EOM-CC effective tools for the study of the ground and excited states of radicals.

In practice, the summations in Eq. (3) for T and in Eqs. (4)–(6) for $\Omega(k)$ are truncated after certain tractable terms. Hence the EOM-CC models are characterized by the truncation orders of T and $\Omega(k)$, and as the operators become closer to complete, the calculated results would systematically approach the full configuration interaction (FCI) results. We have recently analyzed the performance of the EE-EOM-CC models with different truncation orders of T and $\Omega(k)$ with the aid of a determinantal general-order EE-EOM-CC program [24]. We found that generally including the same orders of excitation operators in T and $\Omega(k)$, we arrive at numerically well-balanced EE-EOM-CC models, but we also obtained good results from slightly different treatment of the ground and excited states, attesting to the greater importance of some kinds of excitations in excited states than in the ground state. In this Letter, we report the extension of this analysis to IP-EOM-CC and EA-EOM-CC. We shall examine the performance of these methods as a function of the truncation orders of T and $\Omega(k)$ by comparing the calculated results against FCI results. This is of particular interest as the number of electrons is incremented or decremented upon the ionization or electron-attachment process, and it may not be obvious how T and $\Omega(k)$ should be approximated to handle these processes in a well-balanced manner. We develop general-order IP-EOM-CC and EA-EOM-CC methods that employ a determinantal algorithm, and compute the principal ionization potentials and electron affinities of small diatomic molecules (BH, CH^+, and C_2) across different truncation orders of T and $\Omega(k)$. The excitation energies of diatomic radicals (BH^+ and CH) are also computed as the differences between the first ionization potential (electron affinity) and higher ionization potentials (electron affinities) of the

closed-shell reference state. The results are discussed in the following.

2. Theory

The exponential reference wavefunction $|\Psi_0\rangle = \exp(T)|\Phi_0\rangle$ is determined by the usual CC equations [23]:

$$\langle\Phi_0|H|\Psi_0\rangle = E_0, \tag{7a}$$

$$\left\langle\Phi_i^a|H|\Psi_0\right\rangle = E_0\left\langle\Phi_i^a|\Psi_0\right\rangle, \tag{7b}$$

$$\left\langle\Phi_{ij}^{ab}|H|\Psi_0\right\rangle = E_0\left\langle\Phi_{ij}^{ab}|\Psi_0\right\rangle, \tag{7c}$$

$$\left\langle\Phi_{ijk}^{abc}|H|\Psi_0\right\rangle = E_0\left\langle\Phi_{ijk}^{abc}|\Psi_0\right\rangle, \tag{7d}$$

etc., where H is the Hamiltonian, E_0 the electronic energy of the reference state, and $|\Phi_i^a\rangle$, $|\Phi_{ij}^{ab}\rangle$, and $|\Phi_{ijk}^{abc}\rangle$ represent singly, doubly, and triply substituted determinants, respectively. When T contains single, double,..., m-tuple excitation operators, the chain of equations, (7a)–(7d), terminates after the projection equation onto m-tuply substituted determinants, and we call this method CC(m). For the implementation and calculations of CC(m) at any given order m, the readers are referred to our earlier Letter [25].

The EOM-CC equations are derived by substituting the target wavefunctions into the Schrödinger equation and projecting it onto an appropriate class of determinants. For the kth target state (with the associated energy E_k), we thus start with the equation

$$H\Omega(k)\exp(T)|\Phi_0\rangle = E_k\Omega(k)\exp(T)|\Phi_0\rangle. \tag{8}$$

Operating on both sides of the equation with $\exp(-T)$ from the left-hand side and using the fact that $\Omega(k)$ and T commute, we find

$$\bar{H}\Omega(k)|\Phi_0\rangle = E_k\Omega(k)|\Phi_0\rangle \tag{9}$$

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

$$\bar{H} \equiv \exp(-T)H\exp(T). \tag{10}$$

Eq. (9) is projected onto the basis of determinants that are accessible by the action of $\Omega(k)$ on $|\Phi_0\rangle$.

For IP-EOM-CC, the equations obtained by this projection are

$$\langle\Phi_i|\bar{H}I(k)|\Phi_0\rangle = E_k\langle\Phi_i|I(k)|\Phi_0\rangle, \tag{11a}$$

$$\left\langle\Phi_{ij}^a|\bar{H}I(k)|\Phi_0\right\rangle = E_k\left\langle\Phi_{ij}^a|I(k)|\Phi_0\right\rangle, \tag{11b}$$

$$\left\langle\Phi_{ijk}^{ab}|\bar{H}I(k)|\Phi_0\right\rangle = E_k\left\langle\Phi_{ijk}^{ab}|I(k)|\Phi_0\right\rangle, \tag{11c}$$

etc., where $|\Phi_i\rangle$, $|\Phi_{ij}^a\rangle$, and $|\Phi_{ijk}^{ab}\rangle$ represent one-hole (1h), two-hole-one-particle (2h-1p), and three-hole-two-particle (3h-2p) determinants, respectively, and likewise for EA-EOM-CC. These equations constitute a non-Hermitian CI-like eigenvalue problem, which is to be solved for the amplitudes of $\Omega(k)$.

In what follows, we shall use the notation IP-EOM-CC($m, n+$1h-np) and EA-EOM-CC(m, nh-$n+$1p) to denote specific approximate models of IP-EOM-CC and EA-EOM-CC, respectively. The first parameter m indicates that all connected excitation operators through the connected m-fold excitation operator are included in T; the wavefunction of the reference state is obtained from CC(m). The second parameter nh-$n\mp$1p specifies the truncation order of $\Omega(k)$, which takes such values as 1h, 2h-1p, 3h-2p, etc., for IP-EOM-CC, and 1p, 1h-2p, 2h-3p, etc., for EA-EOM-CC. For example, IP-EOM-CC(3,3h-2p) diagonalizes the effective Hamiltonian $\bar{H}$ obtained from the CC(3) = CCSDT similarity transformation, in the space of 1h, 2h-1p, and 3h-2p determinants. IP-EOM-CC($1, n+$1h-np) and EA-EOM-CC($1, n$h-$n+$1p) employ the CC(1) = HF reference wavefunctions, and are equivalent to the so-called nh-$n\mp$1p CI (see, e.g., Ref. [26]). When we take the largest possible value for n, i.e., when $\Omega(k)$ is complete, IP-EOM-CC($m, n+$1h-np) and EA-EOM-CC(m, nh-$n+$1p) are equivalent to FCI regardless of the choice of m, as the similarity transformation of Eq. (10) does not change the eigenvalues of the original bare Hamiltonian H. The ionization potentials and electron affinities of a molecule M are obtained as the energies of the ground and excited states of M^+ and M^- computed by IP-EOM-CC($m, n+$1h-np) and EA-EOM-CC(m, nh-$n+$1p), respectively, minus the energy of the ground state of M computed by

CC(m). Note that according to this definition one may not necessarily obtain the exact ionization potentials (electron affinities) with complete $\Omega(k)$, because the energy of the ground state of M may not be exact unless T is complete. The differences in ionization potential (electron affinity) between the lowest root (the ground state of the radical) and the other roots (excited states of the radical) amount to the vertical excitation energies of the radical.

3. Demonstrative calculations

The general-order IP/EA-EOM-CC method has been implemented in the POLYMER program [27] by literally following the procedure described in the previous section with a determinantal algorithm. The implementation is parallel to that for the determinantal EE-EOM-CC method, which invokes a non-Hermitian modification [28] of Davidson's iterative subspace method [29] to obtain the several lowest eigenvalues and corresponding eigenvectors of the effective Hamiltonian matrix $\bar{H}$. The wavefunction of the reference state (with N electrons) is stored in an array of the so-called α- and β-strings [30], which address the α- and β-parts of determinants. The wavefunctions of the target states (with $N + 1$ or $N - 1$ electrons) are also represented by arrays of α- and β-strings, but now these strings address the determinants with one more or one less electrons than those for the reference state. The amplitudes of $I(k)$ or $A(k)$ are also conveniently packed into arrays of α- and β-strings for $N + 1$ or $N - 1$ electrons. Therefore, the determinantal EE-EOM-CC program can be readily extended to IP/EA-EOM-CC by replacing appropriately some of the α- and β-strings for N electrons by those for $N + 1$ or $N - 1$ electrons. The details of the implementation of EE-EOM-CC can be found in Ref. [24].

The IP-EOM-CC and EA-EOM-CC calculations are performed for the vertical ionization potentials of BH and for the vertical electron affinities of CH^+, respectively, for all possible combinations of the truncation orders of T and $\Omega(k)$. The calculated results are compiled in Tables 1 and 2, in which we also list the results of CI calcula-

Table 1
The ionization potentials (in eV) of BH ($r_{BH} = 1.232$ Å) calculated by IP-EOM-CC($m, n + $ 1h-np) and CI($m, n + $ 1h-np) with the 6-31G** basis set[a]

Theory	$3\sigma \rightarrow \infty$	$2\sigma \rightarrow \infty$
FCI	9.383	16.643
CI(1,1h)[b]	9.169	19.794
CI(1,2h-1p)[b]	8.097	15.853
CI(1,3h-2p)[b]	7.056	14.390
CI(1,4h-3p)[b,c]	7.016	14.276
CI(2,1h)	11.422	19.680
CI(2,2h-1p)	10.351	18.106
CI(2,3h-2p)	9.310	16.643
CI(2,4h-3p)[c]	9.269	16.529
CI(3,1h)	11.467	19.725
CI(3,2h-1p)	10.395	18.151
CI(3,3h-2p)	9.354	16.688
CI(3,4h-3p)[c]	9.314	16.573
CI(4,1h)[d]	11.535	19.794
CI(4,2h-1p)[d]	10.464	18.220
CI(4,3h-2p)[d]	9.423	16.757
CI(4,4h-3p)[c,d]	9.383	16.643
IP-EOM-CC(1,1h)[b]	9.169	19.794
IP-EOM-CC(1,2h-1p)[b]	8.097	15.853
IP-EOM-CC(1,3h-2p)[b]	7.056	14.390
IP-EOM-CC(1,4h-3p)[b,c]	7.016	14.276
IP-EOM-CC(2,1h)	10.385	18.368
IP-EOM-CC(2,2h-1p)[e]	9.418	16.980
IP-EOM-CC(2,3h-2p)	9.342	16.626
IP-EOM-CC(2,4h-3p)[c]	9.335	16.643
IP-EOM-CC(3,1h)	10.417	18.391
IP-EOM-CC(3,2h-1p)	9.448	17.377
IP-EOM-CC(3,3h-2p)	9.384	16.688
IP-EOM-CC(3,4h-3p)[c]	9.381	16.641
IP-EOM-CC(4,1h)[d]	10.418	18.391
IP-EOM-CC(4,2h-1p)[d]	9.450	17.006
IP-EOM-CC(4,3h-2p)[d]	9.385	16.669
IP-EOM-CC(4,4h-3p)[c,d]	9.383	16.643

[a] The lowest and highest orbitals are kept frozen in the correlation treatment. The FCI energy of the ground state of BH is -25.206212H.
[b] IP-EOM-CC(1,1h) = CI(1,1h) = Koopmans' theorem; IP-EOM-CC(1,2h-1p) = CI(1,2h-1p); IP-EOM-CC(1,3h-2p) = CI(1,3h-2p); IP-EOM-CC(1,4h-3p) = CI(1,4h-3p).
[c] The total energy of any electronic state of BH^+ is exact.
[d] The ground-state total energy of BH is exact.
[e] IP-EOM-CCSD.

tions. CI(m, nh-$n \mp $ 1p) means that the ionization potentials or electron affinities are evaluated as the CI(nh-$n \mp $ 1p) energies of ionized or electron-

Table 2
The electron affinities (in eV) of CH^+ ($r_{CH} = 1.120$ Å) calculated by EA-EOM-CC(m, nh-n + 1p) and CI(m, nh-n + 1p) with the 6-31G* basis set[a]

Theory	$\infty \to 1\pi$	$\infty \to 3\sigma$
FCI	10.109	1.741
CI(1,1p)[b]	8.922	1.159
CI(1,1h-2p)[b]	10.949	2.086
CI(1,2h-3p)[b]	12.551	4.175
CI(1,3h-4p)[b]	12.681	4.288
CI(1,4h-5p)[b,c]	12.709	4.340
CI(2,1p)	6.433	−1.329
CI(2,1h-2p)	8.460	−0.402
CI(2,2h-3p)	10.063	1.687
CI(2,3h-4p)	10.192	1.800
CI(2,4h-5p)[c]	10.220	1.852
CI(3,1p)	6.386	−1.376
CI(3,1h-2p)	8.413	−0.449
CI(3,2h-3p)	10.016	1.640
CI(3,3h-4p)	10.146	1.753
CI(3,4h-5p)[c]	10.173	1.805
CI(4,1p)[d]	6.322	−1.440
CI(4,1h-2p)[d]	8.349	−0.513
CI(4,2h-3p)[d]	9.952	1.575
CI(4,3h-4p)[d]	10.081	1.689
CI(4,4h-5p)[c,d]	10.109	1.741
EA-EOM-CC(1,1p)[b]	8.922	1.159
EA-EOM-CC(1,1h-2p)[b]	10.949	2.086
EA-EOM-CC(1,2h-3p)[b]	12.551	4.175
EA-EOM-CC(1,3h-4p)[b]	12.681	4.288
EA-EOM-CC(1,4h-5p)[b,c]	12.709	4.340
EA-EOM-CC(2,1p)	8.317	0.834
EA-EOM-CC(2,1h-2p)[e]	10.150	1.701
EA-EOM-CC(2,2h-3p)	10.132	1.745
EA-EOM-CC(2,3h-4p)	10.159	1.787
EA-EOM-CC(2,4h-5p)[c]	10.159	1.791
EA-EOM-CC(3,1p)	8.311	0.829
EA-EOM-CC(3,1h-2p)	10.133	1.693
EA-EOM-CC(3,2h-3p)	10.117	1.734
EA-EOM-CC(3,3h-4p)	10.111	1.740
EA-EOM-CC(3,4h-5p)[c]	10.112	1.744
EA-EOM-CC(4,1p)[d]	8.310	0.828
EA-EOM-CC(4,1h-2p)[d]	10.132	1.693
EA-EOM-CC(4,2h-3p)[d]	10.115	1.734
EA-EOM-CC(4,3h-4p)[d]	10.109	1.740
EA-EOM-CC(4,4h-5p)[c,d]	10.109	1.741

[a] The lowest and highest orbitals are kept frozen in the correlation treatment. The FCI energy of the ground state of CH^+ is −37.990913H.
[b] EA-EOM-CC(1,1p) = CI(1,1p) = Koopmans' theorem; EA-EOM-CC(1,1h-2p) = CI(1,1h-2p); EA-EOM-CC(1,2h-3p) = CI(1,2h-3p); EA-EOM-CC(1,3h-4p) = CI(1,3h-4p); EA-EOM-CC(1,4h-5p) = CI(1,4h-5p).
[c] The total energy of any electronic state of CH is exact.
[d] The ground-state total energy of CH^+ is exact.
[e] EA-EOM-CCSD.

Table 3
The ionization potentials (in eV) of C_2 ($r_{CC} = 1.262$ Å) calculated by IP-EOM-CC(m, mh-$m - 1$p) and CI(m, mh-$m - 1$p) with the 6-31G basis set[a]

Theory	$1\pi_u \rightarrow \infty$	$2\sigma_u^- \rightarrow \infty$
FCI	12.131	14.721
CI(1,1h)[b]	12.195	13.942
CI(2,2h-1p)	16.809	18.221
CI(3,3h-2p)	12.070	14.537
CI(4,4h-3p)	12.695	15.063
CI(5,5h-4p)	12.109	14.716
CI(6,6h-5p)	12.136	14.726
CI(7,7h-6p)	12.131	14.721
CI(8,8h-7p)[c]	12.131	14.721
IP-EOM-CC(1,1h)[b]	12.195	13.942
IP-EOM-CC(2,2h-1p)[d]	12.662	15.180
IP-EOM-CC(3,3h-2p)	12.134	14.803
IP-EOM-CC(4,4h-3p)	12.151	14.749
IP-EOM-CC(5,5h-4p)	12.130	14.724
IP-EOM-CC(6,6h-5p)	12.132	14.721
IP-EOM-CC(7,7h-6p)	12.131	14.721
IP-EOM-CC(8,8h-7p)[c]	12.131	14.721

[a] The two lowest and two highest orbitals are kept frozen in the correlation treatment. The FCI energy of the ground state of C_2 is -75.609844H.
[b] IP-EOM-CC(1,1h) = CI(1,1h) = Koopmans' theorem.
[c] The ground-state energies of C_2 and C_2^+ are exact.
[d] IP-EOM-CCSD.

attached states minus the CI(m) energy of the reference state.

By comparing the results of CI(4, nh-$n \mp 1$p) and IP/EA-EOM-CC(4, nh-$n \mp 1$p), we can clearly see the virtue of the similarity transformation of the Hamiltonian in the latter method. The convergence of the calculated ionization potentials and electron affinities with respect to n is remarkably faster in IP/EA-EOM-CC than in CI. As the reference states (the ground states of BH and CH$^+$) are handled exactly by CI(4) = CC(4) = FCI, the difference arises from a better description of the target radicals in IP/EA-EOM-CC(4, nh-$n \mp 1$p) achieved by the effective inclusion of dynamical correlation through the similarity transformation. The IP-EOM-CC(m, mh-$m - 1$p) models appear to be numerically well-balanced models among others. When we increase or decrease the order of T while holding the order of $I(k)$ fixed, we obtain deteriorated results relative to IP-EOM-CC(m, mh-$m - 1$p) except for a few cases. This observation might be expected as these

IP-EOM-CC models include IP-EOM-CC(4,4h-3p) = FCI and IP-EOM-CC(1,1h) = Koopmans' theorem at both ends of the series and also the standard IP-EOM-CCSD = IP-EOM-CC(2,2h-1p). They also correspond to a natural extension of EE-EOM-CC(m, m) in the sense that the excitation energies of Rydberg series obtained from EE-EOM-CC(m, m) should converge at the ionization potentials obtained from IP-EOM-CC(m, mh-$m - 1$p) [16,18,31]. The connection between EA-EOM-CC and EE-EOM-CC is less straightforward [31]. We may consider two different series, i.e., EA-EOM-CC($m, m - 1$h-mp) and EA-EOM-CC(m, mh-$m + 1$p), as candidates for the best-balanced series. The former series includes EA-EOM-CC(1,1p) = Koopmans' theorem (though it performs poorly for electron affinities) and also the standard EA-EOM-CCSD = EA-EOM-CC(2,1h-2p), but not FCI, whereas the latter includes FCI. Overall these two series perform equally well for principal electron affinities, but, as we shall see later, the results for the excitation energies of radicals appear to favor EA-EOM-CC($m, m - 1$h-mp).

Table 3 summarizes the IP-EOM-CC(m, mh-$m - 1$p) and CI(m, mh-$m - 1$p) results for the vertical ionization potentials of C_2. The ground-state wavefunction of C_2 is known to have substantial multi-determinantal character, and is a challenging problem for single-reference theories. The largest absolute amplitude in T occurs at a double (2h-2p) replacement from the ground-state wavefunction, and is as big as 0.39 in the CC(8) wavefunction. Consequently, the wavefunctions of the ionized states, which are predominantly 1h ionization from the ground state, have appreciable contributions from 3h-2p determinants. We notice from the table that IP-EOM-CCSD = IP-EOM-CC(2, 2h-1p) does not provide as accurate principal ionization potentials for C_2 as it does for BH, owing to the multi-determinantal character of the former. However, the deviations from the FCI results are remarkably smaller in IP-EOM-CCSD = IP-EOM-CC(2,2h-1p) (ca. 0.5 eV) than those encountered in the corresponding CI model, i.e., CI(2,2h-1p) (>4 eV), which again attests to the effectiveness of the similarity transformation. IP-EOM-CC(3,3h-2p) includes the 3h-2p operator

among $\Omega(k)$ and yields accurate ionization potentials (within 0.1 eV of the FCI results) for this pathological example.

The vertical excitation energies of BH$^+$ and CH computed by IP-EOM-CC and EA-EOM-CC are compiled in Tables 4 and 5, respectively. The percentage contributions of the 1h (1p) and 2h-1p (1h-2p) determinants in the FCI wavefunctions are also given in these tables. The excited states are categorized into three groups: those that are associated with dominant 1h (1p) transitions from the reference state, those with dominant 2h-1p (1h-2p) transitions, and those with dominant 3h-2p (2h-3p) and higher transitions. The excited states in the first category (the lowest $^2\Sigma^+$ state of BH$^+$ and the third lowest $^2\Sigma^+$ state of CH) are the destinations of the principal ionization or electron-attachment processes. The excitation en-

ergies to these states are reasonably well reproduced by IP-EOM-CC(m, 2h-1p) or EA-EOM-CC(m, 1h-2p), though the deviations from the FCI results for the lowest $^2\Sigma^+$ state of BH$^+$ (0.3–0.5 eV) are appreciably larger than those typically encountered in the EE-EOM-CCSD excitation energies for dominant single replacement transitions (see, e.g., Ref. [32]). This is obviously due to the substantial contributions of 2h-1p determinants in the wavefunction of that state. Most of the excited states listed in the tables are in the second category, which are the destinations of non-Koopmans ionization or electron-attachment processes. Their wavefunctions are predominantly single replacement from the ground-state wavefunctions of the radicals, which in turn are predominantly 1h ionization or 1p electron attachment from the reference states. As one

Table 4

The excitation energies (in eV) of BH$^+$ ($r_{BH} = 1.232$ Å) calculated by IP-EOM-CC(m, $n + $ 1h-np) with the 6-31G** basis set as the differences in the ionization potential of BH between the lowest root (the ground state of BH$^+$) and higher roots (excited states of BH$^+$)[a]

IP-EOM-CC	$^2\Pi$	$^4\Pi$	$^2\Sigma^+$	$^2\Pi$	$^4\Sigma^+$	$^2\Pi$
FCI	3.369	7.073	7.260	10.603	10.698	11.068
(1,1h)[b]	–	–	10.625	–	–	–
(1,2h-1p)[b]	3.530	7.016	7.756	11.007	–	11.607
(1,3h-2p)[b]	3.793	7.083	7.334	10.795	11.022	11.285
(1,4h-3p)[b]	3.369	7.073	7.260	10.603	10.698	11.068
(2,1h)	–	–	7.983	–	–	–
(2,2h-1p)[c]	4.047	7.913	7.562	11.628	–	12.412
(2,3h-2p)	3.415	7.085	7.284	10.591	11.035	11.098
(2,4h-3p)	3.369	7.073	7.260	10.603	10.698	11.068
(3,1h)	–	–	7.974	–	–	–
(3,2h-1p)	4.090	7.959	7.587	11.675	–	12.458
(3,3h-2p)	3.415	7.088	7.304	10.591	11.041	11.100
(3,4h-3p)	3.369	7.073	7.260	10.603	10.698	11.068
(4,1h)	–	–	7.973	–	–	–
(4,2h-1p)	4.059	7.929	7.556	11.645	–	12.427
(4,3h-2p)	3.415	7.089	7.284	10.592	11.041	11.100
(4,4h-3p)	3.369	7.073	7.260	10.603	10.698	11.068
% 1h	0.00	0.00	76.04	0.00	0.00	0.00
% 2h-1p	96.76	96.44	13.09	94.75	0.00	94.98

[a] The lowest and highest orbitals are kept frozen in the correlation treatment. The percentage contributions from the determinants with one hole and two holes and one particle in the FCI wavefunctions are also given as % 1h and % 2h-1p, respectively. The IP-EOM-CC(m, 4h-3p) results are identical to the FCI results irrespective of m.

[b] IP-EOM-CC(1,1h) = CI(1h) = Koopmans' theorem; IP-EOM-CC(1,2h-1p) = CI(2h-1p); IP-EOM-CC(1,3h-2p) = CI(3h-2p); IP-EOM-CC(1,4h-3p) = CI(4h-3p) = FCI.

[c] IP-EOM-CCSD.

might expect, the excitation energies calculated from IP-EOM-CC(m, 2h-1p) and EA-EOM-CC(m, 1h-2p) for these excited states are excessively higher than the FCI results. Quantitative descriptions of these excited states require the inclusion of at least the 3h-2p (2h-3p) operator. Likewise, for those excited states with predominantly 3h-2p (2h-3p) replacement character, the inclusion of the 4h-3p (3h-4p) operator would become necessary. The effect of the similarity transformation on the excitation energies manifests itself in a rather complicated manner. On going from IP-EOM-CC(1,2h-1p) = CI(2h-1p) to IP-EOM-CC(2,2h-1p) = IP-EOM-CCSD, we obtain an improvement only for the lowest $^2\Sigma^+$ state of BH$^+$, which is a dominant 1h replacement

from the reference state, while we deteriorate the results for the rest of the excited states significantly. Comparison between IP-EOM-CC(1,3h-2p) = CI(3h-2p) and IP-EOM-CC(2,3h-2p), on the other hand, indicates that the latter is a uniform improvement over the former. The same trend can be seen in the EA-EOM-CC results. One possible explanation is that the similarity transformation particularly enhances the descriptions of the ionized (electron-attached) states with dominant 1h (1p) character when used in combination with 1h-2p (2h-1p) operator, rendering the energy differences uneven. To obtain reasonable excitation energies for many of the excited states of radicals, we must include 3h-2p (2h-3p) in the ionization or electron-attachment operator.

Table 5
The excitation energies (in eV) of CH (r_{CH} = 1.120 Å) calculated by EA-EOM-CC(m, nh-n + 1p) with the 6-31G* basis set as the differences in the electron affinity of CH$^+$ between the lowest root (the ground state of CH) and higher roots (excited states of CH)[a]

EA-EOM-CC	$^4\Sigma^+$	$^2\Pi$	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Pi$	$^2\Sigma^+$
FCI	0.483	3.144	3.407	4.321	7.900	8.368
(1,1p)[b]	–	–	–	–	–	7.763
(1,1h-2p)[b]	1.106	3.915	4.961	5.115	–	8.862
(1,2h-3p)[b]	0.918	3.569	3.809	5.125	9.393	8.376
(1,3h-4p)[b]	0.466	3.132	3.405	4.347	8.094	8.392
(1,4h-5p)[b]	0.483	3.144	3.407	4.321	7.900	8.368
(2,1p)	–	–	–	–	–	7.483
(2,1h-2p)[c]	2.217	5.067	5.924	6.219	–	8.449
(2,2h-3p)	0.477	3.156	3.498	4.362	9.347	8.387
(2,3h-4p)	0.485	3.145	3.408	4.333	7.930	8.371
(2,4h-5p)	0.483	3.144	3.407	4.321	7.900	8.368
(3,1p)	–	–	–	–	–	7.482
(3,1h-2p)	2.234	5.085	5.930	6.237	–	8.439
(3,2h-3p)	0.504	3.184	3.528	4.374	9.378	8.383
(3,3h-4p)	0.483	3.144	3.407	4.322	7.929	8.371
(3,4h-5p)	0.483	3.144	3.407	4.321	7.900	8.368
(4,1p)	–	–	–	–	–	7.482
(4,1h-2p)	2.235	5.086	5.931	6.238	–	8.439
(4,2h-3p)	0.505	3.184	3.529	4.375	9.379	8.382
(4,3h-4p)	0.484	3.144	3.408	4.322	7.930	8.370
(4,4h-5p)	0.483	3.144	3.407	4.321	7.900	8.368
% 1p	0.00	0.11	0.00	0.16	0.89	87.84
% 1h-2p	94.63	94.58	91.84	93.28	0.45	5.19

[a] The lowest and highest orbitals are kept frozen in the correlation treatment. The percentage contributions from the determinants with one particle and one hole and two particles in the FCI wavefunctions are also given as % 1p and % 1h-2p, respectively. The EA-EOM-CC(m, 4h-5p) results are identical to the FCI results irrespective of m.
[b] EA-EOM-CC(1,1p) = CI(1p) = Koopmans' theorem; EA-EOM-CC(1,1h-2p) = CI(1h-2p); EA-EOM-CC(1,2h-3p) = CI(2h-3p); EA-EOM-CC(1,3h-4p) = CI(3h-4p); EA-EOM-CC(1,4h-5p) = CI(4h-5p) = FCI.
[c] EA-EOM-CCSD.

We now return to the question of the performance of the EA-EOM-CC models. As the truncation order of $\Omega(k)$ largely dictates the performance of the EA-EOM-CC models, it may not be meaningful to compare EA-EOM-CC(m, m-1h-mp) with EA-EOM-CC(m,mh-m+1p) because the latter certainly performs better than the former. Rather we should compare EA-EOM-CC($m + 1, m$h-$m + 1$p) with EA-EOM-CC(m, mh-$m + 1$p). From Table 5, we notice that for a given order of electron-attachment operator mh-$m + 1$p, EA-EOM-CC(m, mh-$m + 1$p) performs appreciably better than EA-EOM-CC($m + 1, m$h-$m + 1$p). For example, EA-EOM-CC(1,1h-2p) provides excitation energies that are in better agreement with the FCI results than EA-EOM-CC(2,1h-2p) does. Likewise the excitation energies obtained from EA-EOM-CC(2,2h-3p) or EA-EOM-CC(3,3h-4p) are systematically closer to the FCI results than those from EA-EOM-CC(3,2h-3p) or EA-EOM-CC(4,3h-4p), respectively. It may be said that for principal electron-attachment transitions both the EA-EOM-CC($m + 1, m$h-$m + 1$p) and EA-EOM-CC(m, mh-$m + 1$p) models perform reasonably well, but for non-Koopmans electron-attachment transitions the latter model is better balanced.

To summarize:

1. IP-EOM-CC(2,2h-1p) = IP-EOM-CCSD is a well-balanced IP-EOM-CC model that provides principal ionization potentials (which are typically of dominant 1h character) with reasonably high accuracy.
2. EA-EOM-CC(2,1h-2p) = EA-EOM-CCSD and EA-EOM-CC(2,2h-3p) perform equally well for principal electron affinities.
3. Despite (1) and (2), for the ground states with considerable multi-determinantal character, IP-EOM-CC(2,2h-1p) = IP-EOM-CCSD performs noticeably worse, and the use of IP-EOM-CC(3,3h-2p) = IP-EOM-CCSDT or higher models will be warranted to obtain accurate principal ionization potentials. Nevertheless, IP-EOM-CC(2,2h-1p) = IP-EOM-CCSD works remarkably better than CI(2,2h-1p) in such pathological cases.
4. For the quantitative descriptions of non-Koopmans ionization or electron-attachment processes, one must go to IP-EOM-CC(3,3h-2p) =

IP-EOM-CCSDT or EA-EOM-CC(2,2h-3p) (the approximate variants of them would be pragmatic choices [18,33–35]). These models provide the excitation energies of radicals within a few hundredths of an electron volt of the FCI results for excited states that are dominant 1h (1p) and 2h-1p (1h-2p) replacements from the reference state.
5. In general, one has to consider the ionization or electron-attachment operator that is one order higher than the dominant rank (the number of electrons involved) of the ionization or electron-attachment process of interest within reasonable accuracy (a few tenth of an electron volt). If one attempts to achieve the similar accuracy with mh-$m \mp 1$p CI, one must consider the ionization or electron-attachment operator that is two orders higher than the dominant rank of the ionization or electron-attachment process.

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