Communication: Accurate excited-state energetics by a combination of Monte Carlo sampling and equation-of-motion coupled-cluster computations

J. Emiliano Deustua,[1] Stephen H. Yuwono,[1] Jun Shen,[1] and Piotr Piecuch[1,2,a)]

[1] *Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA*

[2] *Department of Physics & Astronomy, Michigan State University, East Lansing, MI 48824, USA*

Abstract

The recently proposed idea of identifying the most important higher–than–doubly excited determinants in the ground-state coupled-cluster (CC) calculations through stochastic configuration interaction Quantum Monte Carlo propagations [J.E. Deustua, J. Shen, and P. Piecuch, *Phys. Rev. Lett.* **119**, 223003 (2017)] is extended to excited electronic states via the equation-of-motion (EOM) CC methodology. The advantages of the new approach are illustrated by calculations aimed at recovering the ground- and excited-state energies of the CH^+ molecule at the equilibrium and stretched geometries resulting from the EOMCC calculations with a full treatment of singles, doubles, and triples.

[a)] Corresponding author. Electronic mail: piecuch@chemistry.msu.edu.

One of the most important areas of quantum chemistry is the development of accurate and computationally manageable methods for excited electronic states. This is particularly challenging when excited-state potentials and excited states dominated by two- and other many-electron transitions are examined. Among methods that can be helpful in addressing this challenge are the equation-of-motion (EOM)[1-3] and linear-response (LR)[4-10] extensions of the coupled-cluster (CC) theory[11-15] and their symmetry-adapted-cluster (SAC) configuration interaction (CI) counterpart,[16] in which excited-state wave functions are defined as[17] $|\Psi_\mu\rangle = R_\mu |\Psi_0\rangle = R_\mu \exp(T)|\Phi\rangle$, where $T = \sum_{n=1}^{N} T_n$ and $R_\mu = \sum_{n=0}^{N} R_{\mu,n} = r_{\mu,0}\mathbf{1} + \sum_{n=1}^{N} R_{\mu,n}$ are the cluster and EOM excitation operators, T_n and $R_{\mu,n}$ are the n-body components of T and R_μ, respectively, N is the number of correlated electrons, **1** is the unit operator, and $|\Phi\rangle$ is the reference determinant defining the Fermi vacuum. However, in order to be successful, one needs to come up with robust and computationally tractable ways of incorporating higher–than–two-body components of T and R_μ.

The T_n and $R_{\mu,n}$ components with $n > 2$ become especially important when excited-state wave functions gain a multi-reference character. Indeed, when applied to excited-state potentials along bond breaking coordinates and excited states having significant double excitation contributions, the basic EOMCC method with singles and doubles (EOMCCSD),[3] where T and R_μ are truncated at T_2 and $R_{\mu,2}$, respectively, and its LRCCSD analog,[9,10] which build the excited-state information on top of the ground-state CCSD calculation[18,19] and which are characterized by the relatively inexpensive computational steps that scale as $n_o^2 n_u^4$ [n_o (n_u) is the number of occupied (unoccupied) correlated orbitals], produce errors in the excitation energies that usually exceed 1 eV, being frequently much larger.[20-28] Even when excited-state wave functions are dominated by one-electron transitions, EOMCCSD is not fully quantitative, giving errors on the order of 0.3–0.5 eV.[29] One can rectify these problems by turning to higher CC/EOMCC levels, such as the EOM extension of the CC approach with singles, doubles, and triples (CCSDT),[30,31] abbreviated as EOMCCSDT, where T and R_μ are truncated at T_3 and $R_{\mu,3}$,[21,22,32] or the EOM counterpart of the CC method with singles, doubles, triples, and quadruples (CCSDTQ),[33-36] abbreviated as EOMCCSDTQ, where T and R_μ are truncated at T_4 and $R_{\mu,4}$,[37,38] but methods of this type, although very accurate and in many cases nearly exact,[21,22,32,37,38] are characterized by the iterative computational steps that scale as $n_o^3 n_u^5$ for EOMCCSDT and $n_o^4 n_u^6$ for EOMCCSDTQ, which are usually prohibitively expensive. A lot of effort has gone into developing approximate EOMCC and LRCC models that utilize elements of the many-body perturbation theory to identify the leading post-EOMCCSD contributions in less expensive ways, including the various non-iterative triples corrections to the EOMCCSD or LRCCSD excitation energies[39-42] and their iterative EOMCCSDT-*n*[39,40] and CC3[41-44] counterparts, but approximations of this type are not accurate enough for excited states dominated by two-electron transitions and larger portions of excited-state potentials. The completely renormalized triples corrections to the EOMCCSD total[23,26-28] or excitation[23,29,45] energies and their analogs based on partitioning the similarity-transformed Hamiltonian[46,47] are more robust, but balancing ground- and excited-state energies[23,47] or examining potential surface crossings[48] remains difficult.

One can address the above concerns by turning to the active-space EOMCC approaches,[20-22,24,49] such as EOMCCSDt[20-22,24] or EOMCCSDtq,[20,49] and their extensions to particle non-conserving models,[49-55] where, in analogy to the ground-state case,[36,56-58] one uses small subsets of active orbitals to identify the dominant T_n and $R_{\mu,n}$ amplitudes with $n > 2$ without any reference to perturbation theory or Hamiltonian partitioning (see Ref. 59 for a review), but by relying on the user- and system-dependent active orbitals the active-space EOMCC methods are no longer black-box schemes. We should be able to alleviate at least some of the issues resulting from inadequate choices of active orbitals in EOMCCSDt, EOMCCSDtq, and similar calculations by using the *a posteriori* non-iterative CC(P;Q) corrections[60] to account for the T_3 and $R_{\mu,3}$ or $T_3, R_{\mu,3}$, T_4, and $R_{\mu,4}$ contributions outside the active sets, and we are presently working on extending the CC(P;Q)-based CC(t;3), CC(t,q;3), CC(t,q;3,4), etc. hierarchy[60-63] to excited states, but the problem of the user- and system-dependent active orbitals remains. Questions arise if there is an automated way of capturing the leading T_n and $R_{\mu,n}$ contributions with $n > 2$, without resorting to the active-space ideas, and if this can be done such that the resulting energies of excited states rapidly converge to their high-level EOMCC (e.g., EOMCCSDT) parents at the small fraction of the computational effort, even when the states of interest have significant double excitation or multi-reference character. The present communication addresses these questions by turning to the stochastic CI Quantum Monte Carlo (QMC) framework, as formulated in Refs. 64

and 65, merging it with the deterministic EOMCC computations. In doing so, we draw the inspiration from our recent work on incorporating the stochastic CIQMC methodology and its CC counterpart[66] into the deterministic CC framework.[67] We demonstrate that we can take the merger of the stochastic and deterministic ideas to the next level and produce accurate excited-state energetics closely matching the results of high-level EOMCC computations, represented in this work by EOMCCSDT, after short CIQMC (in this study, full CIQMC = FCIQMC[64,65]) runs.

We recall that the main idea of the CIQMC methodology of Refs. 64 and 65, including the FCIQMC approach employed in this study, is that of a stochastic walker population dynamics that simulates the imaginary-time Schrödinger equation in the many-electron Hilbert space spanned by Slater determinants. The positively or negatively signed walkers populating Slater determinants evolve by spawning, birth or death, and annihilation, attempted in each time step. Upon convergence, the FCIQMC propagation, where walkers are allowed to explore the entire Hilbert space, produces a FCI-level state and energy without any *a priori* knowledge of the nodal structure of the wave function required by traditional QMC considerations.[68-70] Similarly, the truncated CIQMC approximations, where spawning walkers at determinants beyond the specified truncation level is not allowed, converge to the corresponding truncated CI states. Although the FCIQMC and other CIQMC approaches of Refs. 64 and 65 can only be used to converge the ground state or the lowest-energy state of a given symmetry, it is possible to extend the CIQMC population dynamics to excited states of the same symmetry as the ground state. This can be done by adopting a Gram-Schmidt procedure, instantaneously applied to the stochastically evolving distributions of walkers, to orthogonalize higher-energy states against the lower-energy ones, so that the collapse of the dynamically propagated excited states on the lower-energy states within the same irreducible representation is avoided.[71,72] We show in this communication, though, that by combining the stochastic CIQMC and deterministic EOMCC ideas, one can extract accurate excited-state information on the basis of relatively short CIQMC propagations for the ground state or the lowest-energy state of a given symmetry, without having to resort to the more complex excited-state CIQMC framework of Refs. 71 and 72. Several advances have also been made to improve the CIQMC methodology and accelerate its convergence.[65,73-76] Among them is the initiator CIQMC (*i*-CIQMC) approach, exploited in our earlier[67,77] and the present work, where only those determinants that acquire a walker population exceeding a preset value n_a are allowed to spawn new walkers onto empty determinants.[65] The CIQMC ideas can be extended to other many-body theories,[66,78] including high-level CC (CCSDT, CCSDTQ, etc.) methods, resulting in the CCMC approaches,[66] where instead of sampling determinants by walkers, one samples amplitudes of "excitors" by "excips."[79-81] One can further speed-up the convergence of *i*-FCIQMC computations by the perturbative corrections built from the information discarded when applying initiator criteria.[82]

The CIQMC and CCMC methodologies have several appealing features that are useful in the context of the ground-state considerations[67,77] and, as shown in this communication, in designing the stochastically driven excited-state EOMCC framework. In particular, one is not required to have *a priori* knowledge of the determinants that dominate the wave functions of interest, which is normally needed to define the appropriate subspace of the *N*-electron Hilbert space, designated throughout this work as $\mathrm{H}^{(P)}$ and referred to as the *P* space, for the CC and EOMCC calculations. Let the *P* space used in the ground-state CC calculations, abbreviated as CC(*P*), and the corresponding EOMCC calculations for excited states, abbreviated as EOMCC(*P*), be spanned by the excited determinants $|\Phi_K\rangle = E_K |\Phi\rangle$ that together with the reference determinant $|\Phi\rangle$ dominate the wave functions $|\Psi_\mu\rangle$ of interest (E_K is the elementary particle-hole excitation operator generating $|\Phi_K\rangle$ from $|\Phi\rangle$; for now, we are assuming that ground and excited states have the same symmetry; we comment on excited states having different symmetries than the ground state later). Normally, to define the *P* space and the corresponding cluster and EOM excitation operators, $T^{(P)} = \sum_{|\Phi_K\rangle \in \mathrm{H}^{(P)}} t_K E_K$ and $R_\mu^{(P)} = r_{\mu,0}\mathbf{1} + \sum_{|\Phi_K\rangle \in \mathrm{H}^{(P)}} r_{\mu,K} E_K$, respectively, we truncate them at a given many-body rank n, resulting in highly accurate, but usually prohibitively expensive, schemes when $n > 2$, or, to achieve a robust and computationally manageable description, select the dominant T_n and $R_{\mu,n}$ contributions with $n > 2$ using active orbitals. Here, we advocate an alternative route using the CIQMC or CCMC propagations to identify the leading determinants or excitation amplitude types relevant to the target CC/EOMCC level (triples for CCSDT/EOMCCSDT; triples and quadruples for CCSDTQ/EOMCCSDTQ, etc.) and to define the appropriate *P* spaces for the CC(*P*) and subsequent EOMCC(*P*) calculations. As explained in Ref. 67, one may need longer propagation times τ to stabilize and equilibrate walker/excip populations to achieve the desired wave function and energy convergence using purely stochastic means, but the leading determinants or excitation amplitude types, relevant to the electronic states of interest, are identified in the early propagation stages, which require small computational effort compared to the target CC/EOMCC calculations. This is the essence of the stochastic CC(P) methodology of Ref. 67 and its EOMCC(P) extension proposed in this work.

In merging the deterministic CC(P)/EOMCC(P) and stochastic CIQMC or CCMC frameworks, one can envision several algorithmic possibilities. In this preliminary study, focusing on converging the CCSDT/EOMCCSDT energetics, we propose the following procedure:

1. Start a CIQMC (or CCMC) propagation for the ground state and, if the many-electron system under consideration has spin and spatial symmetries, the analogous propagation for the lowest state of each irreducible representation of interest by placing a certain number of walkers (or excips) on the relevant reference functions.

2. After a certain number of MC iterations, i.e., at some propagation time $\tau > 0$, extract a list or, if the system has symmetries, lists of the most important determinants or excitation amplitude types relevant to the CC/EOMCC computations of interest from the CIQMC (or CCMC) propagation/propagations initiated in step 1 to define the P space/spaces for the ground-state CC(P) and subsequent excited-state EOMCC(P) calculations, repeating this list extraction procedure for every irreducible representation considered in the calculation. If the target approach is CCSDT/EOMCCSDT, the P space for the ground-state CC(P) calculations and the EOMCC(P) calculations for excited states of the same symmetry as the ground state is defined as all singles, all doubles, and a subset of triples extracted from the ground-state CIQMC (or CCMC) propagation, where each triple excitation included in the P-space list has at least n_P (in this work, one) positive or negative walkers/excips on it at a given time τ. For the excited states belonging to an irreducible representation other than that of the ground state, the P space needed to solve the underlying CC(P) problem remains the same as for the ground state, but the list of triples for the subsequent EOMCC(P) diagonalization is extracted from the CIQMC (or CCMC) propagation for the lowest-energy state belonging to this irreducible representation. If the target approach is CCSDTQ/EOMCCSDTQ, the P spaces for the CC(P) and EOMCC(P) calculations are obtained in a similar manner, except that in addition to the triples one also extracts the lists of quadruples from the CIQMC (or CCMC) propagations.

3. Solve the ground-state CC(P) and excited-state EOMCC(P) equations using the stochastically determined P spaces in a deterministic manner. If the excited states of interest have the same symmetry as the ground state and if the goal is to converge the CCSDT/EOMCCSDT

energetics, use $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})}$ and $R_\mu^{(P)} = r_{\mu,0}\mathbf{1} + R_{\mu,1} + R_{\mu,2} + R_{\mu,3}^{(\mathrm{MC})}$, where the list of triples entering $T_3^{(\mathrm{MC})}$ and $R_{\mu,3}^{(\mathrm{MC})}$ at a given time τ is extracted from the ground-state CIQMC (or CCMC) propagation. For the excited states belonging to an irreducible representation other than that of the ground state, define the cluster operator $T^{(P)}$ for the CC(P) calculations, needed to construct the similarity-transformed Hamiltonian $\bar{H}^{(P)} = e^{-T^{(P)}} H e^{T^{(P)}}$ for the subsequent EOMCC diagonalization steps, in the same way as for the ground state, but use the CIQMC (or CCMC) propagation for the lowest state belonging to this irreducible representation to determine the triples list entering $R_{\mu,3}^{(\mathrm{MC})}$. Follow similar steps if the target is CCSDTQ/EOMCCSDTQ using $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})} + T_4^{(\mathrm{MC})}$ and $R_\mu^{(P)} = r_{\mu,0}\mathbf{1} + R_{\mu,1} + R_{\mu,2} + R_{\mu,3}^{(\mathrm{MC})} + R_{\mu,4}^{(\mathrm{MC})}$.

4. Check convergence by repeating steps 2 and 3 at some later CIQMC/CCMC propagation time $\tau' > \tau$ and inspecting if the resulting ground- and excited-state energies no longer change within a given threshold. Alternatively, stop the calculation if the propagation time τ in steps 2 and 3 was chosen such that the resulting P space/spaces contains/contain a sufficiently large fraction of higher–than–double excitations of interest. Based on our experiences with the active-space EOMCC calculations[20-22,24,27,50,51,53-55] and the stochastically driven EOMCC(P) computations reported in Tables I–III, we anticipate that to reach millihartree- or submillihartree-level accuracies relative to the target EOMCC energetics it is sufficient to choose τ such that the resulting P spaces accumulate ~20–30 % of higher–than–double excitations of interest. Additional benchmark calculations and trying EOMCC(P) levels beyond EOMCCSDT, which we have not examined yet, will help us determine if this is a good criterion.

In analogy to Ref. 67, the proposed algorithm offers substantial reductions in the computational time compared to the parent EOMCCSDT and similar methods. Indeed, the early stages of CIQMC/CCMC dynamics are very fast compared to the converged propagations and the CC(P) and subsequent EOMCC(P) calculations offer significant speedups when small fractions of higher–than–two-body excitations are involved. For example, if the number of all triples is D and the number of triples in the P space is d, the speedup relative to CCSDT and EOMCCSDT offered by the corresponding CC(P) and EOMCC(P) calculations, when the most expensive $\langle \Phi_{ijk}^{abc} | [H, T_3] | \Phi \rangle$ and $\langle \Phi_{ijk}^{abc} | [\bar{H}^{(P)}, R_{\mu,3}] | \Phi \rangle$ terms in the CCSDT and EOMCCSDT equations are examined, is $(d/D)^2$. Other terms, such as $\langle\Phi_{ijk}^{abc}|[H,T_2]|\Phi\rangle$ and $\langle\Phi_{ijk}^{abc}|[\bar{H}^{(P)},R_{\mu,2}]|\Phi\rangle$ or $\langle\Phi_{ij}^{ab}|[H,T_3]|\Phi\rangle$ and $\langle\Phi_{ij}^{ab}|[\bar{H}^{(P)},R_{\mu,3}]|\Phi\rangle$, offer additional speedups on the order of (d/D).

To examine the performance of the stochastically driven EOMCC(P) formalism, we carried out benchmark computations for the three lowest excited states of the $^1\Sigma^+$ symmetry (designated as 2 $^1\Sigma^+$, 3 $^1\Sigma^+$, and 4 $^1\Sigma^+$; 1 $^1\Sigma^+$ is the ground state), two lowest states of the $^1\Pi$ symmetry (designated as 1 $^1\Pi$ and 2 $^1\Pi$), and two lowest $^1\Delta$ states (designated as 1 $^1\Delta$ and 2 $^1\Delta$) of the CH^+ ion, as described by the [5s3p1d/3s1p] basis set of Ref. 83, at the equilibrium geometry $R = R_e = 2.13713$ bohr (Table I) and two stretches of the C-H bond, $R = 1.5R_e$ (Table II) and $R = 2R_e$ (Table III). Our goal was to recover the EOMCCSDT energetics, which are nearly exact in this case,[21,22] by reading the lists of triples needed to define the corresponding P spaces from the i-FCIQMC propagations. We used the HANDE package[84] for the i-FCIQMC runs and our standalone codes interfaced with the integral and restricted Hartree-Fock (RHF) routines in GAMESS[85] to perform the CC(P) and EOMCC(P) computations. As explained in Refs. 21 and 22, at $R = R_e$, the 2 $^1\Sigma^+$, 1 $^1\Delta$, and 2 $^1\Delta$ states have a significant multi-reference character dominated by two-electron transitions, which manifests itself in large, ~20–35 millihartree, errors in the EOMCCSD energies relative to EOMCCSDT (see Table I). The EOMCCSD description of the 3 $^1\Sigma^+$, 4 $^1\Sigma^+$, and 1 $^1\Pi$ states is better, since they have a single-excitation character at $R = R_e$, but the EOMCCSD energy of the second $^1\Pi$ state is poor again, since it has a mixed character with significant doubly excited components. As shown in Refs. 21 and 22, the situation at $R = 1.5R_e$ and $2R_e$, especially at the latter geometry, where CH^+ is almost dissociated, is even more challenging, resulting in a massive failure of EOMCCSD for all of the excited states considered in this work. This is because at larger C–H distances, the ground state of CH^+ gains a significant multi-reference character, all of the calculated excited states gain large doubly excited components, and the second $^1\Delta$ state becomes a mixture of bi- and triexcitations.[21,22]

Following the above algorithm, for the excited $^1\Sigma^+$ states having the same symmetry as the ground state, we defined the cluster operator $T^{(P)}$ and the EOM excitation operator $R_\mu^{(P)}$ as $T_1 + T_2 + T_3^{(\mathrm{MC})}$ and $r_{\mu,0}\mathbf{1} + R_{\mu,1} + R_{\mu,2} + R_{\mu,3}^{(\mathrm{MC})}$, respectively, where the list of triples entering $T_3^{(\mathrm{MC})}$ and $R_{\mu,3}^{(\mathrm{MC})}$ at a given time τ was extracted from the ground-state i-FCIQMC run at the same τ.

In the case of the excited states of the $^1\Pi$ and $^1\Delta$ symmetries, we defined the cluster operator $T^{(P)}$ for the CC(P) calculations, needed to construct $\bar{H}^{(P)}$, in the same way as for the $^1\Sigma^+$ states, but then we used the *i*-FCIQMC propagation for the lowest-energy state of a given symmetry [the $B_1(C_{2v})$ component of the 1 $^1\Pi$ state in the calculations for the $^1\Pi$ states and the $A_2(C_{2v})$ component of the 1 $^1\Delta$ state in the calculations for the $^1\Delta$ states] to determine the lists of triples for defining the corresponding $R_{\mu,3}^{(\mathrm{MC})}$ operators.

As shown in Tables I–III, using a time step $\Delta\tau = 0.0001$ a.u. and the initiator parameter $n_a = 3$, and placing 1,500 walkers on the RHF, $B_1(C_{2v})$, and $A_2(C_{2v})$ reference functions to initiate the *i*-FCIQMC propagations for the lowest $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$ states [to be precise, the lowest $^1A_1(C_{2v})$, $^1B_1(C_{2v})$, and $^1A_2(C_{2v})$ states], the EOMCC(P) calculations based on the stochastically determined triples lists converge to the corresponding EOMCCSDT energies of excited states so fast that, in analogy to our previous ground-state work,[67] one obtains the EOMCCSDT-level energetics in the early stages of the *i*-FCIQMC propagations. This is true for each calculated state and for each C–H distance examined in this work. By the time we have ~20–30 % of all triples in the P space, the EOMCC(P) energies are within a millihartree from their EOMCCSDT parents. This holds for the excited states dominated by one-electron transitions (the 3 $^1\Sigma^+$, 4 $^1\Sigma^+$, and 1 $^1\Pi$ states of CH^+ at $R = R_e$, shown in Table I), where the effects of triples, defined by forming the difference of the EOMCCSDT [EOMCC(P) $\tau = \infty$] and EOMCCSD [EOMCC(P) $\tau = 0$] energies, are small, as well as for the states having a significant double excitation or multi-reference character, where EOMCCSD produces massive errors relative to EOMCCSDT (the 2 $^1\Sigma^+$, 2 $^1\Pi$, 1 $^1\Delta$, and 2 $^1\Delta$ states of CH^+ at $R = R_e$, shown in Table I, and all states at $R = 1.5R_e$ and $2R_e$ shown in Tables II and III). We anticipate that the fractions of triples needed to achieve millihartree-level accuracies will decrease further once we implement the excited-state variants of the non-iterative CC(P;Q) corrections,[60,61] which will correct the EOMCC(P) energies for the effects of triples outside the stochastically determined P spaces.

In summary, we have extended the recently developed idea of identifying the leading higher–than–double excitations in the ground-state CC calculations via stochastic CIQMC propagations[67] to excited states by merging the CIQMC methodology with the deterministic EOMCC framework. In order to test the proposed merger of the CIQMC and EOMCC approaches, we have performed calculations aimed at recovering the CCSDT/EOMCCSDT energies of the ground and several excited states of the CH^+ molecule at the equilibrium and stretched geometries, in which the required lists of triples were extracted from *i*-FCIQMC propagations for the lowest-energy states in each symmetry category. We have shown that one can accurately reproduce the CCSDT/EOMCCSDT results, including excited states of the same symmetry as the ground state and states of other symmetries, out of the early stages of the *i*-FCIQMC simulations.

Moving forward, in designing the stochastically driven EOMCC(P) framework, we assumed that it is sufficient to use the CIQMC (or CCMC) propagations for the lowest-energy states of the symmetries of interest to determine the P spaces for the EOMCC diagonalizations, keeping the number of MC runs to a minimum and avoiding the more complex excited-state CIQMC computations based on Refs. 71 and 72. Our preliminary calculations to date suggest that this should suffice, at least for the low-lying excitations, but in the future it may be useful to investigate a state-specific version of the above algorithm with as many stochastically determined P spaces as the number of the calculated states, where one would rely on the extension of the CIQMC methodology to excited states of the same symmetry as the ground state.[71,72] Apart from extending this study to higher theory levels beyond EOMCCSDT, such as EOMCCSDTQ, we will implement the excited-state CC(P;Q) corrections,[60,61] which, in analogy to our previous ground-state work,[67] will further speed up the convergence by correcting the EOMCC(P) energies for the missing correlations of interest that were not captured by the CIQMC or CCMC propagations at the time τ the lists of the P-space excitations were created. Finally, we plan to test deterministic ways of identifying the dominant higher–than–doubly excited determinants for the incorporation in the P spaces used in the CC(P) and EOMCC(P) computations, as in adaptive CI[86,87] and adaptive sampling CI,[88,89] which consist of Hamiltonian diagonalizations in increasingly large subspaces of the many-electron Hilbert space.

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TABLE I. Convergence of the ground-state CC(P) energies toward CCSDT and the EOMCC(P) energies of the three lowest-energy excited states of the $^1\Sigma^+$ symmetry, two lowest states of the $^1\Pi$ symmetry, and two lowest $^1\Delta$ states toward EOMCCSDT for the CH^+ ion, as described by the [5s3p1d/3s1p] basis set of Ref. 83, at the equilibrium internuclear separation $R = R_e = 2.13713$ bohr. The P spaces used in the CC(P) and EOMCC(P) calculations for the $^1\Sigma^+$ states consisted of all singles and doubles and subsets of triples identified during the ground-state i-FCIQMC propagation. The P spaces used in the EOMCC(P) diagonalizations for the $^1\Pi$ and $^1\Delta$ states consisted of all singles and doubles and subsets of triples extracted from the i-FCIQMC propagations for the lowest-energy states of the relevant symmetries. Each i-FCIQMC calculation preceding the CC(P) and EOMCC(P) steps was initiated by placing 1,500 walkers on the corresponding reference function [the ground-state RHF determinant for the $^1\Sigma^+$ states, the $3\sigma \rightarrow 1\pi$ state of the $^1B_1(C_{2v})$ symmetry for the $^1\Pi$ states, and the $3\sigma^2 \rightarrow 1\pi^2$ state of the $^1A_2(C_{2v})$ symmetry for the $^1\Delta$ states]. The n_a parameter of the initiator algorithm was set at 3 and the time step $\Delta\tau$ used in each i-FCIQMC run was 0.0001 a.u.

MC Iters.	$1\,^1\Sigma^+$		$2\,^1\Sigma^+$	$3\,^1\Sigma^+$	$4\,^1\Sigma^+$	$1\,^1\Pi$		$2\,^1\Pi$	$1\,^1\Delta$		$2\,^1\Delta$
($\times 10^3$)	ΔE^a	%T^b	ΔE^a	ΔE^a	ΔE^a	ΔE^a	%T^b	ΔE^a	ΔE^a	%T^b	ΔE^a
0^c	1.845	0	19.694	3.856	5.537	3.080	0	11.656	34.304	0	34.685
2	1.071	7	11.004	3.248	4.826	0.772	13	3.746	1.492	10	5.951
4	0.423	15	5.474	1.893	1.980	0.513	20	1.852	0.525	16	2.542
6	0.249	20	4.712	1.268	1.077	0.213	25	0.957	0.471	18	1.892
8	0.181	23	1.371	0.643	0.702	0.170	27	0.743	0.240	22	0.940
10	0.172	24	1.572	0.295	0.385	0.118	29	0.411	0.198	24	0.877
50	0.077	37	0.755	0.139	0.208	0.053	43	0.157	0.039	42	0.133
100	0.044	48	0.277	0.007	0.155	0.021	57	0.063	0.014	56	0.043
150	0.015	59	0.085	0.058	0.041	0.008	71	0.020	0.004	71	0.008
200	0.006	69	0.024	0.014	0.002	0.004	82	0.008	0.003	82	0.003

^{a} The ΔE values are errors relative to the CCSDT and EOMCCSDT energies, in millihartree, obtained in Refs. 21 and 22. The CCSDT energy for the $1\,^1\Sigma^+$ state is −38.019516 hartree. The EOMCCSDT energies for the $2\,^1\Sigma^+$, $3\,^1\Sigma^+$, $4\,^1\Sigma^+$, $1\,^1\Pi$, $2\,^1\Pi$, $1\,^1\Delta$, and $2\,^1\Delta$ states are −37.702621, −37.522457, −37.386872, −37.900921, −37.498143, −37.762113, and −37.402308 hartree, respectively.

^{b} The %T values are the percentages of triples captured during the i-FCIQMC propagations for the lowest-energy state of a given symmetry [the $1\,^1\Sigma^+ = 1\,^1A_1(C_{2v})$ ground state for the $^1\Sigma^+$ states, the $B_1(C_{2v})$ component of the $1\,^1\Pi$ state for the $^1\Pi$ states, and the $A_2(C_{2v})$ component of the $1\,^1\Delta$ state for the $^1\Delta$ states].

^{c} The CC(P) and EOMCC(P) energies at $\tau = 0$ a.u. are identical to the energies obtained in the CCSD and EOMCCSD calculations.

TABLE II. Same as Table I for the stretched internuclear separation $R = 1.5R_e = 3.205695$ bohr.[a]

MC Iters.	$1\,^1\Sigma^+$		$2\,^1\Sigma^+$	$3\,^1\Sigma^+$	$4\,^1\Sigma^+$	$1\,^1\Pi$		$2\,^1\Pi$	$1\,^1\Delta$		$2\,^1\Delta$
($\times 10^3$)	ΔE	%T	ΔE	ΔE	ΔE	ΔE	%T	ΔE	ΔE	%T	ΔE
0	2.815	0	25.344	6.513	10.885	6.769	0	21.380	41.207	0	79.183
2	1.329	4	14.788	2.731	9.417	2.182	10	8.773	1.298	8	7.161
4	0.645	11	5.850	1.597	6.031	1.035	16	4.212	0.534	12	4.002
6	0.321	15	2.489	0.501	1.926	0.447	18	0.557	0.305	15	1.812
8	0.196	17	1.132	0.279	1.122	0.523	21	0.713	0.303	18	1.298
10	0.176	19	0.944	0.325	2.536	0.198	23	0.430	0.209	20	1.007
50	0.087	32	0.399	0.214	0.190	0.037	37	0.097	0.050	33	0.153
100	0.018	44	0.114	0.075	0.118	0.008	49	0.015	0.004	46	0.014
150	0.010	54	0.095	0.056	0.028	0.001	61	0.008	0.002	59	–0.006
200	0.003	65	0.011	0.007	0.008	0.001	73	0.006	0.001	71	0.001

[a] The CCSDT energy for the $1\,^1\Sigma^+$ state is –37.954008 hartree. The EOMCCSDT energies for the $2\,^1\Sigma^+$, $3\,^1\Sigma^+$, $4\,^1\Sigma^+$, $1\,^1\Pi$, $2\,^1\Pi$, $1\,^1\Delta$, and $2\,^1\Delta$ states are –37.696428, –37.609784, –37.438611, –37.890831, –37.650437, –37.736600, and –37.440775 hartree, respectively.[21,22]

TABLE III. Same as Table I for the stretched internuclear separation $R = 2R_e = 4.27426$ bohr.[a]

MC Iters.	$1\,^1\Sigma^+$		$2\,^1\Sigma^+$	$3\,^1\Sigma^+$	$4\,^1\Sigma^+$	$1\,^1\Pi$		$2\,^1\Pi$	$1\,^1\Delta$		$2\,^1\Delta$
($\times 10^3$)	ΔE	%T	ΔE	ΔE	ΔE	ΔE	%T	ΔE	ΔE	%T	ΔE
0	5.002	0	17.140	19.929	32.639	13.552	0	21.200	44.495	0	144.414
2	1.588	3	5.209	12.524	33.400	1.398	7	1.644	1.372	6	13.363
4	0.504	7	4.263	6.383	12.671	0.712	12	0.724	0.451	9	3.338
6	0.275	11	1.405	1.352	5.870	0.409	14	0.612	0.422	12	2.340
8	0.263	12	1.543	1.173	4.406	0.436	16	0.457	0.253	13	2.088
10	0.148	14	0.792	0.613	2.331	0.227	17	0.220	0.122	14	0.862
50	0.030	26	0.302	0.339	0.457	0.061	30	0.079	0.047	26	0.288
100	0.009	39	0.103	0.119	0.110	0.013	41	0.016	0.013	36	0.038
150	0.004	52	0.031	0.035	0.076	0.005	52	0.007	0.005	47	0.014
200	0.001	63	0.024	0.019	–0.006	0.002	65	0.001	0.001	57	0.003

[a] The CCSDT energy for the $1\,^1\Sigma^+$ state is –37.900394 hartree. The EOMCCSDT energies for the $2\,^1\Sigma^+$, $3\,^1\Sigma^+$, $4\,^1\Sigma^+$, $1\,^1\Pi$, $2\,^1\Pi$, $1\,^1\Delta$, and $2\,^1\Delta$ states are –37.704834, –37.650242, –37.495275, –37.879532, –37.702345, –37.714180, and –37.494031 hartree, respectively.[21,22]