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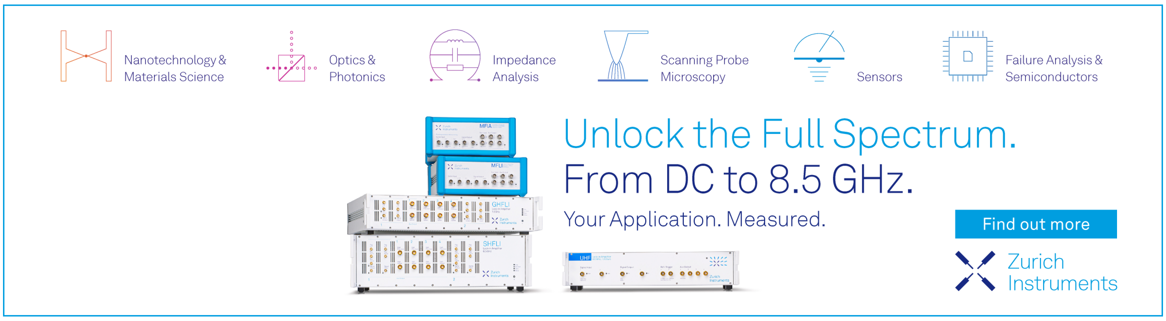

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ABSTRACT

A novel approach to rapidly converging high-level coupled-cluster (CC) energetics in an automated fashion is proposed. The key idea is an adaptive selection of excitation manifolds defining higher–than–two-body components of the cluster operator inspired by CC(P;Q) moment expansions. The usefulness of the resulting methodology is illustrated by molecular examples where the goal is to recover the electronic energies obtained using the CC method with a full treatment of singly, doubly, and triply excited clusters (CCSDT) when the noniterative triples corrections to CCSD fail.

I. INTRODUCTION

It is well established that size extensive approaches that rely on the exponential wave function ansatz[1,2] of coupled-cluster (CC) theory,[3–8]

$$|\Psi_0\rangle = e^{T}|\Phi\rangle, \tag{1}$$

where $|\Phi\rangle$ is the reference determinant defining the Fermi vacuum and

$$T = \sum_{n=1}^{N} T_n \tag{2}$$

is the cluster operator, with T_n designating its n-body (n-particle–n-hole or np–nh) component and N being the number of correlated fermions, and their extensions to excited, open-shell, and multiconfigurational states are among the best ways of tackling many-body correlations in atoms, molecules, and nuclei.[9–14] This is especially true in studies of structural and spectroscopic properties of molecular systems, chemical reaction pathways, noncovalent interactions, and photochemistry. In all these and similar cases, the CC hierarchy, including the CC method with singles and doubles (CCSD), where T is truncated at T_2,[15,16] the CC method with singles, doubles, and triples (CCSDT), where T is truncated at T_3,[17,18] the CC method with singles, doubles, triples, and quadruples (CCSDTQ), where T is truncated at T_4,[19,20] etc., and its equation-of-motion (EOM)[21–26] and linear-response[27–35] extensions rapidly converge to the exact, full configuration interaction (FCI) limit[11] [as usual, letters S, D, T, and Q stand for single (1p–1h), double (2p–2h), triple (3p–3h), and quadruple (4p–4h) excitations relative to $|\Phi\rangle$, respectively]. The problem is that the $\mathscr{N}^8$ computational steps of CCSDT or the $\mathscr{N}^{10}$ operational count of CCSDTQ, where $\mathscr{N}$ is a measure of the system size, make such high-level CC approaches, needed to achieve a quantitative description, prohibitively expensive in the majority of applications of interest. Thus, one of the biggest challenges in the CC theory has been to design numerically efficient ways of incorporating higher–than–two-body components of the cluster operator T and, in the case of excited states, excitation operator

$$R_\mu = r_{\mu,0}\mathbf{1} + \sum_{n=1}^{N} R_{\mu,n} \tag{3}$$

entering the EOMCC wave function ansatz

$$|\Psi_\mu\rangle = R_\mu e^T|\Phi\rangle, \tag{4}$$

where $R_{\mu,n}$ is the np–nh component of R_μ and $\mathbf{1}$ is the unit operator, capable of reducing the enormous costs of CCSDT, CCSDTQ, EOMCCSDT,[23,24] and similar computations, while eliminating failures of the popular perturbative approximations, such as CCSD(T),[36] CCSDT-1,[37,38] CC3,[39] or CCSD(TQ$_\mathrm{f}$),[40] which are more practical, but produce large and often uncontrollable errors in chemical bond stretching and other multireference situations.[9,11,41–43] Solid-state applications of the periodic CC framework[44–47] and nuclear structure CC computations[13,14,48–50] face similar challenges.

In this article, we propose a novel approach to converging high-level CC energetics of the CCSDT, CCSDTQ, and similar types, even in cases of stronger correlations, such as those characterizing stretched chemical bonds and biradical species, where higher–than–two-body components of the cluster operator T become large, in a fully automated, "black-box," manner and at small fractions of the computational costs. The key idea is an adaptive selection of the leading determinants or excitation amplitude types needed to define the T_n (in the case of excited states, also $R_{\mu,n}$) components with $n > 2$, which takes advantage of the intrinsic structure of the moment expansions abbreviated as CC(P;Q), and the associated *a posteriori* energy corrections to capture the remaining correlations, without any reference to the user- and system-dependent or non-CC concepts adopted in our previous CC(P;Q) work.[51–61] Using molecular examples characterized by substantial electronic quasidegeneracies and large and highly nonperturbative T_3 components, we show that the proposed adaptive, self-improving, CC(P;Q) methodology using excitation spaces truncated at triples recovers the parent CCSDT energetics with a relatively small computational effort, which is not very far removed from the noniterative triples corrections to CCSD defining CCSD(T) and its completely renormalized CR-CC(2,3) extension,[62–66] even when these corrections fail or struggle (for other attempts to develop adaptive CC ideas, see Ref. 67).

II. THEORY AND ALGORITHMIC DETAILS

A. Key elements of the CC(P;Q) formalism

We begin with a summary of the CC(P;Q) formalism, as applied to many-electron systems, which was originally formulated in Refs. 51 and 52. Each CC(P;Q) calculation begins by identifying two disjoint subspaces of the N-electron Hilbert space, referred to as the P and Q spaces. The former space, designated as $\mathscr{H}^{(P)}$, is spanned by the excited determinants $|\Phi_K\rangle = E_K|\Phi\rangle$, where E_K is the elementary particle–hole excitation operator generating $|\Phi_K\rangle$ from $|\Phi\rangle$, which, together with $|\Phi\rangle$, dominate the ground state $|\Psi_0\rangle$ or the ground ($\mu = 0$) and excited ($\mu > 0$) states $|\Psi_\mu\rangle$ of the N-electron system of interest. The latter space, designated as $\mathscr{H}^{(Q)}$ [$\mathscr{H}^{(Q)} \subseteq (\mathscr{H}^{(0)} \oplus \mathscr{H}^{(P)})^\perp$, where $\mathscr{H}^{(0)}$ is a one-dimensional subspace spanned by the reference determinant $|\Phi\rangle$], is used to construct the noniterative corrections $\delta_\mu(P;Q)$ to the energies $E_\mu^{(P)}$ obtained in the CC/EOMCC calculations in the P space, abbreviated as CC(P) for the ground state and EOMCC(P) for excited states, due to the higher-order correlation effects not captured by CC(P)/EOMCC(P).

Once the P and Q spaces are defined, we proceed as follows. First, we solve the CC(P) equations,

$$\mathfrak{M}_{0,K}(P) = 0, \quad |\Phi_K\rangle \in \mathscr{H}^{(P)}, \tag{5}$$

to determine the truncated form of the cluster operator T corresponding to the content of the P space,

$$T^{(P)} = \sum_{|\Phi_K\rangle \in \mathscr{H}^{(P)}} t_K E_K, \tag{6}$$

where t_Ks are the relevant cluster amplitudes, and the CC(P) ground-state energy

$$E_0^{(P)} = \langle\Phi|\overline{H}^{(P)}|\Phi\rangle. \tag{7}$$

Here,

$$\mathfrak{M}_{0,K}(P) = \langle\Phi_K|\overline{H}^{(P)}|\Phi\rangle, \tag{8}$$

with

$$\overline{H}^{(P)} = e^{-T^{(P)}} H e^{T^{(P)}}, \tag{9}$$

are the generalized moments of the CC(P) equations.[68–70] We also determine the hole–particle de-excitation operator

$$L_0^{(P)} = \mathbf{1} + \sum_{|\Phi_K\rangle \in \mathscr{H}^{(P)}} l_{0,K}(E_K)^\dagger, \tag{10}$$

which defines the bra ground state $\langle\tilde{\Psi}_0^{(P)}| = \langle\Phi|L_0^{(P)} e^{-T^{(P)}}$ associated with the CC(P) ket state $|\Psi_0^{(P)}\rangle = e^{T^{(P)}}|\Phi\rangle$ satisfying the normalization condition $\langle\tilde{\Psi}_0^{(P)}|\Psi_0^{(P)}\rangle = 1$, by solving the linear system

$$\langle\Phi|L_0^{(P)}\overline{H}^{(P)}|\Phi_K\rangle = E_0^{(P)} l_{0,K}, \quad |\Phi_K\rangle \in \mathscr{H}^{(P)}, \tag{11}$$

where $E_0^{(P)}$ is the CC(P) ground-state energy obtained with Eq. (7). If there is interest in the ground-state as well as excited-state energetics, we follow the CC(P) calculations by the diagonalization of the similarity-transformed Hamiltonian $\overline{H}^{(P)}$, Eq. (9), in the P space $\mathscr{H}^{(P)}$ to obtain the EOMCC(P) energies $E_\mu^{(P)}$ and the corresponding EOM excitation and de-excitation operators,

$$R_\mu^{(P)} = r_{\mu,0}\mathbf{1} + \sum_{|\Phi_K\rangle \in \mathscr{H}^{(P)}} r_{\mu,K} E_K \tag{12}$$

and

$$L_\mu^{(P)} = \delta_{\mu,0}\mathbf{1} + \sum_{|\Phi_K\rangle \in \mathscr{H}^{(P)}} l_{\mu,K}(E_K)^\dagger, \tag{13}$$

respectively, where the amplitudes $r_{\mu,K}$, along with $r_{\mu,0}$, define the EOMCC(P) ket states $|\Psi_\mu^{(P)}\rangle = R_\mu^{(P)} e^{T^{(P)}}|\Phi\rangle$ and their left-eigenstate $l_{\mu,K}$ counterparts define the EOMCC(P) bra states $\langle\tilde{\Psi}_\mu^{(P)}| = \langle\Phi|L_\mu^{(P)} e^{-T^{(P)}}$ satisfying the biorthonormality condition

$\langle \tilde{\Psi}_\mu^{(P)} | \Psi_\nu^{(P)} \rangle = \langle \Phi | L_\mu^{(P)} R_\nu^{(P)} | \Phi \rangle = \delta_{\mu,\nu}$. Once $T^{(P)}$, $L_0^{(P)}$, and $E_0^{(P)}$ and, in the case of excited states, $R_\mu^{(P)}$, $L_\mu^{(P)}$, and $E_\mu^{(P)}$ are known, we proceed to the final step, which is the determination of the CC(P;Q) energies

$$E_\mu^{(P+Q)} = E_\mu^{(P)} + \delta_\mu(P;Q), \tag{14}$$

where corrections $\delta_\mu(P;Q)$ are given by

$$\delta_\mu(P;Q) = \sum_{|\Phi_K\rangle \in \mathscr{H}^{(Q)}} \ell_{\mu,K}(P)\, \mathfrak{M}_{\mu,K}(P). \tag{15}$$

The ground-state moments $\mathfrak{M}_{0,K}(P)$, Eq. (8), and their excited-state counterparts[71–73]

$$\mathfrak{M}_{\mu,K}(P) = \langle \Phi_K | \overline{H}^{(P)} R_\mu^{(P)} | \Phi \rangle \tag{16}$$

entering Eq. (15) correspond to projections of the CC(P) and EOMCC(P) equations on the Q-space determinants $|\Phi_K\rangle \in \mathscr{H}^{(Q)}$. The coefficients $\ell_{\mu,K}(P)$ that multiply these moments are obtained using the Epstein–Nesbet-like formula

$$\ell_{\mu,K}(P) = \langle \Phi | L_\mu^{(P)} \overline{H}^{(P)} | \Phi_K \rangle / D_{\mu,K}^{(P)}, \tag{17}$$

where

$$D_{\mu,K}^{(P)} = E_\mu^{(P)} - \langle \Phi_K | \overline{H}^{(P)} | \Phi_K \rangle. \tag{18}$$

One can replace the denominators $D_{\mu,K}^{(P)}$, Eq. (18), by their Møller–Plesset-like analogs, but, as shown in Refs. 53, 54, 57, 59, 62, 63, 65, and 74, the Epstein–Nesbet-like form of $D_{\mu,K}^{(P)}$ results in a more accurate description.

The CC(P;Q) formalism can be viewed as a generalization of the biorthogonal moment expansions of Refs. 62–64, 66, and 74 and, as such, includes the aforementioned CR-CC(2,3) approach and its higher-order[54,55,75–77] and excited-state[64,74,78] extensions, but its key advantage, which the previous moment expansions did not have, is the possibility of making unconventional choices of the P and Q spaces and relaxing the lower-order T_n and $R_{\mu,n}$ components with $n \leq 2$ in the presence of their higher–than–two-body counterparts, such as T_3 and $R_{\mu,3}$, which CCSD(T), CR-CC(2,3), and other triples or higher-order corrections to CCSD or EOM-CCSD cannot do. There are important problems, including the molecular examples considered in this work and many others, where the decoupling of the higher–than–two-body components of T and R_μ from their lower-order T_n and $R_{\mu,n}$ counterparts with $n \leq 2$, characterizing CCSD(T), CR-CC(2,3), and similar methods, results in large errors in the calculated potential surfaces and activation barriers,[51,52,54,57,59,60] singlet–triplet gaps,[53,61] and electronic excitation spectra.[58] As shown in Refs. 51–61, the CC(P;Q) formalism addresses this issue and is capable of recovering the high-level CC/EOMCC energetics of the CCSDT,[51–61] CCSDTQ,[54–56,59] and EOMCCSDT[58] types at small fractions of the computational costs, even when electronic quasidegeneracies become substantial, by incorporating the dominant triply or triply and quadruply excited determinants in the P space, while using corrections $\delta_\mu(P;Q)$ to account for the remaining correlations of the parent CC/EOMCC approach of interest, but in order to do this, one has to come up with a method of identifying the leading higher–than–doubly excited determinants for inclusion in the P space. So far, this has been accomplished with the help of user-specified active orbitals, resulting in the CC(t;3), CC(t,q;3), CC(t,q;3,4), etc. hierarchy.[51–56] Quantum Monte Carlo (QMC) wave function propagations in the many-electron Hilbert space employing the CIQMC[79–83] and CCMC[84–87] approaches, resulting in the semi-stochastic CC(P;Q) theories[57–59,61] (cf. also Ref. 88), and sequences of Hamiltonian diagonalizations in systematically grown subspaces of the many-electron Hilbert space originating from one of the selected CI schemes,[89–103] abbreviated as CIPSI,[91,102,103] resulting in the CIPSI-driven CC(P;Q) algorithm.[60] All of these attempts to design the appropriate P and Q spaces for accurate CC(P;Q) computations have had their successes, but the adaptive, self-improving, CC(P;Q) framework, which we discuss next, takes us to an entirely new level by freeing us from the user-defined active orbitals and non-CC (CIQMC, CIPSI) or stochastic (CIQMC, CCMC) concepts adopted in our previous CC(P;Q) work.

B. Adaptive CC(P;Q): General considerations

In developing the adaptive CC(P;Q) methodology, we have been inspired by the modern CIPSI algorithm described in Refs. 102 and 103, available in the open-source Quantum Package 2.0,[103] which we exploited in Refs. 60 and 104. As already alluded to above, the main idea of CIPSI is a series of Hamiltonian diagonalizations in increasingly large, iteratively defined, subspaces of the many-electron Hilbert space, which are followed by correcting the resulting energies using expressions originating from the second-order many-body perturbation theory to estimate the remaining correlations.[91,102,103] If $\mathcal{V}_{\text{int}}^{(k)}$, where $k = 0, 1, 2, \ldots$ enumerates the consecutive CIPSI iterations, designates the current diagonalization subspace, the $\mathcal{V}_{\text{int}}^{(k+1)}$ space for the subsequent Hamiltonian diagonalization is constructed by arranging the candidate determinants $|\Phi_\alpha\rangle$ from outside $\mathcal{V}_{\text{int}}^{(k)}$ for a potential inclusion in $\mathcal{V}_{\text{int}}^{(k+1)}$ in descending order according to the absolute values of the perturbative corrections $e_{\alpha,k}^{(2)}$ associated with them, starting from the $|\Phi_\alpha\rangle$s characterized by the largest $|e_{\alpha,k}^{(2)}|$ contributions, moving toward those that have smaller $|e_{\alpha,k}^{(2)}|$ values, and continuing until the number of determinants in $\mathcal{V}_{\text{int}}^{(k+1)}$ reaches a desired dimension (in the CIPSI algorithm of Refs. 102 and 103, until the dimension of $\mathcal{V}_{\text{int}}^{(k+1)}$ exceeds that of $\mathcal{V}_{\text{int}}^{(k)}$ by the user-defined factor $f > 1$). We can adopt a similar strategy in designing P spaces for the CC(P;Q) computations.

Indeed, we can interpret Eq. (15) as a sum of contributions $\delta_{\mu,K}(P;Q)$ due to the individual determinants from the Q space, $|\Phi_K\rangle \in \mathscr{H}^{(Q)}$, evaluated as

$$\delta_{\mu,K}(P;Q) = \ell_{\mu,K}(P)\, \mathfrak{M}_{\mu,K}(P), \tag{19}$$

which, in analogy to the perturbative $e_{\alpha,k}^{(2)}$ corrections that measure the significance of the candidate determinants $|\Phi_\alpha\rangle$ in CIPSI, determine the importance of the Q-space determinants $|\Phi_K\rangle$. One can, therefore, propose an adaptive, self-improving, CC(P;Q) scheme, in which we construct an approximation to the high-level CC/EOMCC approach of interest (in the numerical examples in Sec. III, CCSDT) by a series of CC(P;Q) calculations using increasingly large, iteratively defined, P spaces $\mathscr{H}^{(P)}(k)$, where $k = 0, 1, 2, \ldots$ enumerates the consecutive CC(P;Q) computations, with the corresponding Q subspaces $\mathscr{H}^{(Q)}(k)$ being defined as complementary excitation spaces, such that $\mathscr{H}^{(P)}(k) \oplus \mathscr{H}^{(Q)}(k)$ is always equivalent to the entire excitation manifold appropriate for the CC/EOMCC method we are targeting, independent of k (when targeting CCSDT, all singly, doubly, and triply excited determinants, when targeting CCSDTQ, all singly, doubly, triply, and quadruply excited determinants, etc.). The initial P space $\mathscr{H}^{(P)}(0)$ can be a conveniently chosen zeroth-order excitation manifold, such as the space of singly and doubly excited determinants, $|\Phi_i^a\rangle$ and $|\Phi_{ij}^{ab}\rangle$, respectively, where $i, j, \ldots$ $(a, b, \ldots)$ designate the spin-orbitals occupied (unoccupied) in $|\Phi\rangle$, and the remaining subspaces are constructed via a recursive process analogous to that used in CIPSI, where the P space $\mathscr{H}^{(P)}(k+1)$ is obtained by augmenting its $\mathscr{H}^{(P)}(k)$ predecessor with a subset of the leading Q-space determinants $|\Phi_K\rangle \in \mathscr{H}^{(Q)}(k)$ [when targeting CCSDT, the leading triply excited determinants $|\Phi_{ijk}^{abc}\rangle$ outside $\mathscr{H}^{(P)}(k)$, when targeting CCSDTQ, the leading triply and quadruply excited determinants outside $\mathscr{H}^{(P)}(k)$, etc.] identified with the help of corrections $\delta_{\mu,K}(P;Q)$, Eq. (19). Inspired by the CIPSI algorithm, one can enlarge the current subspace $\mathscr{H}^{(P)}(k)$ to construct the $\mathscr{H}^{(P)}(k+1)$ space for the subsequent CC(P;Q) computation by arranging the candidate determinants $|\Phi_K\rangle \in \mathscr{H}^{(Q)}(k)$ in descending order according to the $\delta_{\mu,K}(P;Q)$ corrections associated with them, starting from the $|\Phi_K\rangle$s characterized by the largest $|\delta_{\mu,K}(P;Q)|$ contributions, moving toward those that have smaller $|\delta_{\mu,K}(P;Q)|$ values, and continuing until the total number of the Q-space determinants in $\mathscr{H}^{(P)}(k+1)$ reaches a certain fraction of all higher-rank determinants relevant to the CC/EOMCC approach of interest (e.g., triples when targeting CCSDT or triples and quadruples when targeting CCSDTQ). Clearly, the adaptive CC(P;Q) procedure, as described above, guarantees convergence toward the high-level CC/EOMCC approach it targets, but, following the computational cost analysis of the CC(P;Q) methods[57–59] (cf. also Refs. 51–56, 60, and 61), in order to be an attractive approach, it has to be capable of recovering the target CC/EOMCC energetics to a very good accuracy with small fractions of higher-rank determinants relevant to the CC/EOMCC method of interest in the underlying P spaces.

C. Adaptive CC(P;Q) and CC(P;Q)$_{(T)}$ approaches aimed at CCSDT and their computational implementation

To illustrate the benefits offered by the approach proposed in Sec. II B, we wrote an adaptive CC(P;Q) code aimed at recovering the ground-state CCSDT energetics, which we incorporated in our open-source CCpy package available on GitHub,[105] implemented in Python and using Numpy and Fortran in the computationally critical parts. In this case, we apply Eq. (15) to a situation where the kth P space $\mathscr{H}^{(P)}(k)$ is spanned by all singly and doubly excited determinants and a subset of triply excited determinants identified by the adaptive CC(P;Q) algorithm and the associated Q space $\mathscr{H}^{(Q)}(k)$ consists of the remaining triples not included in $\mathscr{H}^{(P)}(k)$, i.e.,

$$\delta_0(P^{(k)}; Q^{(k)}) = \sum_{|\Phi_{ijk}^{abc}\rangle \in \mathscr{H}^{(Q)}(k)} \delta_{ijk,abc}(k), \tag{20}$$

where

$$\delta_{ijk,abc}(k) = \ell_{ijk}^{abc}(P^{(k)})\, \mathfrak{M}_{abc}^{ijk}(P^{(k)}) \tag{21}$$

is the contribution to $\delta_0(P^{(k)}; Q^{(k)})$ that corresponds to a given triply excited determinant $|\Phi_{ijk}^{abc}\rangle \in \mathscr{H}^{(Q)}(k)$. The $\ell_{ijk}^{abc}(P^{(k)})$ and $\mathfrak{M}_{abc}^{ijk}(P^{(k)})$ quantities in Eq. (21) are the coefficients $\ell_{0,K}(P)$ and moments $\mathfrak{M}_{0,K}(P)$ entering the ground-state CC(P;Q) correction $\delta_0(P;Q)$, Eq. (15) in which μ is set at 0, adapted to the above definitions of the $\mathscr{H}^{(P)}(k)$ and $\mathscr{H}^{(Q)}(k)$ spaces. For clarity of this description, the P and Q symbols seen in Eqs. (20) and (21), which represent the $\mathscr{H}^{(P)}(k)$ and $\mathscr{H}^{(Q)}(k)$ spaces used in the kth iteration of the adaptive CC(P;Q) procedure, are labeled with the additional superscript (k).

In our current implementation of the adaptive CC(P;Q) approach aimed at recovering the CCSDT-level energetics, we invoked the so-called two-body approximation that was successfully used in some of our earlier CC(P;Q)-related work.[51–54,104] This means that we replaced moments $\mathfrak{M}_{abc}^{ijk}(P^{(k)})$ and coefficients $\ell_{ijk}^{abc}(P^{(k)})$ entering Eq. (21) by $\langle\Phi_{ijk}^{abc}|\overline{H}^{(P)}(2)|\Phi\rangle$ and $\langle\Phi|(\mathbf{1} + L_{0,1} + L_{0,2})\,\overline{H}^{(P)}(2)|\Phi_{ijk}^{abc}\rangle/(E_0^{(P)} - \langle\Phi_{ijk}^{abc}|\overline{H}^{(P)}(2)|\Phi_{ijk}^{abc}\rangle)$, respectively, where $\overline{H}^{(P)}(2) = e^{-T_1-T_2}He^{T_1+T_2}$, with T_1 and T_2 designating the one- and two-body components of the cluster operator $T^{(P)}$ obtained in the CC(P) calculations in $\mathscr{H}^{(P)}(k)$, is an approximation to the true similarity-transformed Hamiltonian $\overline{H}^{(P)} = e^{-T_1-T_2-T_3^{(P)}}He^{T_1+T_2+T_3^{(P)}}$, where $T_3^{(P)}$ is a three-body component of $T^{(P)}$. The one- and two-body de-excitation operators $L_{0,1}$ and $L_{0,2}$, which enter the formula for the $\ell_{ijk}^{abc}(P^{(k)})$ coefficients used in our adaptive CC(P;Q) code, are obtained by solving the left eigenvalue problem involving $\overline{H}^{(P)}(2)$ in the space spanned by singly and doubly excited determinants. Thus, in analogy to $T^{(P)}$, the three-body component $L_{0,3}^{(P)}$ of the de-excitation operator $L_0^{(P)}$ corresponding to the P space $\mathscr{H}^{(P)}(k)$ is neglected. In this way, we preserve the philosophy of the CC(P;Q) algorithm and account for the relaxation of T_1, T_2, $L_{0,1}$, and $L_{0,2}$ in the presence of the three-body components of $T^{(P)}$ obtained in the CC(P) calculations in $\mathscr{H}^{(P)}(k)$, while avoiding the more complex computational steps associated with the use of the complete form of $\overline{H}^{(P)}$ in determining the $\delta_{ijk,abc}(k)$ corrections.

In the adaptive CC(P;Q) code that we incorporated in the CCpy package available on GitHub,[105] the $k = 0$ P space $\mathscr{H}^{(P)}(0)$, used to initiate the calculations, is defined as all singly and doubly excited determinants and the corresponding Q space $\mathscr{H}^{(Q)}(0)$ consists of all triples. This means that the $k = 0$ CC(P) and CC(P;Q) energies are identical to those obtained with CCSD and CR-CC(2,3), respectively. We then follow the recursive procedure described in Sec. II B by moving more and more triply excited determinants from the Q to P spaces. We enlarge the kth subspace $\mathscr{H}^{(P)}(k)$, which consists of all singles and doubles and, when $k > 0$, the subset of triples identified in the previous iteration, to construct the $\mathscr{H}^{(P)}(k+1)$ space for the subsequent CC(P;Q) computation by arranging the candidate triply excited determinants $|\Phi_{ijk}^{abc}\rangle \in \mathscr{H}^{(Q)}(k)$ in descending order according to the $\delta_{ijk,abc}(k)$ corrections associated with them, starting from the triples characterized by the largest $|\delta_{ijk,abc}(k)|$ contributions, moving toward those that have smaller $|\delta_{ijk,abc}(k)|$ values, and continuing until the total number of triply excited determinants in $\mathscr{H}^{(P)}(k+1)$ represents an increase of the number of triples in $\mathscr{H}^{(P)}(k)$ by 1%. We could have chosen any other incremental fraction of triples when enlarging the $\mathscr{H}^{(P)}(k)$, $k = 0, 1, 2, \ldots$, spaces, but, given our desire to use as small fractions of triples in the consecutive CC(P) runs as possible, so that the iterative CC(P) steps preceding the determination of the $\delta_0(P^{(k)}; Q^{(k)})$ corrections are much less expensive than those of the CCSDT target, we felt that 1% is a good incremental fraction to start with in our preliminary numerical tests reported in this initial study (we will explore other incremental fractions of triples in future work). The algorithm that takes full advantage of the speedups offered by the adaptive CC(P;Q) procedure relative to its CCSDT parent, when the underlying P space contains a small fraction of triply excited determinants, along with other information about the CCpy package in which our adaptive CC(P;Q) approach targeting CCSDT has been implemented, will be discussed in a separate publication.

In the adaptive CC(P;Q) computations reported in this work, we distinguish between the relaxed and unrelaxed schemes. In the relaxed variant of the adaptive CC(P;Q), we solve the CC(P) equations for the singly, doubly, and triply excited cluster amplitudes corresponding to the content of each $\mathscr{H}^{(P)}(k)$ space and recompute the corresponding triples corrections $\delta_{ijk,abc}(k)$ accordingly, increasing the number of triples, when going from $\mathscr{H}^{(P)}(k)$ to $\mathscr{H}^{(P)}(k+1)$, by 1%. In the unrelaxed CC(P;Q) approach, we simply pick a particular fraction of triples for inclusion in the P space (say, 3% or 5%) that have the largest initial $|\delta_{ijk,abc}(0)|$ values determined using the T_1 and T_2 amplitudes obtained with CCSD [i.e., the largest absolute values of the $\delta_{ijk,abc}(0)$ contributions to the triples correction of CR-CC(2,3)] and solve the CC(P) equations for the singly, doubly, and triply excited cluster amplitudes with this particular fraction of triples, adding the correction due to the missing T_3 correlations using Eq. (20). The relaxed variant of the adaptive CC(P;Q) approach has an advantage of approaching the target CCSDT energetics as $k \to \infty$, but the unrelaxed scheme, which does not require an iterative construction of multiple $\mathscr{H}^{(P)}(k)$ spaces, is less expensive. One of the goals of this initial study of the adaptive CC(P;Q) approach is to compare the two schemes.

Given the straightforward relationship between the triples corrections of CR-CC(2,3) and CCSD(T), discussed in Refs. 51, 62, 63, 65, and 75, and the fact that the $k = 0$ CC(P;Q) energies are identical to those obtained with CR-CC(2,3), we also implemented the CCSD(T)-like variants of the relaxed and unrelaxed adaptive CC(P;Q) algorithms, abbreviated as CC(P;Q)$_{\text{(T)}}$. One obtains the adaptive CC(P;Q)$_{\text{(T)}}$ approach by replacing moments $\mathfrak{M}_{abc}^{ijk}(P^{(k)})$ and coefficients $\ell_{ijk}^{abc}(P^{(k)})$ in Eq. (21) by $\langle\Phi_{ijk}^{abc}|V_N T_2|\Phi\rangle$ and $\langle\Phi|(T_1^\dagger + T_2^\dagger)V_N|\Phi_{ijk}^{abc}\rangle/(\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c)$, respectively, where V_N is the two-body part of the normal-ordered Hamiltonian, T_1 and T_2 are the singly and doubly excited components of the cluster operator $T^{(P)}$ resulting from the CC(P) calculations in $\mathscr{H}^{(P)}(k)$, and ϵ_p is the single-particle energy associated with the spin-orbital $|p\rangle$ (the diagonal element of the Fock matrix associated with $|p\rangle$). Since the initial P space $\mathscr{H}^{(P)}(0)$ is spanned by all singly and doubly excited determinants and the associated Q space $\mathscr{H}^{(Q)}(0)$ contains all triples, the $k = 0$ CC(P;Q)$_{\text{(T)}}$ energies are identical to those of CCSD(T). One of the objectives of this study is to determine if we could replace the adaptive CC(P;Q) approach by its CCSD(T)-like CC(P;Q)$_{\text{(T)}}$ analog, which uses the somewhat less expensive triples correction $\delta_0(P^{(k)}; Q^{(k)})$ and does not require solving the left eigenvalue problem involving $\overline{H}^{(P)}(2)$, without losing the accuracy of its CR-CC(2,3)-like parent.

III. NUMERICAL EXAMPLES

A. Molecular systems and the reasons for their choice

To test the performance of the relaxed and unrelaxed variants of the adaptive CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ approaches based on Eqs. (20) and (21), especially their ability to recover or accurately approximate the parent CCSDT energetics when the noniterative triples corrections to CCSD, represented in this work by CCSD(T) and CR-CC(2,3), struggle, we applied them to the significantly stretched F_2 and F_2^+ molecules and the reactant (R) and transition-state (TS) species involved in the automerization of cyclobutadiene, along with the corresponding barrier height, for which full CCSDT, as shown, for example, in Refs. 51, 52, 57, 59, 60, 62, 63, and 106–108, works well. In the case of the fluorine molecule and its cation (Tables I and II), for which we used the cc-pVTZ basis set,[109] the respective F–F bond lengths r were stretched to $2r_e$, where r_e represents the equilibrium geometry (2.668 16 bohr for F_2 and 2.498 22 bohr for F_2^+). The geometries of the D_{2h}-symmetric R and D_{4h}-symmetric TS structures adopted in our calculations for cyclobutadiene (Tables III and IV), in which we employed the cc-pVDZ basis,[109] were taken from Ref. 110, where they were optimized using the multireference average-quadratic CC (MR-AQCC) approach.[111,112] With the exception of CCSDT, all CC calculations reported in this work, including CCSD, CCSD(T), and CR-CC(2,3) and the adaptive CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ runs, were performed using the aforementioned CCpy package.[105] In the case of CCSDT, we used our highly efficient in-house code, written in Fortran, developed in the context of our previous active-orbital-based CC(P;Q) studies in Refs. 51, 52, and 54. The computations preceding the CC steps, including the generation of one- and two-electron integrals, the restricted Hartree–Fock (RHF; F_2 and cyclobutadiene) and restricted open-shell Hartree–Fock (ROHF; F_2^+) self-consistent-field (SCF) calculations, and the relevant integral transformations were carried out with the GAMESS package.[113,114] In all post-SCF calculations, the core orbitals correlating with the 1s shells of the F and C atoms were kept frozen.

We chose the significantly stretched fluorine molecule and its cation with $r = 2r_e$ since they are characterized by the enormous and highly nonperturbative T_3 effects, which are estimated, by forming the differences of the CCSDT and CCSD energies, at about

TABLE I. Convergence of the energies resulting from the relaxed (Rel.) and unrelaxed (Unrel.) variants of the adaptive CC(P;Q) approach and the underlying CC(P) computations toward CCSDT for the F_2 and F_2^+ molecules described by the cc-pVTZ basis set, in which the F–F bond lengths r were fixed at $2r_e$, with r_e representing the relevant equilibrium geometries (2.668 16 bohr for F_2 and 2.498 22 bohr for F_2^+). The %T values are the percentages of the $S_z = 0$ triply excited determinants of the $A_{1g}(D_{2h})$, for F_2, and $B_{3g}(D_{2h})$, for F_2^+, symmetries identified by the adaptive CC(P;Q) algorithm and included, alongside all singles and doubles, in the respective P spaces. The Q spaces used in computing the CC(P;Q) corrections were defined as the remaining triples not included in the associated P spaces. In increasing the numbers of triply excited determinants in the P spaces employed in the relaxed calculations, a 1% growth rate was assumed throughout. In all post-RHF (F_2) and post-ROHF (F_2^+) calculations, the two lowest core orbitals were kept frozen.

	F_2				F_2^+			
%T	CC(P) Unrel.[a]	CC(P;Q) Unrel.[a]	CC(P) Rel.[a]	CC(P;Q) Rel.[a]	CC(P) Unrel.[a]	CC(P;Q) Unrel.[a]	CC(P) Rel.[a]	CC(P;Q) Rel.[a]
0	62.819[b]	4.254[c]	62.819[b]	4.254[c]	76.291[b]	10.971[c]	76.291[b]	10.971[c]
1[d]	3.076	0.063	3.076	0.063	6.071	2.173	6.071	2.173
2	2.103	0.089	2.052	0.057	4.061	1.560	2.599	0.191
3	1.586	0.104	1.539	0.070	2.970	1.146	1.707	−0.026
4	1.243	0.098	1.212	0.071	2.100	0.684	1.330	−0.007
5	1.009	0.105	0.985	0.080	1.680	0.549	1.077	0.010
100	−199.238 344[e]				−198.606 409[e]			

[a] The CC(P) and CC(P;Q) energies are reported as errors relative to CCSDT in millihartree.

[b] Equivalent to CCSD.

[c] Equivalent to CR-CC(2,3).

[d] For %T = 1, the CC(P) and CC(P;Q) energies obtained in the relaxed and unrelaxed calculations are identical.

[e] Total CCSDT energy in hartree.

TABLE II. Same as Table I except that the CC(P;Q) corrections to the CC(P) energies are replaced by their CCSD(T)-like CC(P;Q)$_{(T)}$ counterparts. As in Table I, the F–F bond lengths r in F_2 and F_2^+ were fixed at $2r_e$, where r_e designates the corresponding equilibrium geometries (2.668 16 bohr for F_2 and 2.498 22 bohr for F_2^+).

	F_2				F_2^+			
%T	CC(P) Unrel.[a]	CC(P;Q)$_{(T)}$ Unrel.[a]	CC(P) Rel.[a]	CC(P;Q)$_{(T)}$ Rel.[a]	CC(P) Unrel.[a]	CC(P;Q)$_{(T)}$ Unrel.[a]	CC(P) Rel.[a]	CC(P;Q)$_{(T)}$ Rel.[a]
0	62.819[b]	−26.354[c]	62.819[b]	−26.354[c]	76.291[b]	−8.985[c]	76.291[b]	−8.985[c]
1[d]	3.274	−0.789	3.274	−0.789	7.758	1.802	7.758	1.802
2	2.205	−0.471	2.316	−0.514	5.861	1.991	3.513	0.010
3	1.669	−0.309	1.593	−0.349	4.740	1.892	1.971	−0.445
4	1.314	−0.205	1.253	−0.233	3.930	1.697	1.478	−0.367
5	1.061	−0.145	1.009	−0.166	3.285	1.466	1.200	−0.264
100	−199.238 344[e]				−198.606 409[e]			

[a] The CC(P) and CC(P;Q)$_{(T)}$ energies are reported as errors relative to CCSDT in millihartree.

[b] Equivalent to CCSD.

[c] Equivalent to CCSD(T).

[d] For %T = 1, the CC(P) and CC(P;Q)$_{(T)}$ energies obtained in the relaxed and unrelaxed calculations are identical.

[e] Total CCSDT energy in hartree.

−63 and −76 millihartree, respectively, when the cc-pVTZ basis set is employed (see Tables I and II). As shown, for example, in Ref. 51 and as further discussed in Refs. 59 and 60, the T_3 effects in the stretched F_2 and F_2^+ molecules at $r = 2r_e$ are so large that they exceed (F_2) or are not much smaller than (F_2^+) the depths of the corresponding CCSDT potential wells (estimated in the case of the cc-pVTZ basis at about 57 and 116 millihartree, respectively[51,59,60]). The nonperturbative character of T_3 correlations in the stretched F_2 and F_2^+ systems considered in this study is best illustrated by examining the large errors relative to CCSDT obtained in the CCSD(T) calculations, which in the cc-pVTZ basis used in this work are −26.354 and −8.985 millihartree, respectively[51,59,60] (cf. Table II). The CR-CC(2,3) triples correction to CCSD, equivalent to the initial, $k = 0$, CC(P;Q) calculation, improves the CCSD(T) [$k = 0$ CC(P;Q)$_{(T)}$] result for the stretched F_2 molecule in a substantial manner, but, as shown in Table I and Refs. 51, 59, and 60, the 4.254 millihartree error relative to CCSDT remains. The same table (see also Ref. 51) demonstrates that the $r = 2r_e$ F_2^+ system presents an even greater challenge since in this case, the CR-CC(2,3) approach, while placing the energy above its CCSDT parent, does not reduce the

TABLE III. Convergence of the energies resulting from the relaxed (Rel.) and unrelaxed (Unrel.) variants of the adaptive CC(P;Q) approach and the underlying CC(P) computations toward CCSDT for the reactant (R) and transition-state (TS) structures involved in the automerization of cyclobutadiene, as described by the cc-pVDZ basis set, optimized in the MR-AQCC calculations reported in Ref. 110, along with the corresponding barrier heights. The %T values are the percentages of the $S_z = 0$ triply excited determinants of the $A_{1g}(D_{2h})$ symmetry identified by the adaptive CC(P;Q) algorithm and included, alongside all singles and doubles, in the respective P spaces. In analogy to F_2 and F_2^+, the Q spaces adopted in computing the CC(P;Q) corrections consisted of the triply excited determinants not included in the associated P spaces, and in increasing the numbers of triples in the P spaces used in the relaxed calculations, a 1% growth rate was assumed throughout. In all post-RHF calculations, the four lowest core orbitals were kept frozen.

	R				TS				Barrier height	
%T	CC(P) Unrel.[a]	CC(P;Q) Unrel.[a]	CC(P) Rel.[a]	CC(P;Q) Rel.[a]	CC(P) Unrel.[a]	CC(P;Q) Unrel.[a]	CC(P) Rel.[a]	CC(P;Q) Rel.[a]	CC(P;Q) Unrel.[b]	CC(P;Q) Rel.[b]
0	26.827[c]	0.848[d]	26.827[c]	0.848[d]	47.979[c]	14.636[d]	47.979[c]	14.636[d]	8.653[d]	8.653[d]
1[e]	12.622	−0.055	12.622	−0.055	12.622	0.601	12.622	0.601	0.412	0.412
2	10.143	−0.013	10.121	−0.030	10.180	0.598	9.250	−0.169	0.384	−0.087
3	8.610	0.016	8.588	−0.002	8.643	0.561	7.821	−0.111	0.343	−0.068
4	7.501	0.037	7.482	0.022	7.571	0.568	6.827	−0.040	0.334	−0.038
5	6.637	0.050	6.620	0.035	6.722	0.559	6.052	0.010	0.320	−0.016
100	−154.244 157[f]				−154.232 002[f]				7.627[g]	

[a] The CC(P) and CC(P;Q) energies of the R and TS species are reported as errors relative to CCSDT in millihartree.

[b] The CC(P;Q) values of the barrier height are reported as errors relative to CCSDT in kcal/mol.

[c] Equivalent to CCSD.

[d] Equivalent to CR-CC(2,3).

[e] For %T = 1, the CC(P) and CC(P;Q) energies obtained in the relaxed and unrelaxed calculations are identical.

[f] Total CCSDT energy in hartree.

[g] The CCSDT barrier height in kcal/mol.

TABLE IV. Same as Table III except that the CC(P;Q) corrections to the CC(P) energies are replaced by their CCSD(T)-like CC(P;Q)$_{(T)}$ counterparts. As in Table III, the reactant (R) and transition-state (TS) structures of cyclobutadiene adopted in the calculations, optimized using the MR-AQCC approach, were taken from Ref. 110.

	R				TS				Barrier height	
%T	CC(P) Unrel.[a]	CC(P;Q)$_{(T)}$ Unrel.[a]	CC(P) Rel.[a]	CC(P;Q)$_{(T)}$ Rel.[a]	CC(P) Unrel.[a]	CC(P;Q)$_{(T)}$ Unrel.[a]	CC(P) Rel.[a]	CC(P;Q)$_{(T)}$ Rel.[a]	CC(P;Q)$_{(T)}$ Unrel.[b]	CC(P;Q)$_{(T)}$ Rel.[b]
0	26.827[c]	1.123[d]	26.827[c]	1.123[d]	47.979[c]	14.198[d]	47.979[c]	14.198[d]	8.205[d]	8.205[d]
1[e]	12.650	−0.347	12.650	−0.347	12.829	−1.618	12.829	−1.618	−0.798	−0.798
2	10.171	−0.254	10.131	−0.263	10.394	−1.009	9.138	−1.417	−0.473	−0.723
3	8.638	−0.193	8.603	−0.202	8.894	−0.685	7.729	−1.126	−0.309	−0.579
4	7.530	−0.147	7.498	−0.156	7.802	−0.491	6.746	−0.905	−0.216	−0.470
5	6.666	−0.113	6.637	−0.121	6.964	−0.347	5.991	−0.735	−0.146	−0.385
100	−154.244 157[f]				−154.232 002[f]				7.627[g]	

[a] The CC(P) and CC(P;Q)$_{(T)}$ energies of the R and TS species are reported as errors relative to CCSDT in millihartree.

[b] The CC(P;Q)$_{(T)}$ values of the barrier height are reported as errors relative to CCSDT in kcal/mol.

[c] Equivalent to CCSD.

[d] Equivalent to CCSD(T).

[e] For %T = 1, the CC(P) and CC(P;Q)$_{(T)}$ energies obtained in the relaxed and unrelaxed calculations are identical.

[f] Total CCSDT energy in hartree.

[g] The CCSDT barrier height in kcal/mol.

large unsigned error relative to CCSDT characterizing CCSD(T). In fact, the CR-CC(2,3) calculation makes it somewhat larger [10.971 millihartree, as opposed to 8.985 millihartree obtained with CCSD(T)]. This is indicative of a substantial increase in the coupling between the lower-rank T_1 and T_2 clusters and the higher-rank T_3 component compared to the similarly stretched F_2 species, which none of the noniterative triples corrections to CCSD can capture.

In the case of cyclobutadiene, the T_3 effects, again estimated by forming the differences between the CCSDT and CCSD energies, which are −26.827 millihartree for the R and −47.979 millihartree for the TS structures when the cc-pVDZ basis set is employed (see Tables III and IV), are not only very large but also difficult to balance, resulting in a massive, 13.274 kcal/mol, error relative to CCSDT in the CCSD value of the barrier height characterizing the automerization process, which exceeds the CCSDT activation energy of 7.627 kcal/mol by more than 170%.[52,57,59,60] Furthermore, the more challenging TS structure is characterized by a large coupling of the lower-rank T_1 and T_2 components with their higher-rank T_3 counterpart, so large that none of the noniterative triples corrections to CCSD provide a reasonable description of the barrier height.[52,107,115] This, in particular, applies to the CR-CC(2,3) approach, which places the activation barrier at 16.280 kcal/mol when the cc-pVDZ basis set is employed, instead of less than 8 kcal/mol obtained with CCSDT[52,57,59,60] (see Table III). Once again, CR-CC(2,3) does not improve the results of the CCSD(T) calculations, which give a similarly poor barrier height (15.832 kcal/mol; see Table IV). The failure of the CR-CC(2,3) and CCSD(T) methods to provide accurate activation energies for the automerization of cyclobutadiene is a consequence of the poor performance of both approaches in the calculations for the TS species. As shown in Refs. 52, 57, 59, and 60 and Tables III and IV, the difference between the CR-CC(2,3) and CCSDT energies at the TS geometry obtained with the cc-pVDZ basis, of 14.636 millihartree, and the analogous 14.198 millihartree difference between the CCSD(T) and CCSDT energy values are much larger than the ~1 millihartree errors relative to CCSDT characterizing the CR-CC(2,3) and CCSD(T) calculations for the R species.

B. Performance of the adaptive CC(P;Q) and CC(P;Q)$_{(\mathrm{T})}$ approaches: Energetics

In our previous studies,[51,52,57,59,60] we demonstrated that the active-orbital-based CC(P;Q) scheme abbreviated as CC(t;3) and the semi-stochastic, CIQMC- and CCMC-based, and CIPSI-driven CC(P;Q) approaches are capable of greatly improving the CCSD(T) and CR-CC(2,3) results for the significantly stretched F_2 molecule and the automerization of cyclobutadiene, generating the CCSDT-quality data at small fractions of the computational effort associated with the conventional CCSDT calculations. In our initial CC(P;Q) work reported in Ref. 51, we showed that the CC(t;3) method can do the same for the stretched F_2^+. We now show that the fully automated, "black-box," adaptive CC(P;Q) methodology, as implemented in our CCpy package,[105] performs equally well or can even be more efficient.

Indeed, as shown in Tables I and III, the convergence of the adaptive CC(P;Q) calculations toward the parent CCSDT energetics is very fast. This includes the more challenging multireference situations created by the stretched F_2 and F_2^+ molecules and the TS structure of cyclobutadiene, where, as explained above, T_3 correlations are large, nonperturbative, and difficult to capture, resulting in failures of CCSD(T) and, in the case of the latter two systems, of CR-CC(2,3), as well as the weakly correlated cyclobutadiene R species, which the CCSD(T) and CR-CC(2,3) methods can handle, although not perfectly. The relaxed variant of the adaptive CC(P;Q) algorithm is generally most accurate. For the most demanding cases of the stretched F_2^+ and TS species of cyclobutadiene, where the coupling of the lower-rank T_1 and T_2 clusters with their higher-rank T_3 counterpart is the largest, it reduces the 10.971 and 14.636 millihartree errors relative to CCSDT obtained with CR-CC(2,3) and the similarly large errors obtained with CCSD(T) to a 0.1 millihartree level using as little as 2–3% of all triply excited determinants in the underlying P spaces. With only 2% of all triples in the P space, the difference between the activation energies characterizing the automerization of cyclobutadiene obtained with the relaxed variant of the adaptive CC(P;Q) approach and full CCSDT is less than 0.1 kcal/mol, as opposed to the orders of magnitude larger, 8–9 kcal/mol, errors relative to CCSDT resulting from the CR-CC(2,3) and CCSD(T) calculations. The rate with which the energies resulting from the adaptive CC(P;Q) calculations based on the relaxed algorithm approach the parent CCSDT energetics, observed in Tables I and III, is certainly most encouraging.

As one might anticipate and as confirmed in Tables I and III, the unrelaxed variant of the adaptive CC(P;Q) methodology, in which one picks a particular fraction of triples for inclusion in the P space based on their contributions to the CR-CC(2,3) correction to CCSD, is less accurate for the stretched F_2^+ molecule, the TS structure of cyclobutadiene, and the associated barrier height than its relaxed counterpart, which reaches a desired fraction of triply excited determinants in the P space through a sequence of recursively generated subspaces, but the results of the unrelaxed CC(P;Q) calculations, especially given their simplicity and lower computational costs, are excellent too. As shown in Tables I and III, with only 2–3% of all triply excited determinants in the underlying P spaces, the adaptive CC(P;Q) computations based on the unrelaxed algorithm reduce the 9–11 millihartree, 14–15 millihartree, and 8–9 kcal/mol unsigned errors relative to CCSDT characterizing the CCSD(T) and CR-CC(2,3) calculations for the $r = 2r_e$ F_2^+ system, the TS species involved in the automerization of cyclobutadiene, and the corresponding barrier height, respectively, to a chemical accuracy (1 millihartree or 1 kcal/mol) level. Compared to the adaptive CC(P;Q) calculations using the relaxed scheme, the convergence rate toward the parent CCSDT energetics characterizing the unrelaxed approach is slower, but the fact that one can obtain such high accuracies with just a few percent of all triples in the underlying P spaces, when the CCSD(T) and CR-CC(2,3) corrections to CCSD fail or struggle, is encouraging. It is worth noting that with only 1% of all triply excited determinants in the relevant P spaces, which is the smallest fraction of triples considered in this work, the adaptive CC(P;Q) computations reduce the 10.971 millihartree, 14.636 millihartree, and 8.653 kcal/mol errors obtained with CR-CC(2,3) for the challenging $r = 2r_e$ F_2^+ system, the TS structure of cyclobutadiene, and the activation energy characterizing the automerization of cyclobutadiene relative to CCSDT to 2.173 millihartree, 0.601 millihartree, and 0.412 kcal/mol, respectively. Given the fact that 1% is also the incremental fraction of triples used to enlarge the $\mathscr{H}^{(P)}(k)$ spaces in the relaxed CC(P;Q) calculations reported in this study, the relaxed and unrelaxed CC(P;Q) computations using the leading 1% of all triply excited determinants identified by the adaptive CC(P;Q) algorithm are equivalent.

While the P spaces containing only 1% of all triply excited determinants may not be rich enough to bring the errors characterizing the adaptive CC(P;Q) calculations for the stretched F_2^+ ion and the TS structure of cyclobutadiene relative to CCSDT to a 0.1 millihartree level, they are sufficient for achieving high accuracies of this type in the adaptive CC(P;Q) computations for the stretched fluorine molecule and the cyclobutadiene R species. As shown in Tables I and III, the adaptive CC(P;Q) calculations for the $r = 2r_e$ F_2 system and the R structure of cyclobutadiene using only 1% of all triply excited determinants in the underlying P spaces reduce the 4.254 and 0.848 millihartree differences between the CR-CC(2,3) and CCSDT energies and the 26.354 and 1.123 millihartree unsigned errors relative to CCSDT obtained with CCSD(T) to about 60 microhartree. Clearly, these are dramatic improvements, especially given the small computational effort involved. Furthermore, unlike in the $r = 2r_e$ F_2^+ and cyclobutadiene TS systems, the results of the adaptive CC(P;Q) computations for the stretched fluorine molecule and the R species of cyclobutadiene using larger fractions of triples in the corresponding P spaces do not change much when the relaxed algorithm is replaced by its simpler unrelaxed counterpart. We can rationalize these observations as follows. In the case of the stretched F_2 molecule, T_3 correlations are large and nonperturbative, so that one is much better off by using the CR-CC(2,3) triples correction to CCSD instead of CCSD(T), but the coupling of T_1 and T_2 clusters with T_3 is not as well pronounced as in the stretched F_2^+ and TS species of cyclobutadiene and can, therefore, be captured by injecting a tiny fraction of the leading triply excited determinants into the CC(P) calculations preceding the determination of the noniterative $\delta_0(P;Q)$ correction. As a result, the incorporation of a larger fraction of triples in the underlying P space and the iterative construction of the P space via the relaxed algorithm are not necessary to obtain high accuracies in the adaptive CC(P;Q) computations for the stretched F_2. In the case of the R species of cyclobutadiene, T_3 correlations are relatively small, perturbative, and largely decoupled from those captured by T_1 and T_2 clusters and their powers entering the CC wave function ansatz, making the need for the use of larger fractions of triples in the P space and the iteratively constructed $\mathscr{H}^{(P)}(k)$ spaces even smaller.

It is interesting to observe that many of the above comments also apply to the CCSD(T)-like variant of the adaptive CC(P;Q) methodology, abbreviated as CC(P;Q)$_{\text{(T)}}$, which is obtained by approximating moments $\mathfrak{M}^{ijk}_{abc}(P^{(k)})$ and coefficients $\ell^{abc}_{ijk}(P^{(k)})$ in Eq. (21) such that the initial, $k = 0$, CC(P;Q)$_{\text{(T)}}$ energies are identical to those obtained with CCSD(T). As shown in Tables II and IV, the adaptive CC(P;Q)$_{\text{(T)}}$ computations using as little as 1–3% of all triply excited determinants in the underlying P spaces, identified with the help of the relaxed or unrelaxed variants of the CC(P;Q)$_{\text{(T)}}$ algorithm, offer major error reductions relative to CCSDT compared to the CCSD(T) and CR-CC(2,3) calculations. As one might anticipate, the results of the CC(P;Q)$_{\text{(T)}}$ calculations are not as accurate as those obtained with the more complete form of the adaptive CC(P;Q) formalism used in Tables I and III, in which the approximations in moments $\mathfrak{M}^{ijk}_{abc}(P^{(k)})$ and coefficients $\ell^{abc}_{ijk}(P^{(k)})$ entering Eq. (21) that we invoked when implementing these quantities in our CCpy code are much less drastic than in the CC(P;Q)$_{\text{(T)}}$ case. Nevertheless, it is encouraging to observe that the replacement of Eq. (21) by its CCSD(T)-like counterpart does not result in an erratic behavior characterizing the CCSD(T) calculations for the stretched F_2 and F_2^+ molecules and the cyclobutadiene TS species, where electronic quasidegeneracies are substantial and T_3 correlations become large and nonperturbative. The reduction of the large unsigned errors relative to CCSDT obtained with CCSD(T) for the $r = 2r_e$ F_2 and F_2^+ systems, the TS structure of cyclobutadiene, and the corresponding barrier height, of about 26, 9, and 14 millihartree and more than 8 kcal/mol, respectively, to 1–2 millihartree and <1 kcal/mol levels by the adaptive CC(P;Q)$_{\text{(T)}}$ approach using only 1% of all triples in the underlying P spaces is certainly promising. Similarly encouraging are the major improvements in the energies of the $r = 2r_e$ F_2^+ system and the TS species of cyclobutadiene, where one has to relax the lower-rank T_1 and T_2 amplitudes in the presence of their higher-rank T_3 counterparts to obtain a reliable description, resulting from the replacement of the CR-CC(2,3) triples correction to CCSD by the adaptive CC(P;Q)$_{\text{(T)}}$ scheme using tiny fractions of triples in the underlying P spaces.

The fact that the adaptive CC(P;Q)$_{\text{(T)}}$ approach works as well as it does is a consequence of including the largest triply excited cluster amplitudes in the iterative CC(P) steps preceding the determination of the noniterative $\delta_0(P;Q)$ corrections [which take care of the remaining T_3 correlations not included in the CC(P) calculations]. The largest triply excited cluster amplitudes engage valence shells that become quasidegenerate in multireference situations and cannot, as such, be accurately estimated using the arguments originating from the many-body perturbation theory exploited in the design of the (T) correction of CCSD(T) because of the smallness of the Møller–Plesset-type denominators. They are the ones causing failures of the triples corrections of CCSD(T). After solving for the largest triply excited cluster amplitudes using the iterative CC(P) approach, one is left with the remaining, generally much smaller and largely perturbative, T_3 contributions that can be reasonably well described by the CCSD(T)-like expressions (cf. Refs. 116 and 117 for similar considerations). One might argue that the adaptive CC(P;Q)$_{\text{(T)}}$ approach using a simplified form of the triples correction $\delta_0(P;Q)$, reminiscent of that adopted by CCSD(T), which does not, for example, require solving the left eigenvalue problem involving $\overline{H}^{(P)}(2)$ to construct the coefficients $\ell^{abc}_{ijk}(P^{(k)})$ entering Eq. (21), is a good substitute for its more complete CC(P;Q) parent used in Tables I and III, but we prefer the latter approach for the following two reasons. First, a direct comparison of the results of the adaptive CC(P;Q)$_{\text{(T)}}$ calculations reported in Tables II and IV with their CC(P;Q) counterparts shown in Tables I and III demonstrates that the more complete treatment of moments $\mathfrak{M}^{ijk}_{abc}(P^{(k)})$ and coefficients $\ell^{abc}_{ijk}(P^{(k)})$ in Eq. (21), adopted in the latter scheme, results in generally higher accuracies. Second, all the computational timings that we have analyzed to date, including those presented in Table V, which we discuss next, show that savings in the computational effort offered by the CCSD(T)-like CC(P;Q)$_{\text{(T)}}$ scheme, compared to its CR-CC(2,3)-like CC(P;Q) counterpart, are not large enough to favor the adaptive CC(P;Q)$_{\text{(T)}}$ treatment over its slightly more expensive, but also more robust, CC(P;Q) parent.

C. Performance of the adaptive CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ approaches: Computational effort

To illustrate the computational benefits of employing the adaptive CC(P;Q) methodology as a substitute for full CCSDT, which the adaptive CC(P;Q) computations using tiny fractions of triples in the underlying P spaces approximate so well, in Table V, we show the timings characterizing the various CC calculations carried out in this study for the challenging TS structure of cyclobutadiene, as described by the cc-pVDZ basis. As in the case of Tables I–IV, the information about the adaptive CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ calculations and the associated CCSD, CCSD(T), and CR-CC(2,3) runs included in Table V was obtained with our standalone CCpy package implemented in Python and available on GitHub,[105] which uses the Numpy library and Fortran routines in the numerically intensive

TABLE V. Computational timings characterizing the various CC calculations for the cyclobutadiene/cc-pVDZ system in the transition-state (TS) geometry optimized with MR-AQCC in Ref. 110, including CCSD, CCSD(T), CR-CC(2,3), and CCSDT, and the unrelaxed variants of the adaptive CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ approaches, abbreviated as CC(P;Q)$[\%\text{T} = x]$ and CC(P;Q)$_{\text{(T)}}[\%\text{T} = x]$, respectively, where $x = 1, 3$, and 5, which used the leading x percent of triply excited determinants, identified on the basis of the largest $\delta_{ijk,abc}(0)$ contributions to the CR-CC(2,3) and CCSD(T) triples corrections, in addition to all singles and doubles, in constructing the respective P spaces. The Q spaces used to determine the CC(P;Q)$[\%\text{T} = x]$ and CC(P;Q)$_{\text{(T)}}[\%\text{T} = x]$ corrections to the CC(P)$[\%\text{T} = x]$ energies consisted of the remaining $(100 - x)$ percent of triples not included in the corresponding P spaces. In all post-RHF calculations, the four lowest core orbitals were kept frozen.

Method	CPU time[a]			
	P space determination[b]	Iterative steps[c]	Noniterative steps[d]	Total
CCSD	⋯	0.5	⋯	0.5
CCSD(T)	⋯	0.5	0.1	0.6
CR-CC(2,3)	⋯	0.8	0.3	1.1
CC(P;Q)$[\%\text{T} = 1]$	1.9[e] (2.4)[f]	3.4	0.3	5.6[g] (6.1)[h]
CC(P;Q)$[\%\text{T} = 3]$	1.9[e] (9.3)[f]	4.0	0.3	6.2[g] (13.6)[h]
CC(P;Q)$[\%\text{T} = 5]$	2.0[e] (21.3)[f]	4.5	0.3	6.8[g] (26.1)[h]
CC(P;Q)$_{\text{(T)}}[\%\text{T} = 1]$	1.5[e] (2.0)[f]	3.1	0.2	4.8[g] (5.3)[h]
CC(P;Q)$_{\text{(T)}}[\%\text{T} = 3]$	1.5[e] (8.9)[f]	3.7	0.2	5.4[g] (12.8)[h]
CC(P;Q)$_{\text{(T)}}[\%\text{T} = 5]$	1.6[e] (20.9)[f]	4.1	0.2	5.9[g] (25.2)[h]
CCSDT	⋯	455.8	⋯	455.8

[a] All reported timings, in CPU minutes, correspond to single-core runs on the Precision 7920 workstation from Dell equipped with Intel Xeon Silver 4114 2.2 GHz processor boards. No advantage of the D_{4h} symmetry of the TS structure of cyclobutadiene or its D_{2h} Abelian subgroup was taken in the post-RHF steps. The computational times associated with the execution of the integral, RHF, and integral transformation and sorting routines preceding the CC steps are ignored.

[b] The timings associated with determining the P spaces for the unrelaxed CC(P;Q)$[\%\text{T} = x]$ and CC(P;Q)$_{\text{(T)}}[\%\text{T} = x]$ computations, where $x = 1, 3$, and 5, include the times required to execute the corresponding initial CR-CC(2,3) and CCSD(T) runs plus the times spent on analyzing the $\delta_{ijk,abc}(0)$ contributions to the resulting triples corrections to CCSD needed to identify the top x percent of triply excited determinants. The timings associated with constructing the P spaces for the iterative steps of the CCSD, CCSD(T), CR-CC(2,3), and CCSDT calculations are not reported since in these four cases, these spaces are *a priori* known [consisting of all singly and doubly excited determinants in the case of the CCSD, CCSD(T), and CR-CC(2,3) methods and of all singly, doubly, and triply excited determinants in the CCSDT case].

[c] In executing the iterative steps of each CC calculation, a convergence threshold of 10^{-7} hartree was assumed. The timings corresponding to the iterative steps include the times required to construct and solve the relevant CC amplitude equations and, in the case of CR-CC(2,3) and CC(P;Q), the times needed to construct and solve the companion left eigenstate problems involving the respective similarity-transformed Hamiltonians [using, in the case of CC(P;Q), the two-body approximation discussed in the text].

[d] In the language of Q spaces adopted by the CC(P;Q) formalism, the computational times required to determine the noniterative triples corrections of CCSD(T), CR-CC(2,3), CC(P;Q), and CC(P;Q)$_{\text{(T)}}$ correspond to all triples in the case of CCSD(T) and CR-CC(2,3) and the remaining $(100 - x)$ percent of triples not included in the relevant P spaces in the case of CC(P;Q)$[\%\text{T} = x]$ and CC(P;Q)$_{\text{(T)}}[\%\text{T} = x]$ ($x = 1, 3$, and 5).

[e] Timing obtained with the faster, but also more memory intensive, determinant selection algorithm that, in the case of the unrelaxed CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ computations, first constructs and stores an array of all $\delta_{ijk,abc}(0)$ contributions to the CR-CC(2,3) or CCSD(T) triples correction, calculated prior to the final CC(P;Q)$[\%\text{T} = x]$ or CC(P;Q)$_{\text{(T)}}[\%\text{T} = x]$ run, in memory. The resulting array of all $\delta_{ijk,abc}(0)$ contributions is subsequently sorted to identify the leading x percent of triply excited determinants, for inclusion in the P space needed to set up and solve the CC(P) equations of the target unrelaxed CC(P;Q)$[\%\text{T} = x]$ or CC(P;Q)$_{\text{(T)}}[\%\text{T} = x]$ calculation, which are characterized by the largest $|\delta_{ijk,abc}(0)|$ values.

[f] Timing obtained with the low-memory determinant selection algorithm that captures the leading x percent of triply excited determinants, for inclusion in the P space needed to carry out the desired unrelaxed CC(P;Q)$[\%\text{T} = x]$ or CC(P;Q)$_{\text{(T)}}[\%\text{T} = x]$ calculation, on the fly. In this algorithm, when applied to the unrelaxed computations, an array that has a dimension equal to the number of triples used in the iterative CC(P) steps of the target CC(P;Q)$[\%\text{T} = x]$ or CC(P;Q)$_{\text{(T)}}[\%\text{T} = x]$ run is populated and continually repopulated with the small subsets of $\delta_{ijk,abc}(0)$ contributions to the CR-CC(2,3) or CCSD(T) triples correction as they are being successively computed, analyzed, and filtered out to identify those with the largest $|\delta_{ijk,abc}(0)|$ values. In this procedure, the $\delta_{ijk,abc}(0)$ contribution associated with the candidate triply excited determinant for potential inclusion in the P space is compared with the $\delta_{ijk,abc}(0)$ contribution in the array that has the smallest absolute value. If the absolute value of $\delta_{ijk,abc}(0)$ characterizing the candidate triply excited determinant is larger than the smallest absolute value of $\delta_{ijk,abc}(0)$ in the array, the triply excited determinant associated with the smallest $|\delta_{ijk,abc}(0)|$ is removed from the P space and replaced by the candidate determinant. At the same time, the $\delta_{ijk,abc}(0)$ contribution in the array characterized by the smallest absolute value is replaced by the $\delta_{ijk,abc}(0)$ corresponding to the candidate determinant and the process is repeated by examining the next triply excited determinant for potential inclusion in the P space, and so on.

[g] Total CPU time resulting from the utilization of the faster, but also more memory intensive, P-space determination algorithm described in footnote (e).

[h] Total CPU time resulting from the utilization of the low-memory P-space determination algorithm described in footnote (f).

parts, whereas the computational (CPU) time needed to converge the reference CCSDT energy was determined using the highly efficient Fortran code developed in the context of our CC(t;3) and other active-orbital-based CC(P;Q) studies in Refs. 51, 52, and 54. All the CPU timings shown in Table V correspond to single-core runs without taking advantage of the D_{4h} spatial symmetry of the TS structure of cyclobutadiene or its D_{2h} Abelian subgroup in the post-RHF steps. The computational times associated with the execution of the integral, SCF, and integral transformation routines used to generate the one- and two-electron molecular integrals in the RHF basis, which was carried out using GAMESS, and the integral sorting operations preceding the CC steps performed using CCpy are ignored in Table V.

To facilitate our discussion, in reporting the computational timings that characterize our adaptive CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ runs for the cyclobutadiene/cc-pVDZ system in its TS geometry, we focus on the calculations using 1%, 3%, and 5% of the $S_z = 0$ triply excited determinants of the $\text{A}_{1g}(D_{2h})$ symmetry in the corresponding

P spaces identified by the unrelaxed variants of the adaptive CC(P;Q) and CC(P;Q)$_{(\mathrm{T})}$ algorithms, which, as shown in Tables III and IV, reduce the 14.198 and 14.636 millihartree errors relative to CCSDT obtained with CCSD(T) and CR-CC(2,3) to as little as 0.601, 0.561, and 0.559 millihartree, respectively, in the case of CC(P;Q) and −1.618, −0.685, and −0.347 millihartree, respectively, when the unrelaxed CC(P;Q)$_{(\mathrm{T})}$ approach is employed. To get useful insights, in addition to the total CPU times, we report the timings associated with the three key stages of the adaptive CC(P;Q) and CC(P;Q)$_{(\mathrm{T})}$ calculations. In the case of the unrelaxed CC(P;Q) and CC(P;Q)$_{(\mathrm{T})}$ algorithms considered in Table V, these three key stages include (i) the P space determination, which consists of the initial CR-CC(2,3) or CCSD(T) run followed by the analysis of the $\delta_{ijk,abc}(0)$ contributions to the resulting triples correction to CCSD, needed to identify a desired fraction of triply excited determinants for inclusion in the subsequent CC(P) computation; (ii) the iterative CC(P) calculation using the P space $\mathscr{H}^{(P)}(1)$ consisting of all singly and doubly excited determinants and a subset of triply excited determinants identified in stage (i); and (iii) the determination of the noniterative $\delta_0(P;Q)$ correction to the CC(P) energy obtained in stage (ii) to capture the remaining T_3 correlations with the help of the complementary Q space $\mathscr{H}^{(Q)}(1)$ using Eq. (20) in which we set k at 1.

At this point, we can handle the preparatory stage (i), needed to filter out a particular fraction of the triply excited determinants characterized by the largest $|\delta_{ijk,abc}(k)|$ [in the unrelaxed calculations considered in Table V, $|\delta_{ijk,abc}(0)|$] values, in two different ways. In a faster, but also more memory intensive, scheme, further elaborated on in footnote (e) of Table V, we identify a desired fraction of the triply excited determinants for inclusion in the P space $\mathscr{H}^{(P)}(k)$ [in the unrelaxed case, $\mathscr{H}^{(P)}(1)$] after storing all $\delta_{ijk,abc}(k)$ [in Table V, $\delta_{ijk,abc}(0)$] contributions in memory. As shown in Table V, the CPU timings associated with this scheme are small, considerably smaller than the computational times required by the CC(P) iterations, and barely dependent on the fraction of triples one is interested in identifying. In the second determinant selection scheme, which is characterized by the minimum memory requirements that are as low as the fraction of triples one would like to include in the iterative CC(P) steps, described in further detail in footnote (f) of Table V, an array that has a dimension equal to the number of triples included in the P space of a given CC(P;Q) or CC(P;Q)$_{(\mathrm{T})}$ run is populated and continually repopulated with the small subsets of $\delta_{ijk,abc}(k)$ [in the unrelaxed case, $\delta_{ijk,abc}(0)$] contributions as they are being computed, analyzed, and filtered out to identify those with the largest $|\delta_{ijk,abc}(k)|$ values. The main advantage of this scheme, when applied to small fractions of triples included in the relevant P spaces, is the fact that its memory requirements are consistent with the small numbers of triples included in the CC(P) iterations. The problem with this scheme is a steep increase of the computational time with the fraction of triples included in the P space, which may, as shown in Table V, substantially exceed the time spent on the remaining steps of the adaptive CC(P;Q) and CC(P;Q)$_{(\mathrm{T})}$ runs. This is not an issue when the fraction of triples included in the P space is 1–2%, but it may become a problem when larger fractions must be considered. This does not appear to be a major obstacle since the convergence of the adaptive CC(P;Q) calculations toward CCSDT is fast and the results obtained with 1–2% of triples in the P space are already in excellent agreement with the parent CCSDT data, greatly improving the CCSD(T) and CR-CC(2,3) energetics at very small fractions of the costs of CCSDT computations. Nevertheless, we will continue working on our low-memory determinant selection algorithm to reduce the CPU timings associated with it. One of the ideas that we plan to experiment with is the use of somewhat larger arrays that are populated and repopulated with subsets of $\delta_{ijk,abc}(k)$ contributions in our low-memory determinant selection scheme, which could, for example, store as many $\delta_{ijk,abc}(k)$ values as a desired fraction of triples to be included in the P space multiplied by a small prefactor to reduce the operation count compared to the current minimalistic implementation. We will also investigate if one can reduce the number of the candidate Q-space determinants screened by our low-memory selection algorithm, which might substantially improve its efficiency too. In particular, we will examine if it is possible to adopt the determinant selection procedures analogous to those discussed in Sec. III.D.2 of Ref. 103, used in CIPSI, or exclude the unimportant triply excited determinants characterized by tiny $|\delta_{ijk,abc}(k)|$ values from the set of the Q-space triples screened by the low-memory selection algorithm described in footnote (f) of Table V. Although the faster, but also much more memory intensive, determinant selection algorithm summarized in footnote (e) of Table V is quite efficient as is, as far as the operation count is concerned, excluding the unimportant triply excited determinants from the set of the Q-space triples prior to filtering out those that are characterized by the largest $|\delta_{ijk,abc}(k)|$ values will benefit this algorithm too, speeding it up and reducing its memory requirements.

The illustrative CPU timings included in Table V, combined with the previously discussed energetics compared to CCSDT in Tables I–IV, clearly demonstrate the enormous benefits of using the adaptive CC(P;Q) methodology proposed in this study. If we focus on the faster determinant selection algorithm, as summarized above, the adaptive CC(P;Q) runs using 1–5% of triples in the underlying P spaces accelerate the parent CCSDT computations for the cyclobutadiene/cc-pVDZ system in its TS geometry with only minimal loss of accuracy by factors on the order of 67–81, reducing the >14 millihartree errors relative to CCSDT obtained with the CCSD(T) and CR-CC(2,3) triples corrections to CCSD to small fractions of a millihartree. The speedups offered by the adaptive CC(P;Q) runs using the slower, minimum-memory, P space determination algorithm are not as good when the fractions of triples in the P space are larger, but they are still quite impressive, reducing the CPU time required by the CCSDT calculation for the cyclobutadiene/cc-pVDZ TS species by factors of 34 and 17 when 3% and 5% of all triples, respectively, are included in the underlying P spaces. We believe that we will be able to considerably improve these speedups, while keeping the memory requirements associated with the P space determination algorithm at low levels. In the case of having 1% of all triples in the P space, the performance of our low-memory P space determination algorithm is excellent. The resulting adaptive CC(P;Q) calculations for the cyclobutadiene/cc-pVDZ system in its TS geometry are 75 times faster than the parent CCSDT run, while reducing the >14 millihartree errors relative to CCSDT obtained in the CCSD(T) and CR-CC(2,3) computations to about 0.6 millihartree.

The computational timings collected in Table V allow us to draw a few other conclusions. While we will continue working on improving our codes, the results in Table V already show a reasonably high efficiency of our current implementation of the adaptive CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ approaches incorporated in the CCpy package available on GitHub.[105] This is particularly true in the case of the most challenging CC(P) routines, which, in analogy to the previously formulated semi-stochastic[57–59,61] and CIPSI-driven[60] CC(P;Q) approaches, are used to solve the CC equations in the P spaces containing spotty subsets of triply excited determinants that do not form continuous manifolds labeled by occupied and unoccupied orbitals from the respective ranges of indices assumed in conventional CC programming. We did discuss some of the key algorithmic ingredients that must be considered when coding the CC(P;Q) approaches, if we are to benefit from the potentially enormous speedups offered by methods in this category when the excitation manifolds used in the iterative CC(P) steps [and their excited-state EOMCC(P) counterparts] are small and spotty, in Refs. 57–59 (cf. also Ref. 88), but we will return to this topic in a separate publication, where the coding strategies adopted in our current implementation of the adaptive CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ methods in the CCpy package will be discussed in detail. One of the most useful consequences of our current implementation of the adaptive CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ approaches aimed at accurately approximating the full CCSDT energetics, in addition to the major savings in the computational effort compared to CCSDT, is the observation that the CPU timings characterizing the CC(P) calculations preceding the determination of the noniterative $\delta_0(P;Q)$ corrections grow slowly with the fraction of triply excited determinants included in the underlying P spaces (see Table V). This is consistent with the computational cost analysis of the CC(P;Q) methods using small fractions of higher–than–doubly excited cluster and excitation amplitudes in the iterative CC(P) and EOMCC(P) steps in Refs. 57–59 and 88.

Among other observations worth mentioning here, which are clearly reflected in the CPU timings shown in Table V and the results of the adaptive CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ calculations reported in Tables I–IV and which are also consistent with our earlier active-orbital-based,[51–56] semi-stochastic,[57–59,61] and CIPSI-driven[60] CC(P;Q) studies, is the fact that one is much better off by adding the $\delta_0(P;Q)$ corrections to the CC(P) energies. The uncorrected CC(P) energies approach their CCSDT parents as the number of triply excited determinants in the P space increases, improving the associated initial CCSD energetics and the CCSD(T) and CR-CC(2,3) results, but the $\delta_0(P;Q)$-corrected CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ energy values are much more accurate, converging to CCSDT much faster, while the computational costs of determining the $\delta_0(P;Q)$ corrections are only small fractions of those associated with the underlying CC(P) steps. We must also realize that we have to determine the $\delta_0(P;Q)$ [in general, $\delta_\mu(P;Q)$] corrections in the adaptive CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ schemes anyway since we need them to construct the underlying P spaces, so using the uncorrected CC(P) [in the case of excited states, EOMCC(P)] energies does not make much sense and is not recommended. This is in a way similar to the selected CI calculations, such as the CIPSI approach used as an inspiration in the development of the adaptive CC(P;Q) framework in this study, which rely on the perturbative corrections to the variational CI energies in the process of constructing the underlying Hamiltonian diagonalization spaces. It is also clear from the timings reported in Table V and comparisons with the CCSDT energetics in Tables I–IV that there are no major benefits of using the CCSD(T)-like CC(P;Q)$_{\text{(T)}}$ approximation to the adaptive CC(P;Q) methodology, which relies on a much more complete and robust treatment of moments $\mathfrak{M}^{ijk}_{abc}(P^{(k)})$ and coefficients $\ell^{abc}_{ijk}(P^{(k)})$ in Eq. (21) compared to that employed in CC(P;Q)$_{\text{(T)}}$. The adaptive CC(P;Q)$_{\text{(T)}}$ energies are generally less accurate, while the savings in the computational effort offered by the CC(P;Q)$_{\text{(T)}}$ approach compared to its more complete, CR-CC(2,3)-like, CC(P;Q) counterpart are small.

Last, but not least, it is interesting to observe in Table V that the CPU timings characterizing the adaptive CC(P;Q) computations capable of providing the near-CCSDT energetics, while larger than those required by their CCSD(T) and CR-CC(2,3) counterparts, are not very far removed from the costs of the CCSD(T) and CR-CC(2,3) calculations, which are generally less robust and much less accurate, especially when T_3 correlations are larger and nonperturbative and the coupling between the lower-rank T_1 and T_2 and higher-rank T_3 clusters becomes significant. This is mainly because the CPU times needed to complete the iterative CC(P) steps, when the fraction of triples incorporated in the P space is as tiny as 1–3%, which is, as shown in Tables I–IV, enough to recover the CCSDT energetics to within fractions of a millihartree, even when CCSD(T) and CR-CC(2,3) fail or struggle, are only a few times longer than those characterizing CCSD. This is not too surprising. When the fraction of triples in the P space is tiny, the noniterative triples corrections of the adaptive CC(P;Q) and CR-CC(2,3) calculations have virtually identical costs since the corresponding Q spaces, which are spanned by either all [CR-CC(2,3)] or nearly all [CC(P;Q)] triply excited determinants, are very similar. One can, therefore, anticipate that much of the difference between the CPU timings characterizing the CR-CC(2,3) and adaptive CC(P;Q) runs, especially if we put aside the P space determination steps, is driven by the time spent on the CC(P) iterations, and this is exactly what we see in Table V. Similar remarks apply to the relative costs of the CCSD(T) vs adaptive CC(P;Q)$_{\text{(T)}}$ computations. The storage requirements characterizing the adaptive CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ calculations are not far removed from those required by their CCSD(T) and CR-CC(2,3) counterparts either, if the fractions of triples in the underlying P spaces are tiny, since the vectors representing the $T^{(P)} = T_1 + T_2 + T_3^{(P)}$ operators are not much longer than those used to store $T_1 + T_2$. In summary, it is encouraging that with the introduction of the adaptive CC(P;Q) methodology, which is only a few times more expensive than the CCSD(T) and CR-CC(2,3) approaches, we can accelerate the full CCSDT computations by orders of magnitude with only minimal loss of accuracy, even when T_3 effects are highly nonperturbative, causing CCSD(T) to fail, and even when the coupling among T_1, T_2, and T_3 components of the cluster operator becomes so large that the CR-CC(2,3) correction to CCSD is no longer reliable.

IV. SUMMARY, CONCLUDING REMARKS, AND FUTURE OUTLOOK

One of the most important topics in the CC theory and its EOM and linear-response extensions to excited electronic states has been the development of accurate and robust ways of incorporating higher–than–two-body components of the cluster and excitation operators that would avoid large, usually prohibitive, computational costs of methods such as CCSDT, CCSDTQ, EOMCCSDT, etc., which treat these operators fully, while eliminating failures of the more practical perturbative approximations of the CCSD(T) type in typical multireference situations, such as chemical bond stretching or breaking, biradicals, and excited states dominated by two-electron transitions. Among the most promising ideas in this area has been the CC(P;Q) formalism,[51–61] in which one solves the CC/EOMCC equations in a subspace of the many-electron Hilbert space, called the P space, spanned by the excited determinants that, together with the reference determinant, dominate the ground or the ground and excited states of interest, and then improves the resulting CC(P) or CC(P) and EOMCC(P) energies using the *a posteriori* noniterative $\delta_\mu(P;Q)$ corrections due to higher-order correlation effects not captured by the CC(P)/EOMCC(P) computations, determined with the help of another subspace of the Hilbert space, called the Q space. The CC(P;Q) methodology is a generalization of the biorthogonal moment expansions of Refs. 62–64, 66, and 74, which have resulted in methods such as CR-CC(2,3), but unlike its predecessors, it permits unconventional choices of the P and Q spaces that relax the lower-rank T_n and $R_{\mu,n}$ components in the presence of their higher-rank counterparts, which CR-CC(2,3), CCSD(T), and their higher-order and excited-state extensions cannot do.

In this work, we have introduced a novel category of the CC(P;Q) formalism, called adaptive CC(P;Q), which applies to ground and excited states and which results in methods that are expected to converge or accurately approximate high-level CC/EOMCC energetics of the CCSDT, CCSDTQ, EOMCCSDT, etc. types at small fractions of the computational costs. The adaptive CC(P;Q) approaches should work equally well in cases of weaker as well as stronger correlations, from nondegenerate ground states and excited states dominated by one-electron transitions to bond stretching or breaking, biradicals, and excited states having substantial double excitation character, where higher–than–two-body components of the cluster and EOM excitation operators become large and can be strongly coupled to their lower-rank counterparts. The adaptive CC(P;Q) methodology discussed in this paper is a “black-box” and self-improving framework. The key idea behind its design is an adaptive selection of the leading determinants or excitation amplitude types needed to define the T_n (in the case of excited states, also $R_{\mu,n}$) components with $n > 2$ that enter the CC(P) and EOMCC(P) calculations, which relies on the intrinsic mathematical structure of the moment expansions defining the noniterative $\delta_\mu(P;Q)$ corrections to the CC(P) and EOMCC(P) energies. This makes the process of identifying the leading higher–than–doubly excited determinants for inclusion in the P space fully automated. Prior to this work, in our quest to find an efficient and robust procedure for selecting the appropriate subset of higher–than–doubly excited determinants for inclusion in the P space, we have relied on active orbitals,[51–56] CIQMC and CCMC wave function propagations,[57–59,61,88] and sequences of Hamiltonian diagonalizations employed in the modern formulation of CIPSI,[60] and all of these efforts have been successful, allowing us to recover or accurately approximate the CCSDT,[51–61] CCSDTQ,[54–56,59] and EOMCCSDT, etc.[58] energetics at small fractions of the computational costs, but the adaptive CC(P;Q) formalism, introduced and tested in this study, by eliminating the need for reliance on user-defined active orbitals, non-CC (CIQMC, CIPSI) wave functions, and stochastic (CIQMC, CCMC) concepts, moves us to an entirely new level.

In defining the adaptive CC(P;Q) methodology, especially its relaxed variant, we have been inspired by the modern implementation of the CIPSI approach in Quantum Package 2.0, where one grows the relevant, recursively generated, Hamiltonian diagonalization spaces by arranging the candidate determinants from outside the current space according to the magnitude of their contributions to perturbative corrections to the Hamiltonian eigenvalues, using those characterized by the largest contributions to enlarge the variational space. Thus, we define our adaptive CC(P;Q) algorithm by interpreting the CC(P;Q) correction $\delta_\mu(P;Q)$, Eq. (15), as a sum of contributions due to the individual determinants from the Q space. We then use the Q-space determinants characterized by the largest (in absolute value) contributions to $\delta_\mu(P;Q)$ to enlarge the current P space, repeating the process, if need be, to generate the CIPSI-style sequence of the slowly growing P spaces and slowly shrinking Q spaces adding up to the excitation manifold of the parent high-level CC/EOMCC theory of interest.

To illustrate the benefits of the adaptive CC(P;Q) framework, we have developed the adaptive CC(P;Q) code targeting the ground-state CCSDT energetics, which we incorporated in our open-source CCpy package available on GitHub.[105] The initial P space in this code is spanned by singly and doubly excited determinants and the initial Q space consists of all triples, so that our sequence of CC(P;Q) calculations starts from CR-CC(2,3), and then, we follow the above recursive procedure by transferring more and more triply excited determinants from the Q to P spaces. In the adaptive CC(P;Q) computations reported in this article, we have distinguished between the relaxed algorithm, in which one reaches a desired fraction of triply excited determinants in the P space through a sequence of systematically grown smaller subspaces, relaxing the one-, two-, and three-body components of the underlying cluster operator accordingly, and a one-shot unrelaxed approach, in which one picks a target fraction of triples for inclusion in the P space based on their contributions to the CR-CC(2,3) correction to CCSD. We have also considered the relaxed and unrelaxed variants of the adaptive CC(P;Q)$_{\text{(T)}}$ approach, in which the CC(P;Q) correction to the CC(P) energy is calculated using the CCSD(T)-like formulas.

The relaxed and unrelaxed variants of the adaptive CC(P;Q) and CC(P;Q)$_{\text{(T)}}$ methods aimed at converging the ground-state CCSDT energetics have been tested using the significantly stretched F_2 and F_2^+ molecules, in which T_3 correlations are large and highly nonperturbative, causing CCSD(T) to fail, and the reactant and transition-state structures involved in the automerization of cyclobutadiene. In analogy to the stretched F_2^+ system, the transition-state structure of cyclobutadiene is characterized by large and nonperturbative T_3 effects, which are also strongly coupled to those captured by T_1 and T_2 and their powers, so that both CCSD(T) and CR-CC(2,3) fail in these two cases. The CCSD(T) and CR-CC(2,3) methods work well for the cyclobutadiene molecule in its reactant, i.e., equilibrium, geometry, but some nonnegligible errors relative to CCSDT, which has been treated in our numerical work as a reference, remain. Our calculations show that independent of the system considered in the calculations, the adaptive CC(P;Q) scheme using the relaxed algorithm, in which the numbers of triples in the relevant P spaces are increased using tiny 1% increments, recovers the target CCSDT energetics to within 0.1 millihartree or so using only 2–3% of all triples in the final P spaces, i.e., after 3–4 cycles of the algorithm. This applies to all four systems included in our tests, including the most challenging stretched F_2^+ species and the transition state of cyclobutadiene and the activation barrier associated with it, where both CCSD(T) and CR-CC(2,3) fail. The simpler unrelaxed variant of the adaptive CC(P;Q) approach is less accurate and displays slower convergence toward CCSDT, but with similar fractions of triples in the underlying P spaces, it has no problem with reaching chemical accuracy levels relative to CCSDT. Even with a tiny 1% of all triply excited determinants in the P spaces, the adaptive CC(P;Q) algorithm proposed in this study works excellent, recovering the CCSDT energetics to within 1–2 millihartree, even when the errors in the CCSD(T) and CR-CC(2,3) data relative to CCSDT reach ~10–30 millihartree and the CR-CC(2,3) method struggles. Our current implementation of the relaxed and unrelaxed adaptive CC(P;Q) schemes aimed at CCSDT is efficient enough to allow us to recover the CCSDT energetics with the above accuracy levels using computational times that are orders of magnitude smaller than those characterizing CCSDT and that are not very far removed from those characterizing the corresponding CCSD(T) and CR-CC(2,3) calculations. While the CC(P;Q)$_{(\mathrm{T})}$ approximation to the adaptive CC(P;Q) works well too, one is better off using its more complete CC(P;Q) counterpart since the adaptive CC(P;Q)$_{(\mathrm{T})}$ energies are generally less accurate, while the savings in the computational effort offered by CC(P;Q)$_{(\mathrm{T})}$ are comparatively small.

The results obtained in this study are most encouraging, but, given the novelty of the adaptive CC(P;Q) methodology proposed in this work and the limited numerical evidence to date, we have to examine greater numbers of molecular examples and a wider range of situations, especially those where T_3 and other higher–than–two-body clusters become large and difficult to converge, and extend our current adaptive CC(P;Q) codes to higher levels of the CC theory, such as CCSDTQ. In analogy to our semi-stochastic CC(P;Q) efforts,[58] we will also implement and test excited-state extensions of the adaptive CC(P;Q) approaches, starting with those aimed at the EOMCCSDT energetics. The present article has already demonstrated that the adaptive CC(P;Q) formalism applies to ground as well as excited states and that extending the adaptive CC(P;Q) codes to excited states within the EOMCC framework is feasible. Ultimately, we will examine if it is practical to extend the adaptive CC(P;Q) algorithm discussed in this article to converge the full CC/EOMCC, meaning full CI, data, using the Q spaces which are orthogonal complements to the P spaces used in the CC(P)/EOMCC(P) and CC(P;Q) considerations. In all of the relaxed CC(P;Q) calculations reported in this article, we have assumed a 1% growth rate in the fractions of triples added to the underlying P spaces, but we are planning to explore other (smaller as well as larger) incremental fractions of triples used to grow P spaces in the relaxed variant of the adaptive CC(P;Q) algorithm as well, to see if they can substantially affect any of the conclusions of this study. All the above plans will be accompanied by improvements in the adaptive CC(P;Q) code incorporated in the CCpy software package available on GitHub,[105] especially the low-memory variant of the determinant selection algorithm needed to filter out the leading triply (in the future also quadruply) excited determinants for inclusion in the P spaces used in the adaptive CC(P;Q) computations.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Karthik Gururangan: Conceptualization (equal); Data curation (lead); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (lead); Validation (equal); Writing – original draft (supporting); Writing – review & editing (equal). **Piotr Piecuch**: Conceptualization (equal); Data curation (supporting); Formal analysis (equal); Funding acquisition (lead); Investigation (equal); Methodology (equal); Project administration (lead); Resources (lead); Software (supporting); Supervision (lead); Validation (equal); Writing – original draft (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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