

Coupled-cluster methods with internal and semi-internal triply and quadruply excited clusters: CCSD*t* and CCSD*tq* approaches

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(Received 23 July 1998; accepted 8 December 1998)

Extension of the closed-shell coupled-cluster (CC) theory to studies of bond breaking and general quasidegenerate situations requires the inclusion of the connected triply and quadruply excited clusters, T_3 and T_4 , respectively. Since the complete inclusion of these clusters is expensive, we explore the possibility of incorporating dominant T_3 and T_4 contributions by limiting them to active orbitals. We restrict T_3 and T_4 clusters to internal or internal and semi-internal components using arguments originating from the multireference formalism. A hierarchy of approximations to standard CCSDT (CC singles, doubles, and triples) and CCSDTQ (CC singles, doubles, triples, and quadruples) schemes, designated as the CCSD*t* and CCSD*tq* approaches, is proposed and tested using the H₂O and HF molecules at displaced nuclear geometries and C₂ at the equilibrium geometry. It is demonstrated that the CCSD*t* and CCSD*tq* methods provide an excellent description of bond breaking and nondynamic correlation effects. Unlike perturbative CCSDT and CCSDTQ approaches, the CCSD*t* and CCSD*tq* approaches do not fail at large internuclear separations, in spite of using the restricted Hartree–Fock reference. All CCSD*t* and CCSD*tq* approaches are essentially n^6 procedures and yet they are shown to provide reliable information about T_3 and T_4 components, whose standard evaluation requires expensive n^8 and n^{10} steps. © 1999 American Institute of Physics. [S0021-9606(99)30410-4]

I. INTRODUCTION

The success of the single-reference (SR) CC theory^{1–5} in describing nondegenerate ground states of molecules, for which the basic CCSD (CC singles and doubles)⁶ approximation provides very good results, has stimulated considerable research activity aimed at the extension of CC theory to quasidegenerate states via either a multireference (MR) formalism,^{5,7–11} or SRCC approaches that explicitly include the connected tri- and tetraexcited clusters.^{12–17}

The genuine MRCC theories may be quite useful in general open-shell situations. However, it is formally much easier to describe quasidegenerate ground states, including difficult cases of bond breaking, by including higher-than-pair clusters in the standard SRCC formalism. In SRCC calculations, all nondynamic correlation effects related to the quasidegenerate nature of the electronic state of interest can be treated dynamically. In consequence, the SRCC calculations do not suffer from the convergence and intruder-state problems that plague genuine MRCC theories (cf., e.g., Refs. 18 and 19). Furthermore, they have an ease of application that is not matched by MRCC approaches or multireference configuration interaction (MRCI) methods. The newly developed state-specific MRCC approaches (cf., e.g., Refs. 20–22), which are based on a genuine MR formulation, may change this situation, but none of the existing state-specific

methods is simple or general enough to be as widely applicable as approaches that are based on the standard SRCC description.

Unfortunately, a full account of triply and quadruply excited clusters, T_3 and T_4 , respectively, is computationally very demanding. The complete CCSDT (CC singles, doubles, and triples) method^{12–14} requires steps that scale as $n_o^3 n_u^5$, where n_o (n_u) is the number of occupied (unoccupied) spatial orbitals. The CCSDTQ (CC singles, doubles, triples, and quadruples) approach^{15,16} (see, also, Ref. 17) scales as $n_o^4 n_u^6$, which should be compared to a much more favorable, $n_o^2 n_u^4$ scaling of the CCSD method. While the performance of CCSDT and CCSDTQ programs can be greatly improved by using the idea of recursively generated intermediates and fast matrix multiplication routines,¹⁵ little, other than orthogonal spin-adaptation,^{23,24} can be done to reduce large storage requirements for tri- and tetraexcited cluster amplitudes. As a result, the CCSDT and CCSDTQ calculations are limited to relatively small systems.

The large costs of CCSDT and CCSDTQ calculations have inspired a considerable research activity towards the formulation and implementation of various approximate CCSDT and CCSDTQ schemes, which are less expensive than their complete counterparts. In the iterative perturbative CC approaches termed CCSDT- n ,^{24–26} ACCSDT-1 (approximate CCSDT-1 methA)~ACPTQ (approximate coupled-pair theory with connected triples and quadruples),²⁴ and CCSDTQ-1,²⁷ and their noniterative variants, referred to as the CCSD+T(CCSD)=CCSD[T]=CC4SD[T],^{24,28–30} ACCSD+T(ACCSD)=ACCSD[T],³¹ CCD+ST(CCD)=CCD[ST],^{24,29,32} ACCD+ST(ACCD)=ACCD[ST],^{24,29}

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CCSD(T)=CC4SD(T),^{30,33,34} CCSDQ'+T(CCSDQ')=CCSDQ'[T],³¹ CCSDT+Q(CCSDT)=CCSDT[Q],²⁷ CCSD+TQ*(CCSD)=CCSD[TQ*],³⁵ CC5SD[TQ],³⁰ and CC5SD(TQ)³⁰ methods, the T_3 and T_4 clusters are related to lower-order T_1 and T_2 clusters using arguments originating from many-body perturbation theory (MBPT). This allows us to reduce the $n_o^3 n_u^5$ scaling of the CCSDT approach to $n_o^3 n_u^4$, when the CCSDT-1, CCSD[T], and CCSD(T) methods are employed.

In another approach, attempts have been made to externally correct the CCSD method.^{31,36–42} In this case, the T_3 and T_4 clusters are obtained by a cluster analysis of the projected unrestricted Hartree–Fock (PUHF),^{31,36} valence bond (VB),^{37,38} multiconfigurational self-consistent-field (MCSCF) or complete active space SCF (CASSCF),^{31,39–41} and MRCI⁴² wave functions. These approaches are not much more expensive than the standard CCSD scheme provided that the calculation used to generate T_3 and T_4 components is significantly less expensive than the CCSD calculation. The externally corrected CCSD methods are related to a recently proposed split-amplitude strategy of solving CC equations,⁴³ in which part of the cluster operator is obtained from external sources, while the other part is determined from a set of quasilinearized CC equations.

The problem with perturbative CC schemes is that they typically fail to describe bond breaking (cf. Refs. 44–47). In more complicated quasidegenerate situations, such as those found in cyclic polyenes, the CCSD approach becomes singular,⁴⁸ so that the T_1 and T_2 components needed to estimate T_3 and T_4 clusters in perturbative CC schemes are simply not available. Replacing the restricted Hartree–Fock (RHF) reference by its unrestricted Hartree–Fock (UHF) analog improves the results (cf., e.g., Refs. 44 and 45), but the corresponding CC wave functions are spin-contaminated. Although the level of spin-contamination of CC wave functions is significantly reduced compared to UHF wave functions, potential energy curves or surfaces (PECs or PESs) resulting from CC/UHF calculations exhibit nonanalytic behavior in the vicinity of a triplet instability^{44,49} (for classification of Hartree–Fock instabilities, see, e.g., Ref. 50).

The externally corrected CCSD schemes do not fail upon bond breaking but they have other kinds of problems. The most important one is that information is taken from outside the CC structure. In addition, the PUHF wave function can only be used to estimate the effect of T_4 clusters, but no information about important T_3 components can be extracted from PUHF calculations.^{31,36} The VB wave functions provide information about both T_3 and T_4 clusters,^{37,38} but then we have to deal with the problem of nonorthogonal orbitals used by the VB method. The MCSCF (CASSCF) method is a rather inefficient source of information about T_3 and T_4 clusters if one chooses to use MCSCF (CASSCF) orbitals in CC calculations,⁴¹ even though PESs obtained in MCSCF-corrected (CASSCF-corrected) CCSD calculations are better than their CCSD analogs^{40,41} (the CASSCF-corrected CCSD scheme employing the CASSCF wave function to extract T_3 and T_4 components and a RHF configuration to define the reference and orbitals for CC calculations, which was proposed in Ref. 31, has not yet been tested). Finally, the

MRCISD (MRCI singles and doubles) calculations used in the MRCI-corrected CCSD scheme (referred to as the reduced MRCCSD or RMRCCSD approach⁴²) are significantly more expensive than the corresponding CCSD calculations, if the MRCISD and CCSD methods are properly encoded (the cost of MRCISD calculation is proportional to $M n_o^2 n_u^4$, where $M > 1$ is the dimension of the multidimensional reference space), even though RMRCCSD results for small molecules represent a significant improvement over the CCSD ones.⁴² Moreover, the MRCISD approach is not size-extensive, so that the T_3 and T_4 clusters resulting from cluster analysis of the MRCISD wave function introduce unlinked terms into the CC formalism. Another problem with all externally corrected CCSD schemes is that it is practically impossible to formulate efficient analytic gradient techniques once different types of wave functions (in this case, wave functions of CC and non-CC origin) are combined together. It is much easier to develop analytic gradient codes for perturbative CC methods.^{34,45,51}

In this paper, we investigate the possibility of incorporating the dominant T_3 and T_4 contributions by combining SRCC concepts with a limitation to active orbitals for higher-than-pair clusters. Our aim is to design approximations, which scale as $n_o^2 n_u^4$, while allowing us to describe quasidegenerate systems in a *completely size-extensive* manner. By utilizing the well-known concept of active orbitals, we restrict T_3 and T_4 clusters to internal or internal and semi-internal (see the next section) components using arguments originating from the MRCC theory. We base our analysis on the observation that any MRCC technique, once restricted to the ground state, can be regarded as a clever way of selecting the most important high-order excitations from all high-order excitations entering the SRCC expansion. In a wealth of MRCI applications and in some CC calculations,^{46,52–57} it has been documented that the restriction of T_3 and T_4 clusters to internal and semi-internal components can lead to an excellent description of single- and multiple bond breaking in small molecules.

In order to learn which cluster selection schemes are most efficient, we propose a hierarchy of approximations to standard CCSDT and CCSDTQ methods, which we commonly designate as the CCSD*t* and CCSD*tq* approaches (lower case *t* and *q* indicate that not all T_3 and T_4 amplitudes have been included). The CCSD*t* and CCSD*tq* methods including internal and semi-internal T_3 and T_4 clusters are equivalent to the so-called state-selective (SS) CCSD(T) and CCSD(TQ) methods of Refs. 52, 53, and 58 (for the most general formulation of the SSCC method, see Ref. 58; for earlier developments, see, also, Ref. 59). We propose, however, other CCSD*t* and CCSD*tq* approximations, which have not been studied before, including approaches that use internal T_3 and T_4 components only and approaches that combine perturbative concepts with the concept of an active space. Our implementation of all CCSD*t* and CCSD*tq* schemes allows us to use (for the first time in the context of CC studies) larger active spaces and basis sets.

All methods discussed in this paper have been tested on a number of molecular systems, including the H₂O and HF molecules at displaced nuclear geometries and the difficult

example of the C_2 molecule. All systems studied in this paper are characterized by a large T_3 effect. The stretched H_2O molecule and C_2 are also characterized by a significant T_4 effect.

In the following Sec. II, we describe the CCSD t and CCSD tq methods. The relevant computational details are presented in Sec. III. In Sec. IV, we present the results of calculations, and in the last Sec. V, we summarize our findings.

II. THEORY

In the SRCC theory, the ground state Ψ of the N -electron system is written in the following form:

$$\Psi = e^T \Phi, \quad (1)$$

where

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

is the cluster operator and Φ is a single-determinantal reference configuration which we choose as the Fermi vacuum (usually, the RHF or UHF wave function). Many-body components T_k ($k=1,2,\dots,N$) of the cluster operator T are defined in terms of the excitation operators

$$E_{i_1 \dots i_k}^{a_1 \dots a_k} = \prod_{\kappa=1}^k \hat{a}_{i_\kappa}^\dagger \hat{i}_\kappa, \quad (3)$$

and the corresponding cluster amplitudes $t_{a_1 \dots a_k}^{i_1 \dots i_k}$ as follows:

$$T_k = \left(\frac{1}{k!} \right)^2 t_{a_1 \dots a_k}^{i_1 \dots i_k} E_{i_1 \dots i_k}^{a_1 \dots a_k}. \quad (4)$$

We use \hat{i}_κ (\hat{a}_κ^\dagger) to designate the annihilation (creation) operators. We use letters i, j, k, l to designate the spin-orbitals which are occupied in the reference Φ and a, b, c, d designate the unoccupied spin-orbitals. We also use the Einstein summation convention to indicate the summation over repeated indices.

The CCSD approach⁶ is obtained if we restrict the operator T to singly and doubly excited clusters, i.e., if we assume that $T = T_1 + T_2$. The CCSDT model^{12–14} is obtained if we assume that $T = T_1 + T_2 + T_3$ and in the CCSDTQ model^{15–17,53} we assume that $T = T_1 + T_2 + T_3 + T_4$. As explained in the Introduction, the CCSD method requires steps that scale as $n_o^2 n_u^4$, the CCSDT approach scales as $n_o^3 n_u^5$, and the scaling of the complete CCSDTQ procedure is $n_o^4 n_u^6$. The corresponding storage requirements for the doubly excited amplitudes t_{ab}^{ij} , triply excited amplitudes t_{abc}^{ijk} , and quadruply excited amplitudes t_{abcd}^{ijkl} are $n_o^2 n_u^2$, $n_o^3 n_u^3$, and $n_o^4 n_u^4$, respectively.

In order to reduce the computer cost associated with complete inclusion of T_3 and T_4 cluster components, we have to decouple the CCSD part of the CCSDT or CCSDTQ system of equations from equations projected on tri- and (in case of the CCSDTQ scheme) tetraexcited configurations. In the following we focus on simplifying the CCSDTQ scheme. A similar analysis applies to the CCSDT method.

The CCSDTQ equations have the following general form:

$$\langle \Phi_i^a | \text{CCSD} + (H_N T_3)_C | \Phi \rangle = 0, \quad (5)$$

$$\langle \Phi_{ij}^{ab} | \text{CCSD} + [H_N (T_3 + T_1 T_3 + T_4)]_C | \Phi \rangle = 0, \quad (6)$$

$$\langle \Phi_{ijk}^{abc} | \text{CCSD} + [H_N (T_3 + T_1 T_3 + T_4 + T_1 T_4 + T_2 T_3 + \frac{1}{2} T_1^2 T_3)]_C | \Phi \rangle = 0, \quad (7)$$

$$\langle \Phi_{ijkl}^{abcd} | \text{CCSD} + [H_N (T_3 + T_1 T_3 + T_4 + T_1 T_4 + T_2 T_3 + \frac{1}{2} T_1^2 T_3 + T_2 T_4 + \frac{1}{2} T_3^2 + \frac{1}{2} T_1^2 T_4 + T_1 T_2 T_3 + \frac{1}{6} T_1^3 T_3)]_C | \Phi \rangle = 0, \quad (8)$$

where **CCSD** designates all terms that contain T_1 and T_2 clusters only and terms that do not contain cluster operators at all, $H_N = H - \langle \Phi | H | \Phi \rangle$ is the electronic Hamiltonian in the normal-product form, the subscript C designates the connected components of the corresponding operator expression, and

$$\Phi_{i_1 \dots i_k}^{a_1 \dots a_k} = E_{i_1 \dots i_k}^{a_1 \dots a_k} \Phi, \quad (9)$$

are excited configurations. Notice that higher-than-quadruply excited clusters do not enter Eqs. (5) and (6) if the Hamiltonian contains at most two-body terms. This means that if T_3 and T_4 clusters are exact (i.e., they correspond to a full CI solution), then T_1 and T_2 clusters obtained by solving Eqs. (5) and (6) are also exact, and so is the resulting energy, which can be expressed solely in terms of T_1 and T_2 cluster components

$$E = \langle \Phi | H | \Phi \rangle + \langle \Phi | [H_N (T_1 + T_2 + \frac{1}{2} T_1^2)]_C | \Phi \rangle. \quad (10)$$

This observation^{31,37} allows us to decouple Eqs. (5) and (6) from the rest of the CCSDTQ chain. Indeed, once we find a good approximation for T_3 and T_4 , we no longer have to use the complete set of the CCSDTQ equations, Eqs. (5)–(8), to obtain very good (nearly full CI) energy values. We can rely on Eqs. (5) and (6), in which we iterate T_1 and T_2 components in the presence of terms containing information about higher-order T_3 and T_4 clusters. This is the basic mechanism of reducing the computer cost of the full CCSDTQ calculation to $n_o^2 n_u^4$ steps or steps that are only moderately more expensive than the CCSD steps. This idea has been recently used with a factorized form of T_4 in another approach.⁶⁰

The question remains how to find good approximations for T_3 and T_4 . As mentioned in the Introduction, we can use the MBPT arguments to express T_3 and T_4 clusters in terms of their lower-order analogs, T_1 and T_2 (we can also think of expressing T_4 clusters in terms of T_1 , T_2 , and T_3 , as is done in the CCSDTQ-1 method²⁷). For example, in the well-known and highly successful CCSDT-1 scheme,²⁵ (cf. also, Ref. 24 for the orthogonally spin-adapted formulation) we approximate T_3 as follows:

$$T_3 = R_0^{(3)} (W_N T_2)_C, \quad (11)$$

where $R_0^{(3)}$ designates the three-body part of the reduced resolvent used in the standard MBPT formalism and W_N is the two-body part of H_N . This allows us to replace the CCSDT system of equations, Eqs. (5)–(7) (with $T_4=0$), by Eqs. (5) and (6), in which T_3 is given by Eq. (11) (and, of course, $T_4=0$). The resulting CCSDT-1 scheme scales as $n_o^3 n_u^4$, which should be compared to much more expensive

$n_o^3 n_u^5$ steps of the full CCSDT formalism. In addition, the CCSDT-1 t_{abc}^{ijk} amplitudes do not have to be stored, since we can calculate them on the fly using Eq. (11). A similar reduction in the computer effort applies to noniterative counterparts of the CCSDT-1 scheme, such as the CCSD[T] method^{28,30} (for the orthogonally spin-adapted formulation, see Refs. 24 and 29) or its somewhat more popular CCSD(T) analog.^{30,33,34} The examples of other perturbative CC methods were given in the Introduction. All perturbative CC methods work very well if the ground electronic state under consideration has a nondegenerate character. For example, the CCSDT-1, CCSD[T], and CCSD(T) results for molecules near their equilibrium geometries are practically identical to full CCSDT results. Unfortunately, as mentioned in the Introduction, all perturbative CC approaches fail at large inter-nuclear separations, since MBPT arguments are no longer valid when bonds are being broken.⁶¹

In order to respond to this, somewhat unsatisfactory, situation, we decided to propose and investigate a new category of CCSDT-like and CCSDTQ-like CC methods, which (i) are size extensive and are solely based on the CC exponential ansatz, (ii) provide a correct description of bond breaking and quasidegenerate states, (iii) offer substantial savings in computer effort compared to full CCSDT and CCSDTQ approaches, and (iv) do not use perturbative concepts, even though we leave room for various perturbative approximations that can be introduced later. As is often done in CASSCF or MRCI/MRMBPT/MRCC approaches, we divide all spin-orbitals into three sets of core, active, and virtual spin-orbitals. We designate core spin-orbitals by $\mathbf{i}, \mathbf{j}, \mathbf{k}, \mathbf{l}, \dots$, active spin-orbitals occupied in reference Φ (active holes) by $\mathbf{I}, \mathbf{J}, \mathbf{K}, \mathbf{L}, \dots$, active spin-orbitals unoccupied in reference Φ (active particles) by $\mathbf{A}, \mathbf{B}, \mathbf{C}, \mathbf{D}, \dots$, and virtual spin-orbitals by $\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{d}, \dots$. The number of active spatial orbitals occupied in reference Φ is designated by N_o and the number of active spatial orbitals unoccupied in Φ is designated by N_u . Clearly, if the core and virtual sets are not empty, we have $N_o < n_o$ and $N_u < n_u$.

With this partitioning of the one-electron space, we introduce various approximations (commonly termed the CCSD*t* and CCSD*tq* schemes), in which T_3 and T_4 clusters are restricted to certain, relatively narrow classes defined in terms of active spin-orbitals (T_1 and T_2 clusters are treated exactly, i.e., all available spin-orbitals are used to define these clusters). We are interested in a significant reduction of the computer time, so that active spaces satisfying the condition $N_u \ll n_u$ and, if possible, the condition $N_o \ll n_o$, are preferred. We distinguish between schemes using internal triples and quadruples only, in which T_3 and T_4 components are defined using excitations within the active space, and schemes using semi-internal tri- and tetraexcitations, in which at least one spin-orbital index defining t_{abc}^{ijk} and t_{abcd}^{ijkl} amplitudes is inactive (core or virtual). The CCSD*t* and CCSD*tq* approximations tested by us so far are described in Secs. II A–II D below.

A. CCSD{ t }, CCSD{ tq }, CCSD{ t' }, and CCSD{ $t'q'$ } schemes

In each of these approaches, we proceed as follows. We first solve the complete CCSDT or CCSDTQ system of equations, Eqs. (5)–(7) or (5)–(8), respectively, using active orbitals only (Step 1). In the next Step 2, we solve Eqs. (5) and (6) with T_3 or T_3 and T_4 obtained in Step 1. There is a minor difference between CCSD{ t } or CCSD{ tq } and CCSD{ t' } or CCSD{ $t'q'$ } schemes. For example, Step 2 of the CCSD{ tq } procedure requires that we solve the following system of equations:

$$\langle \Phi_i^a | \text{CCSD} + (H_N \mathbf{t}_3^{(0)})_C | \Phi \rangle = 0, \quad (12)$$

$$\langle \Phi_{ij}^{ab} | \text{CCSD} + [H_N(\mathbf{t}_3^{(0)} + T_1 \mathbf{t}_3^{(0)} + \mathbf{t}_4^{(0)})]_C | \Phi \rangle = 0, \quad (13)$$

where

$$\mathbf{t}_3^{(0)} \equiv T_3^{(0)} \begin{pmatrix} \mathbf{ABC} \\ \mathbf{IJK} \end{pmatrix} \quad (14)$$

and

$$\mathbf{t}_4^{(0)} \equiv T_4^{(0)} \begin{pmatrix} \mathbf{ABCD} \\ \mathbf{IJKL} \end{pmatrix}, \quad (15)$$

are internal T_3 and T_4 components obtained in Step 1. In Step 2 of the CCSD{ $t'q'$ } procedure, along with T_3 and T_4 clusters, we extract from Step 1 the $T_1 T_3$ term entering Eq. (6). As a result, Eq. (13) of the CCSD{ tq } scheme simplifies in the CCSD{ $t'q'$ } approach to

$$\langle \Phi_{\mathbf{IJ}}^{\mathbf{AB}} | \text{CCSD} + [H_N(\mathbf{t}_3^{(0)} + \mathbf{t}_1^{(0)} \mathbf{t}_3^{(0)} + \mathbf{t}_4^{(0)})]_C | \Phi \rangle = 0 \quad (16)$$

and

$$\langle \Phi_{ij}^{ab} | \text{CCSD} | \Phi \rangle = 0, \quad (17)$$

if Φ_{ij}^{ab} contains at least one inactive index. This means that in the CCSD{ $t'q'$ } procedure, we simply add the entire $\langle \Phi_{\mathbf{IJ}}^{\mathbf{AB}} | [H_N(\mathbf{t}_3^{(0)} + \mathbf{t}_1^{(0)} \mathbf{t}_3^{(0)} + \mathbf{t}_4^{(0)})]_C | \Phi \rangle$ term generated in Step 1 to the CCSD equations projected on internal (all-active) double excitations without storing internal $t_{\mathbf{ABC}}^{\mathbf{IJK}}$ and $t_{\mathbf{ABCD}}^{\mathbf{IJKL}}$ amplitudes and without modifying the Step 2-CCSD equations projected on semi-internal and external excitations. We might add that the $\langle \Phi_i^a | (H_N \mathbf{t}_3^{(0)})_C | \Phi \rangle$ term, which modifies the CCSD equations projected on singly excited configurations, changes only these equations in Eq. (12) which correspond to projections on internal, monoexcited configurations.

An obvious advantage of all four CCSD{ t }, CCSD{ tq }, CCSD{ t' }, and CCSD{ $t'q'$ } schemes (apart from their inherent simplicity) is their minimum cost. Step 1 of these procedures scales as $N_o^3 N_u^5$ or $N_o^4 N_u^6$. Step 2 consists of regular $n_o^2 n_u^4$ and less expensive steps of the standard CCSD procedure. If $N_u \ll n_u$ and $N_o \ll n_o$, the CPU cost associated with Step 1 is negligible compared to Step 2. For example, Step 1 of the CCSD{ t } and CCSD{ t' } procedures is no more expensive than Step 2 provided that (more or less) $N_o \ll n_o^{2/3}$ and $N_u \ll n_u^{4/5}$. This means that we can actually use fairly large active spaces in this case and still obtain procedures which are not much more expensive than the standard CCSD approach. The relevant CPU timings that illustrate this statement are presented in Sec. IV.

Notice that $\text{CCSD}\{t\}$, $\text{CCSD}\{tq\}$, $\text{CCSD}\{t'\}$, and $\text{CCSD}\{t'q'\}$ schemes are genuine CC analogs of the CASSCF-corrected CCSD scheme of Refs. 39–41. In the CASSCF-corrected CCSD approach of Refs. 39–41, one first has to solve the full CI (FCI) equations within the active space (CASFCI equations) to obtain the t_{ABC}^{IJK} and t_{ABCD}^{IJKL} amplitudes (which is done by analyzing the cluster structure of this all-active FCI or CASSCF solution). This might become a very expensive step if the active space is large. We replace this step by a much simpler CCSDT or CCSDTQ calculation within the active space, since for all practical purposes the CCSDT or CCSDTQ approaches (particularly the latter one) are almost as good as the FCI method. Thus, we reduce the cost associated with the CASSCF (or CASFCI) calculation, which is an integral part of the method of Refs. 39–41, and completely eliminate the need for a cluster analysis, since all the information about cluster components defining the CCSDT or the CCSDTQ wave functions is directly obtained by solving the CCSDT or CCSDTQ equations. In consequence, we can study much larger active spaces than the authors of Refs. 39–41. This is very important, since one cannot reproduce a significant portion of the T_3 and T_4 effects using a CASSCF-corrected CCSD scheme of Refs. 39–41 if the active space is small (cf. Ref. 41). In our methods, we also use (in the closed-shell case) standard RHF orbitals, instead of the CASSCF orbitals used in Refs. 39–41, although our programs are general and allow us to use orbitals of any type (see Sec. IV for more comments related to the use of CASSCF orbitals in SRCC calculations).

B. CCSDt' and CCSDt'q' schemes

In these two procedures, we solve the CCSDT or CCSDTQ system of equations, Eqs. (5)–(7) or (5)–(8), respectively, using the complete sets of t_a^i and t_{ab}^{ij} amplitudes and the t_{abc}^{ijk} or t_{abcd}^{ijkl} amplitudes restricted to internal types only, i.e., t_{ABC}^{IJK} or t_{ABCD}^{IJKL} . Thus, in the $\text{CCSDt}'q'$ case, we solve the following system of equations:

$$\langle \Phi_i^a | \text{CCSD} + (H_N \mathbf{t}_3^{\text{int}})_C | \Phi \rangle = 0, \quad (18)$$

$$\langle \Phi_{ij}^{ab} | \text{CCSD} + [H_N(\mathbf{t}_3^{\text{int}} + T_1 \mathbf{t}_3^{\text{int}} + \mathbf{t}_4^{\text{int}})]_C | \Phi \rangle = 0, \quad (19)$$

$$\langle \Phi_{\text{IJK}}^{\text{ABC}} | \text{CCSD} + [H_N(\mathbf{t}_3^{\text{int}} + T_1 \mathbf{t}_3^{\text{int}} + \mathbf{t}_4^{\text{int}} + T_1 \mathbf{t}_4^{\text{int}} + T_2 \mathbf{t}_3^{\text{int}} + \frac{1}{2} T_1^2 \mathbf{t}_3^{\text{int}})]_C | \Phi \rangle = 0, \quad (20)$$

$$\langle \Phi_{\text{IJKL}}^{\text{ABCD}} | \text{CCSD} + [H_N(\mathbf{t}_3^{\text{int}} + T_1 \mathbf{t}_3^{\text{int}} + \mathbf{t}_4^{\text{int}} + T_1 \mathbf{t}_4^{\text{int}} + T_2 \mathbf{t}_3^{\text{int}} + \frac{1}{2} T_1^2 \mathbf{t}_3^{\text{int}} + T_2 \mathbf{t}_4^{\text{int}} + \frac{1}{2} (\mathbf{t}_3^{\text{int}})^2 + \frac{1}{2} T_1^2 \mathbf{t}_4^{\text{int}} + T_1 T_2 \mathbf{t}_3^{\text{int}} + \frac{1}{6} T_1^3 \mathbf{t}_3^{\text{int}})]_C | \Phi \rangle = 0, \quad (21)$$

where

$$\mathbf{t}_3^{\text{int}} \equiv T_3 \begin{pmatrix} \text{ABC} \\ \text{IJK} \end{pmatrix} \quad (22)$$

and

$$\mathbf{t}_4^{\text{int}} \equiv T_4 \begin{pmatrix} \text{ABCD} \\ \text{IJKL} \end{pmatrix}. \quad (23)$$

The only essential difference between the CCSDt' or $\text{CCSDt}'q'$ approaches and methods described in Sec. II A is the fact that we now iterate the restricted set of $\mathbf{t}_3^{\text{int}}$ or $\mathbf{t}_3^{\text{int}}$ and $\mathbf{t}_4^{\text{int}}$ components, Eqs. (22) and (23), in the presence of all t_a^i and t_{ab}^{ij} amplitudes, whereas in methods described in Sec. II A we calculate the internal T_3 and T_4 clusters in the presence of internal T_1 and T_2 components prior to solving for the actual set of all t_a^i and t_{ab}^{ij} amplitudes. As a result, the cost of the CCSDt' and $\text{CCSDt}'q'$ calculations is more or less identical to the cost of the corresponding $\text{CCSD}\{t\}$, $\text{CCSD}\{tq\}$, $\text{CCSD}\{t'\}$, and $\text{CCSD}\{t'q'\}$ calculations ($\sim N_o^3 N_u^5 + n_o^2 n_u^4$ in the CCSDt' case and $\sim N_o^4 N_u^6 + n_o^2 n_u^4$ in the $\text{CCSDt}'q'$ case). Compared to the simplest $\text{CCSD}\{t'\}$ and $\text{CCSD}\{t'q'\}$ schemes, we now have to store the internal t_{ABC}^{IJK} or t_{ABCD}^{IJKL} amplitudes. As explained in Sec. II A, there is no need to store these amplitudes in the $\text{CCSD}\{t'\}$ and $\text{CCSD}\{t'q'\}$ calculations (of course, there are relatively few t_{ABC}^{IJK} and t_{ABCD}^{IJKL} amplitudes, so the need for their storage is not a major limitation). On the other hand, it should be easier to implement the analytic gradient techniques for the CCSDt' and $\text{CCSDt}'q'$ methods, since the only difference between CCSDt' and $\text{CCSDt}'q'$ equations and their complete CCSDT and CCSDTQ analogs are loops over orbital indices describing tri- and tetraexcited clusters, which in the CCSDt' and $\text{CCSDt}'q'$ cases are restricted to active indices only.

C. CCSDt and CCSDtq schemes

The complete CCSDt and CCSDtq schemes arise from solving the CCSDT or CCSDTQ systems of equations, Eqs. (5)–(7) or (5)–(8), respectively, with T_3 or T_3 and T_4 clusters restricted to internal and semi-internal excitations of the following type (cf. Refs. 52, 53, and 58):

$$\mathbf{t}_3 = T_3 \begin{pmatrix} abC \\ \text{Ijk} \end{pmatrix}, \quad (24)$$

$$\mathbf{t}_4 = T_4 \begin{pmatrix} abCD \\ \text{Ijkl} \end{pmatrix}. \quad (25)$$

The CCSDtq system of equations for t_a^i , t_{ab}^{ij} , t_{abC}^{Ijk} , and t_{abCD}^{Ijkl} has the following form:

$$\langle \Phi_i^a | \text{CCSD} + (H_N \mathbf{t}_3)_C | \Phi \rangle = 0, \quad (26)$$

$$\langle \Phi_{ij}^{ab} | \text{CCSD} + [H_N(\mathbf{t}_3 + T_1 \mathbf{t}_3 + \mathbf{t}_4)]_C | \Phi \rangle = 0, \quad (27)$$

$$\langle \Phi_{\text{Ijk}C}^{\text{ab}C} | \text{CCSD} + [H_N(\mathbf{t}_3 + T_1 \mathbf{t}_3 + \mathbf{t}_4 + T_1 \mathbf{t}_4 + T_2 \mathbf{t}_3 + \frac{1}{2} T_1^2 \mathbf{t}_3)]_C | \Phi \rangle = 0, \quad (28)$$

$$\langle \Phi_{\text{Ijkl}C}^{\text{ab}CD} | \text{CCSD} + [H_N(\mathbf{t}_3 + T_1 \mathbf{t}_3 + \mathbf{t}_4 + T_1 \mathbf{t}_4 + T_2 \mathbf{t}_3 + \frac{1}{2} T_1^2 \mathbf{t}_3 + T_2 \mathbf{t}_4 + \frac{1}{2} \mathbf{t}_3^2 + \frac{1}{2} T_1^2 \mathbf{t}_4 + T_1 T_2 \mathbf{t}_3 + \frac{1}{6} T_1^3 \mathbf{t}_3)]_C | \Phi \rangle = 0, \quad (29)$$

where \mathbf{t}_3 and \mathbf{t}_4 are defined by Eqs. (24) and (25), respectively. The CCSDt system of equations is obtained by eliminating Eq. (29) from the CCSDtq system and by setting $\mathbf{t}_4 = 0$ in the remaining equations. As explained in Ref. 58 (cf. also, Refs. 52 and 53), the internal and semi-internal tri- and tetraexcited clusters defined by Eqs. (24) and (25) are needed

if we want to describe all single and double excitations from the configurations spanning the multidimensional reference space

$$\mathcal{M}_0 = \text{span}\{\Phi, \Phi_{\mathbf{I}}^{\mathbf{A}}, \Phi_{\mathbf{IJ}}^{\mathbf{AB}}\}_{\mathbf{I} > \mathbf{J}, \mathbf{A} > \mathbf{B}}. \quad (30)$$

Thus, the choice of triples and quadruples described by Eqs. (24) and (25) leads to an SRCC scheme which has a MR cluster structure of the ground-state electronic wave function built directly into T . In fact, the CCSD t and CCSD tq wave functions have a much richer structure than the wave functions corresponding to mono- and bi-excitations from \mathcal{M}_0 , Eq. (30). This is an immediate consequence of the exponential nature of the SRCC ansatz. In particular, various higher-than-quadruply excited disconnected clusters of internal and semi-internal type are present in the CCSD tq wave function (clearly, the highest rank of the internal cluster components is limited by the number of occupied and unoccupied orbitals included in the active space).

It can be shown⁵⁸ that the choice of triples and quadruples according to Eqs. (24) and (25) is equivalent to decomposing the SR cluster operator T into internal and external parts, T^{int} and T^{ext} , respectively, which in the CCSD tq case are defined as follows:

$$T^{\text{int}} = T_1^{\text{int}} + T_2^{\text{int}} + T_3^{\text{int}} + T_4^{\text{int}}, \quad (31)$$

$$T^{\text{ext}} = T_1^{\text{ext}} + T_2^{\text{ext}} + T_3^{\text{ext}} \begin{pmatrix} ab\mathbf{C} \\ \mathbf{I}jk \end{pmatrix} + T_4^{\text{ext}} \begin{pmatrix} ab\mathbf{CD} \\ \mathbf{I}jkl \end{pmatrix}, \quad (32)$$

where the amplitudes defining T^{int} carry only active spin-orbital labels, and the amplitudes defining many-body components of T^{ext} carry at least one inactive (core or virtual) label. With this decomposition, we obtain⁵⁸

$$\Psi = e^{T^{\text{ext}}} \Phi^{\text{int}}, \quad (33)$$

where

$$\Phi^{\text{int}} = e^{T^{\text{int}}} \Phi, \quad (34)$$

is the multiconfigurational reference state satisfying the intermediate normalization $\langle \Phi^{\text{int}} | \Phi \rangle = 1$. With T^{int} defined by Eq. (31) (the CCSD tq approach), the multiconfigurational reference state Φ^{int} is practically identical or, in some cases, (if the active space contains no more than two occupied and no more than two unoccupied spatial orbitals) identical to the renormalized CAS reference state

$$\Phi_{\text{CAS}}^{\text{int}} = (1 + C^{\text{int}}) \Phi, \quad (35)$$

where

$$C^{\text{int}} = C_1^{\text{int}} + C_2^{\text{int}} + \dots + C_{N_o}^{\text{int}}, \quad (36)$$

is a FCI excitation operator within the active space. This equivalence (or approximate equivalence) of CAS and CCSD tq multiconfigurational reference states is an immediate consequence of the fact that the multiconfigurational reference state Φ^{int} characterizing the CCSD tq approach is a CCSDTQ state corresponding to excitations within the active space and for all practical purposes the CCSDTQ solution within the active space is identical to a FCI solution within the same space, which is in turn the same as the renormalized CAS reference $\Phi_{\text{CAS}}^{\text{int}}$, Eq. (35).

One might of course argue that for severe cases of multiple bond breaking, such as dissociation of N_2 , where the active space should consist of more than two occupied and more than two unoccupied spatial orbitals, one needs to include higher-than-quadruply excited connected clusters of internal type (T_5^{int} , T_6^{int} , etc.) to make the reference state (34) fully equivalent to a CAS reference state (35). In fact, this can easily be accomplished within our formalism by adding the relevant T_5^{int} , T_6^{int} , etc. cluster components to Eq. (31) (cf. Ref. 58). Since these high-order clusters would only be evaluated within the active space, their addition should not increase the cost of calculations significantly. On the other hand, methods such as CCSDT or CCSDTQ, which do not use higher-than-quadruply excited connected clusters, are capable of describing the bond breaking in N_2 and similar systems quite reasonably,⁴⁵ so that the issue of the relative importance of T_5^{int} , T_6^{int} , and other higher-order cluster components in these kinds of studies can be debated. We should keep in mind that many high-order cluster components of connected and disconnected type are included in our CCSD t and CCSD tq approaches. The T_5^{int} , T_6^{int} , etc. components are included in the recently proposed RMRCCSD method⁴² through cluster analysis of the MRCISD wave function. Unfortunately, the resulting procedure is not size extensive and this will eventually limit its applicability when larger systems are investigated. As demonstrated in this paper, we can use large active spaces in our CCSD t and CCSD tq calculations. The RMRCCSD calculations are limited to fairly small active spaces, since MRCISD calculations become prohibitively expensive when the number of active orbitals increases.

Clearly, the multiconfigurational reference state $\Phi^{\text{int}} = e^{T^{\text{int}}} \Phi$, Eq. (34), of the CCSD tq approach and its analog characterizing the CCSD $t'q'$ method discussed in Sec. II B are identical [the same Eq. (31) applies to both methods]. The only difference between both approaches lies in the definition of T^{ext} [if we assume the viewpoint based on Eqs. (31)–(34)]. In the CCSD $t'q'$ case, we would have to replace Eq. (32) by the formula

$$T^{\text{ext}} = T_1^{\text{ext}} + T_2^{\text{ext}}. \quad (37)$$

This is of course what makes the CCSD $t'q'$ and CCSD t' procedures less expensive than the corresponding CCSD tq and CCSD t approaches based on internal and semi-internal triples and quadruples. The CCSD tq approach scales as $N_o^2 N_u^2 n_o^2 n_u^4$, which should be compared to $\sim N_o^4 N_u^6 + n_o^2 n_u^4$ scaling of the CCSD $t'q'$ scheme. The CCSD t approach scales as $N_o N_u n_o^2 n_u^4$, which should be compared to $\sim N_o^3 N_u^5 + n_o^2 n_u^4$ scaling of the CCSD t' scheme. Typically, the scaling of the CCSD tq method is almost identical to the scaling of the MRCISD approach (the CCSD t method, however, is usually less expensive than MRCISD). On the other hand, neglect of semi-internal components $T_3^{\text{ext}} \begin{pmatrix} ab\mathbf{C} \\ \mathbf{I}jk \end{pmatrix}$ and $T_4^{\text{ext}} \begin{pmatrix} ab\mathbf{CD} \\ \mathbf{I}jkl \end{pmatrix}$ in Eq. (37) must worsen the accuracy of the CCSD $t'q'$ and CCSD t' schemes, compared to the CCSD tq and CCSD t approaches, respectively, if the same active space is employed in both kinds of calculations.

The CCSD t and CCSD tq approaches are a lot less expensive than their complete CCSDT and CCSDTQ analogs,

both in terms of scaling and storage requirements for cluster amplitudes. We will return to issues related to costs of CCSD t and CCSD tq calculations when we discuss the numerical results in Sec. IV.

D. CCSD t -1 scheme

We also decided to explore the possibility of combining the above selection schemes for triples and quadruples, which are based on a concept of a multidimensional active space, with simple perturbative estimates of the T_3 and T_4 contributions discussed earlier. An example of such an approach, in which perturbative and active space concepts are mixed together, would be the CCSD t -1 scheme proposed below. In this method, we solve the regular CCSD T -1 equations²⁵ (cf. also, Ref. 24) with Eq. (11) replaced by its semi-internal analog

$$T_3 \begin{pmatrix} abC \\ \mathbf{I}jk \end{pmatrix} = R_0^{(3)} \begin{pmatrix} abC \\ \mathbf{I}jk \end{pmatrix} (W_N T_2)_C. \quad (38)$$

The difference between the complete three-body resolvent $R_0^{(3)}$ and its semi-internal analog $R_0^{(3)} \begin{pmatrix} abC \\ \mathbf{I}jk \end{pmatrix}$ lies in the fact that the latter resolvent includes the summation over the internal and semi-internal triexcited configurations $\Phi_{\mathbf{I}jk}^{abC}$, whereas the former resolvent includes all triexcited configurations Φ_{ijk}^{abc} . In other words, the CCSD t -1 scheme is a CCSD T -1 analog of the complete CCSD t scheme discussed in Sec. II C. Other perturbative CCSD t and CCSD tq procedures can be proposed as well (cf. Sec. V), but in this preliminary study we only focus on the CCSD t -1 method.

The study of perturbative CCSD t and CCSD tq approaches has two purposes. First of all, we want to demonstrate that selection schemes for triples and quadruples based on the concept of an active space can be used in conjunction with any CC procedure that includes T_3 and T_4 clusters. Cluster analysis of the quasidegenerate ground-state wave functions tells us that the most important T_3 and T_4 clusters are those of the internal and semi-internal types.^{46,53} Other types of T_3 and T_4 clusters are much less important and can be safely neglected. This should be true for all CC schemes accounting for T_3 and T_4 , including those which use MBPT arguments to approximate T_3 and T_4 clusters. Second, at least some perturbative CCSD t and CCSD tq methods may prove useful in practical applications, since they offer significant CPU time savings. For example, the $n_o^3 n_u^4$ step of the CCSD T -1 approach reduces to a $N_o N_u n_o^2 n_u^3$ step in the CCSD t -1 case. In other words, the n^7 step of the CCSD T -1 procedure ($n = n_o + n_u$ is the number of molecular orbitals used in the calculation) becomes an inexpensive n^5 step if the CCSD t -1 method is employed. Thus, the scaling of the CCSD t -1 method is practically identical to the scaling of the CCSD approach. We would never be able to state anything like that if the complete CCSD T -1 approach were employed, since the CCSD T -1 procedure is significantly more expensive than the CCSD approach.

The CCSD t -1 method may become a useful alternative to the well-known CCSD T -1 approach provided that the CCSD t -1 and CCSD T -1 results are of comparable accuracy. Performance of the CCSD t -1 approach in actual calculations

is discussed in Sec. IV. Performance of other CCSD t and CCSD tq methods, which we described in Secs. II A–II C, is discussed in Sec. IV as well.

III. COMPUTATIONAL DETAILS

All methods discussed in Sec. II have been implemented by utilizing our closed-shell CCSD T and CCSD TQ programs¹⁶ (cf. also, Ref. 15) and ACES II⁶² routines. Although ACES II routines were primarily used to perform the ground-state RHF calculations and to generate the transformed one- and two-electron molecular integrals, we also took advantage of ACES II routines when converging the CC equations.

Since this is only our initial implementation of various CCSD t and CCSD tq methods, our codes do not fully utilize the spatial symmetry of the Hamiltonian. On the other hand, our codes are completely vectorized, since we fully exploit the idea of recursively generated intermediates, which are efficiently evaluated using fast matrix multiplication routines.¹⁵ Our CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, and CCSD $\{t'q'\}$ programs are, thus, as efficient as they could normally be. Implementation of the remaining CCSD t' , CCSD $t'q'$, CCSD t , CCSD tq , and CCSD t -1 methods discussed in Secs. II B–II D is less efficient at this point, even though we can already study large active spaces and use large basis sets.

In all calculations reported in this paper, we use the RHF determinant as a reference configuration. This includes cases where bonds are significantly stretched or broken, so that the RHF solution becomes triplet unstable.⁵⁰ We do not use the UHF reference, since it is our aim to prove that all CCSD t and CCSD tq methods have an ability to describe bond breaking, even if the RHF wave function is used as a reference. By using RHF orbitals, we can avoid problems associated with the use of UHF orbitals mentioned in the Introduction. The RHF-based CC approaches are also less expensive than the corresponding UHF-based CC schemes and can be adapted to all available symmetries of the Hamiltonian (including the spin symmetry).

The results reported in this paper include three systems: The H₂O molecule with both O–H bonds stretched to twice the equilibrium bond length, the C₂ molecule at the equilibrium geometry, and the entire potential energy curve for the HF molecule. The stretched H₂O molecule and C₂ are characterized by a large effect due to T_3 and a significant T_4 effect. Thus, these two systems should allow us to illustrate the effectiveness of various CCSD t and CCSD tq methods in reproducing large T_3 and T_4 contributions (by comparing the CCSD t and CCSD tq results with their complete CCSD T and CCSD TQ analogs). By comparing the results of various CCSD t and CCSD tq calculations with the available FCI results for H₂O and C₂, we should be able to test the performance of CCSD t and CCSD tq approaches in cases where quasidegeneracy of the ground electronic state is severe. The potential energy curve for HF should allow us to illustrate the effectiveness of methods discussed in this paper in describing single bond breaking.

Two different basis sets are employed to describe H₂O.

TABLE I. Correlation energies (in mE_h) for the DZP model of H_2O^a ($n_o = 4$, $n_u = 20$). The O–H bond length is fixed at twice the equilibrium value. Numbers in parentheses represent correlation energies obtained in CCSDT or CCSDTQ calculations using active orbitals only.

Method	Active space (N_o, N_u)		
	(3,3)	(3,8)	(4,8)
CCSD $\{t'\}$	–349.846 (–212.594)	–356.304 (–274.486)	–358.817 (–301.911)
CCSD $\{t\}$	–348.930 (–212.594)	–356.304 (–274.486)	–358.819 (–301.911)
CCSD t'	–348.850	–355.632	–358.020
CCSD t -1	–372.363	–372.580	–372.580
CCSD t	–372.094	–372.394	–372.394
CCSD $\{t'q'\}$	–347.003 (–209.703)	–352.957 (–271.051)	–355.427 (–298.468)
CCSD $t'q'$	–348.475	–354.798	–357.517
CCSD tq	–369.471	–369.886	–369.886
CCSD		–348.579	
CCSDT-1		–372.629	
CCSDT		–372.455	
CCSDTQ		–369.998	
FCI ^a		–369.983	

^aThe basis set, geometry, and FCI energy were taken from Ref. 63. In all correlated calculations, the lowest $1a_1$ orbital was kept frozen.

We use a DZP (double zeta plus polarization) basis set, consisting of twenty five orbitals, as described in Ref. 63, so that we can compare our results with the results of the exact FCI calculation⁶³ and with several earlier CC results, including the full CCSDT¹² and CCSDTQ¹⁶ calculations. We also use the much larger cc-pVTZ basis set of Ref. 64 consisting of fifty eight orbitals, for which a comparison could be made with the complete CCSDT result (obtained in this study). The calculations for C_2 are performed using the modified aug-cc-pVDZ basis set⁶⁵ of Ref. 66 (designated here as pVDZ+ basis set), for which the exact FCI results⁶⁶ as well as numerous CC results^{30,66,67} are available. Finally, we use a DZP basis set described in Ref. 68 (twenty orbitals) in the calculations for HF. In this case, the exact FCI energies are available for three internuclear separations, the equilibrium bond length R_e and two stretches of the H–F bond, $1.5R_e$ and $2R_e$.⁶⁸ For the remaining H–F distances studied in this work, we rely on our own CCSDT results.

IV. RESULTS

A. The DZP model of H_2O

The results for the DZP model of H_2O are summarized in Table I. Here and elsewhere in the present paper, we use a notation in which $X(N_o, N_u)$ designates the calculation performed with method X and employing an active space spanned by N_o active orbitals occupied in reference Φ and N_u active orbitals unoccupied in Φ (we assume the orbital ordering in which active orbitals occupied in Φ are the highest energy occupied orbitals and active orbitals unoccupied in Φ are the lowest energy unoccupied orbitals). For example, CCSD $\{tq\}(3,8)$ symbolizes the CCSD $\{tq\}$ calcula-

tion based on an active space spanned by the three highest energy occupied orbitals and eight lowest energy unoccupied orbitals.

When both O–H bonds in H_2O are simultaneously stretched by a factor of 2 (i.e., $R = 2R_e$, where R is the O–H bond length and R_e is the equilibrium value of R), we create a situation in which the effect due to T_3 , as measured by the difference between the CCSDT and CCSD energies, is $23.9mE_h$. Clearly, this large T_3 effect is related to a quasidegenerate (multireference) nature of the ground-state electronic wave function at $R = 2R_e$. For comparison, the T_3 contribution at the equilibrium geometry equals $3.6mE_h$. The T_4 contribution to the energy is also large when $R = 2R_e$. For the DZP model of H_2O with $R = 2R_e$, the effect due to T_4 , as obtained by forming a difference between CCSDTQ and CCSDT energies, equals $2.5mE_h$, which should be compared to $0.5mE_h$ at $R = R_e$. Higher-than-quadruply excited clusters are negligible, as a comparison of the CCSDTQ and FCI results in Table I clearly indicates. As it often (but not always) happens, the signs of T_3 and T_4 energy contributions are opposite.

The results collected in Table I show that all CCSD t and CCSD tq calculations improve the CCSD results. The most accurate description of T_3 and T_4 effects is provided by the CCSD t and CCSD tq approaches using internal as well as semi-internal tri- and tetraexcited clusters (cf. Sec. II C). In this case, it is sufficient to use a small active space, $(N_o, N_u) = (3,3)$, which is more or less equivalent to a valence shell of H_2O . The active space (3,3) consists of the three highest energy occupied orbitals ($1b_2$, $1b_1$, and $3a_1$ orbitals if the C_{2v} symmetry is employed; the ordering of molecular orbitals in the RHF configuration is $|(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2(3a_1)^2|$) and the three lowest energy unoccupied orbitals ($2b_1$, $2b_2$, and $4a_1$). Indeed, the difference between the full CCSDT and CCSD $t(3,3)$ energies is less than $0.4mE_h$ and the difference between full CCSDTQ and CCSD $tq(3,3)$ energies is only $0.5mE_h$. When larger active spaces are employed, the full CCSDT and CCSD t energies become virtually identical. For example, the difference between CCSDT and CCSD $t(3,8)$ energies equals $0.061mE_h$. The same observation applies to the CCSD tq approach. The difference between CCSDTQ and CCSD $tq(3,8)$ energies is only $0.112mE_h$. None of the other methods provides results which are as good as the CCSD t and CCSD tq ones. The choice of eight active orbitals from the total number of twenty unoccupied orbitals in the examples presented in Table I is justified by the orbital energy spacings, which increase to almost $370mE_h$ for the energies of the eighth and ninth unoccupied orbitals.

The remarkably good performance of the CCSD t and CCSD tq approaches observed for the DZP model of H_2O at $R = 2R_e$ is certainly very promising from the point of view of potential applications of these methods, since the cost of each CCSD t or CCSD tq calculation is comparable to the cost of a standard MRCISD calculation employing the same active space (in fact, the CCSD t calculations are less expensive than the corresponding MRCISD calculations). A similar behavior of the CCSD t and CCSD tq approaches in calculations for H_2O was observed earlier,⁵⁷ even though the

authors of Ref. 57 tested only a small DZ basis set and active spaces consisting of at most two active orbitals of occupied and unoccupied types. Here, we can consider relatively large active spaces, although the CCSD t and CCSD tq methods are capable of providing excellent results even when small active spaces are employed.

Interestingly enough, inclusion of perturbative internal and semi-internal triples in the CC approach, as is done in the CCSD t -1 scheme [cf. Sec. IID, Eq. (38)], gives remarkably good results. Part of this success can be attributed to the fact that the CCSDT-1 method itself provides a very good estimate of the T_3 effect at $R=2R_e$. For this geometry, the difference between CCSDT and CCSDT-1 energies is only $0.174mE_h$ (cf. Table I). It should be noticed, however, that the CCSDT-1 method slightly overestimates the T_3 contribution. This should be regarded as the first sign of the breakdown of the perturbative description of T_3 effects at larger internuclear distances. For larger stretches of the O–H bonds ($R>2R_e$), the CCSDT-1 method using RHF orbitals would fail altogether.

Although the CCSDT-1 method must eventually fail at large internuclear distances, the CCSD t -1 results presented in Table I are most encouraging. The CCSD t -1 and CCSDT-1 energies are practically identical, even when a small active space, such as (3,3), is employed. The difference between CCSDT-1 and CCSD t -1(3,3) energies for the DZP model of H₂O at $R=2R_e$ is only $0.266mE_h$. This indicates that we can reproduce the CCSDT-1 results by considering the internal and semi-internal perturbative triples only. As explained in Sec. IID, the cost of the CCSD t -1 calculation is small when compared with the full CCSDT-1 calculation. In the CCSD t -1 method, the n^7 step of the CCSDT-1 approach is replaced by an inexpensive n^5 step, so that the CCSD t -1 approach is as inexpensive as the standard CCSD method. It is interesting to see that we do not have to compromise the accuracy of the CCSDT-1 approach by switching to its CCSD t -1 analog.

The results in Table I indicate that the CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, CCSD $\{t'q'\}$, CCSD t' , and CCSD $t'q'$ methods using internal T_3 and T_4 clusters only provide worse results than the CCSD t and CCSD tq approaches using internal as well as semi-internal triples and quadruples, if identical active spaces are employed. For example, the negligible $0.061mE_h$ error in describing the T_3 effect, obtained when the CCSD t (3,8) method is employed, increases to $16.151mE_h$ when the CCSD $\{t'\}$ (3,8) approach is used (the total T_3 effect equals $23.9mE_h$). On the other hand, it is very easy to improve the CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, CCSD $\{t'q'\}$, CCSD t' , and CCSD $t'q'$ results by employing larger active spaces. For example, the $16.151mE_h$ error in describing the T_3 effect, obtained when the CCSD $\{t'\}$ (3,8) method is employed, reduces to $13.638mE_h$ when the CCSD $\{t'\}$ (4,8) calculation is performed. A similar observation applies to the CCSD $\{t'q'\}$ scheme. The difference between the CCSDTQ and CCSD $\{t'q'\}$ (4,8) energies is $14.571mE_h$, which should be compared to $21.419mE_h$ representing the total T_3 plus T_4 effect. For comparison, if the smaller (3,8) active space is employed, the difference between the CCSDTQ and

CCSD $\{t'q'\}$ energies increases to $17.041mE_h$.

There seems to be a correlation between the quality of the CCSD $\{t'\}$ and CCSD $\{t'q'\}$ results and the fraction of the correlation energy reproduced in Step 1 of these calculations, in which we solve the CCSDT or CCSDTQ equations using active orbitals only. For example, the fraction of the T_3 contribution to the energy reproduced in various CCSD $\{t'\}$ calculations, which we carried out for the DZP model of H₂O at $R=2R_e$, increases from 5.3%, obtained when the (3,3) active space is employed, to 32.4% and 42.9%, respectively, obtained when the CCSD $\{t'\}$ (3,8) and CCSD $\{t'\}$ (4,8) calculations are performed. For comparison, the CCSDT calculations using the (3,3), (3,8), and (4,8) orbital spaces give 57.5%, 74.2%, and 81.6% of the FCI correlation energy, respectively. This would indicate that an active space employed in the CCSD $\{t'\}$ and CCSD $\{t'q'\}$ calculations should be large enough to enable us to reproduce more than 70%–80% of the total correlation energy in the preliminary CCSDT or CCSDTQ calculations using active orbitals only, if we want the CCSD $\{t'\}$ and CCSD $\{t'q'\}$ approaches to reproduce a significant portion of the T_3 and T_4 contributions.

There is practically no difference between the CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' results on the one hand and the CCSD $\{tq\}$, CCSD $\{t'q'\}$, and CCSD $t'q'$ results on the other. The fact that there is no difference between the CCSD $\{t\}$ and CCSD $\{t'\}$ or CCSD $\{tq\}$ and CCSD $\{t'q'\}$ energies would imply that it is not important how we treat the T_1T_3 contribution to Eq. (13). In principle, we should only extract the T_3 and T_4 clusters from the CCSDT or CCSDTQ calculations using active orbitals and iterate the T_1 cluster component entering the T_1T_3 contribution to Eq. (13) in the same way as we iterate the remaining T_1 and T_2 components. This is what we do in the CCSD $\{t\}$ and CCSD $\{tq\}$ approaches. It seems, however, that we can be less rigorous. We can simply pull out the entire T_1T_3 term entering Eq. (6) (along with the corresponding T_3 and T_4 contributions) from the CCSDT or CCSDTQ calculations in the active space. The resulting CCSD $\{t'\}$ and CCSD $\{t'q'\}$ approaches are significantly simpler (we only have to extract the $\langle\Phi_{\text{IT}}^{\text{AB}}|[H_N(\mathbf{t}_3^{(0)}+\mathbf{t}_1^{(0)}\mathbf{t}_3^{(0)}+\mathbf{t}_4^{(0)})]_C|\Phi\rangle$ term from the CCSDT or CCSDTQ calculations in the active space and modify the equations of the final CCSD calculation accordingly without even storing the $t_{\text{ABC}}^{\text{IJK}}$ and $t_{\text{ABCD}}^{\text{IJKL}}$ amplitudes) and yet, as Table I shows, they yield results which are almost identical to the CCSD $\{t\}$ and CCSD $\{tq\}$ ones. It also seems that there is no need to iterate the internal T_3 and T_4 components with all singly and doubly excited cluster amplitudes, as Eqs. (18)–(21) of the CCSD t' and CCSD $t'q'$ approaches require. The CCSD t' and CCSD $t'q'$ results are of the same quality as the CCSD $\{t\}$ and CCSD $\{tq\}$ or CCSD $\{t'\}$ and CCSD $\{t'q'\}$ ones. Thus, it is totally sufficient to extract the internal T_3 and T_4 components from the CCSDT or CCSDTQ solution using active orbitals only in these types of calculations. The simplest CCSD $\{t'\}$ and CCSD $\{t'q'\}$ approaches seem to represent the optimum computational strategy if we do not want to use the semi-internal T_3 and T_4 components of the complete CCSD t and CCSD tq schemes.

The results in Table I indicate that the efficiency of the

CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, and CCSD $\{t'q'\}$ methods in estimating the T_3 and T_4 effects is comparable to the efficiency of the CASSCF-corrected CCSD approach advocated in Refs. 39–41. For example, the authors of Ref. 41 could not reduce the $12.699mE_h$ error in the CCSD result for the DZP model of OH at $R=2R_e$ (the ground state of OH is $^2\Pi$) by more than $3-5mE_h$ using their CASSCF-corrected CCSD scheme. The only case where the reduction was somewhat larger (error relative to FCI of $5.115mE_h$ or 40% of the difference between CCSD and FCI results) was a calculation employing seven active electrons [all electrons in OH except for two electrons that occupy the O($1s$) core] and six unoccupied orbitals in the active space, which is 37.5% of the total number of unoccupied orbitals (the total number of unoccupied orbitals is sixteen in this case). Our results for H₂O (and other results discussed in this paper) seem to be consistent with this observation. For the DZP model of H₂O with $R=2R_e$, we can easily reduce the $21.404mE_h$ error in the CCSD result relative to FCI by 30%–50% by using our CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, and CCSD $\{t'q'\}$ methods and by including 40% of all unoccupied orbitals ($N_u=8$) in the active space. A better description of the T_3 and T_4 effects by the CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, and CCSD $\{t'q'\}$ methods can only be obtained if larger active spaces are employed. This implies that internal T_3 and T_4 cluster components used in the CASSCF-corrected CCSD approach and in our CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, and CCSD $\{t'q'\}$ methods can only be used to describe a portion of the total T_3 and T_4 effects. Neither our CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, and CCSD $\{t'q'\}$ approaches nor the CASSCF-corrected CCSD approach of Refs. 39–41 can describe the important T_3 and T_4 components of the semi-internal type. These can only be described by the CCSD t and CCSD tq methods of Sec. II C and, somewhat less efficiently (although quite accurately) by the MRCISD-corrected CCSD method of Ref. 42 (referred to as the RMRCCSD approach). We must remember, however, that the latter method steps outside the CC structure and is not size extensive, which should worsen the performance of the RMRCCSD method for large systems.

Using any kind of orbitals from a multireference wave function in a SRCC approach is counterproductive, since multireference wave functions emphasize other configurations than the reference function. In particular, the use of CASSCF orbitals in the CASSCF-corrected CCSD calculations of Refs. 39–41 is of no significance for the quality of the results, as the authors of Ref. 41 indicate. In other words, in CASSCF-corrected CCSD calculations it is sufficient to use the RHF [or restricted open-shell Hartree–Fock (ROHF)] orbitals and extract T_3 and T_4 clusters from the FCI calculation within the active space defined in terms of RHF (or ROHF) orbitals. The same is observed in our CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, and CCSD $\{t'q'\}$ calculations, in which instead of performing FCI calculations within the active space and analyzing the cluster structure of the resulting wave function, we extract T_3 and T_4 clusters directly from the less expensive CCSDT or CCSDTQ calculations, which we also perform in the active space (clearly, the use of CCSDT and CCSDTQ methods instead of FCI allows us to

TABLE II. Correlation energies (in mE_h) for the cc-pVTZ model of H₂O^a ($n_o=4$, $n_u=53$). The O–H bond length is set to twice the experimental equilibrium value [$R(\text{O–H})=1.94 \text{ \AA}$, $\angle(\text{H–O–H})=106^\circ$]. Numbers in parentheses represent correlation energies obtained in CCSDT or CCSDTQ calculations using active orbitals only.

Method	Active space (N_o, N_u)			
	(3,3)	(3,14)	(4,14)	(4,20)
CCSD $\{t'\}$	–379.414 (–170.750)	–384.520 (–247.434)	–387.495 (–278.614)	–394.897 (–326.614)
CCSD $\{t\}$	–378.842 (–170.750)	–384.482 (–247.434)	–387.310 (–278.614)	–394.767 (–326.614)
CCSD t'	–378.725	–383.732	–386.133	–393.967
CCSD $t-1$	–404.872	–407.277	–407.277	–407.604
CCSD t	–404.505	–406.806	–406.806	–407.121
CCSD		–378.541		
CCSDT-1		–407.748		
CCSDT		–407.232		

^aThe basis set was taken from Ref. 64. In all correlated calculations, the lowest $1a_1$ orbital was kept frozen.

study large active spaces; the CASSCF-corrected CCSD method^{39–41} becomes very expensive if larger active spaces are employed). In fact, to further elaborate on this issue, we tried to use CASSCF orbitals in our CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, and CCSD $\{t'q'\}$ calculations. Following the prescription described in Refs. 39–41, we defined the reference configuration Φ as the dominant configuration in the CASSCF wave function (we used GAMESS⁶⁹ to generate the CASSCF solution). The results for the DZP model of H₂O discussed here barely changed compared to calculations employing RHF orbitals (independently of the active space employed, the energies never changed by more than a fraction of a milihartree). The fact that nothing can be gained in our calculations by using CASSCF orbitals is an immediate consequence of the presence of T_1 components in the cluster operator T , plus the undue emphasis of other configurations in the wave function. It is well-known that T_1 clusters make various approximate CC methods including T_1 almost insensitive to orbital rotations, even if mixing of occupied and unoccupied orbitals is involved.^{3(c)} This “numerical insensitivity” of CC theory applies, in particular, to our CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, and CCSD $\{t'q'\}$ schemes. The insensitivity of the CCSD t and CCSD tq approaches employing internal as well as semi-internal triples and quadruples with respect to CASSCF orbital rotations has been demonstrated in Ref. 54. As suspected above, CASSCF orbitals are actually a handicap, as their use in CC calculations makes it more difficult to converge the CC equations due to relatively large T_1 components, which in the RHF case they do not contribute to the first-order MBPT wave function.

Next, we report results obtained with larger, cc-pVTZ basis.

B. The cc-pVTZ model of H₂O

The results for the cc-pVTZ model of H₂O with $R=2R_e$ are given in Table II. Since no FCI result is available in this case, and since and it would be rather difficult to

obtain the full CCSDTQ result for a basis set of cc-pVTZ quality, we decided to focus on the effectiveness of various approaches in describing the T_3 effect.

Typically, the magnitude of the T_3 effect increases when the size of the basis set increases. This is what we observe for the cc-pVTZ model of H_2O at $R=2R_e$. In this case, the effect due to T_3 , as measured by forming a difference between CCSDT and CCSD energies, equals $28.7mE_h$, which should be compared to $23.9mE_h$ characterizing the DZP model of H_2O with the same geometry. It is interesting to see how various CCSDT approaches describe the T_3 effect which is so large.

Let us first discuss the performance of the CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' approaches, in which we consider internal T_3 components only. As in the DZP model of H_2O , there seems to be a correlation between the quality of the CCSD $\{t\}$ and CCSD $\{t'\}$ results and the fraction of the correlation energy reproduced in the CCSDT calculation employing active orbitals only. Clearly, the small active spaces, such as (3,3), are too small to provide us with a good estimate of the T_3 effect. The CCSDT calculation using three occupied and three unoccupied active orbitals gives only 41.9% of the total CCSDT correlation energy obtained with all orbitals. This is too little to provide us with a great deal of information about T_3 components. The situation dramatically changes when we use larger active spaces, such as (4,20). In this case, the CCSDT calculation based on active orbitals reproduces 80.2% of the correlation energy obtained using the CCSDT approach and all orbitals. In consequence, the $28.7mE_h$ difference between the CCSDT and CCSD energies reduces to a difference of $12.3mE_h$ between the CCSDT and the CCSD $\{t'\}$ (4,20) energies. This means that the CCSD $\{t'\}$ (4,20) calculation reproduces almost 60% of the total T_3 contribution to the correlation energy, which is a very good result, particularly if we realize that the total cost of the CCSD $\{t'\}$ (4,20) calculation is still comparable to the cost of the CCSD calculation (examples of timings are discussed in Sec. IV C). Although an active space containing twenty unoccupied orbitals seems to be very large (the total number of unoccupied orbitals equals fifty three), the $n_o^3 n_u^5$ scaling of the CCSDT approach (used only in Step 1 of the CCSD $\{t\}$ and CCSD $\{t'\}$ procedures) makes the initial CCSDT calculation employing four occupied orbitals and twenty unoccupied orbitals many times less expensive than the CCSDT calculation in the full orbital space. It would certainly be very difficult to perform the CASSCF-corrected CCSD calculation using an active space consisting of four occupied and twenty unoccupied orbitals, since the FCI problem using four occupied and twenty unoccupied orbitals is already extremely demanding. Indeed, the FCI calculation in an active space of this size would be identical to a FCI calculation for the DZP model of H_2O , in which case one needs to consider 6 740 280 spin and symmetry adapted configuration state functions (CSFs) or 28 233 466 determinants;⁶³ the CCSDT calculation in the same orbital space, which constitutes Step 1 of CCSD $\{t\}$ and CCSD $\{t'\}$ calculations, requires as little as 15 520 CSFs and the corresponding CCSDTQ calculation would need 151 248 CSFs, which is only 2% of the total number of CSFs defining the

FCI problem. In consequence, it would be rather difficult (and certainly very expensive) to reproduce 50%–60% of the total T_3 effect characterizing the cc-pVTZ model of H_2O at $R=2R_e$ using the CASSCF-corrected CCSD scheme of Refs. 39–41. We have no problem whatsoever with performing our CCSD $\{t\}$ (4,20) and CCSD $\{t'\}$ (4,20) calculations, which reproduce 60% of the T_3 contribution to the energy. One might argue, of course, that the CCSDT-1 approach is a better solution in this case, since the difference between the CCSDT-1 and CCSDT energies is only $0.5mE_h$, but we must remember that the CCSDT-1 method will eventually fail when the O–H bonds are broken (the CCSDT-1 approach overestimates the magnitude of the T_3 effect already for $R=2R_e$). As we demonstrate in Sec. IV D, the CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' procedures describe the bond breaking process correctly, since they account for most of the nondynamic correlation effects through inclusion of internal T_3 components.

As observed in the calculations for the DZP model of H_2O , all three CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' methods provide results which are virtually identical. For this reason, the simplest CCSD $\{t'\}$ approach, in which we add the entire $\langle \Phi_{\text{tr}}^{\text{AB}} | [H_N(\mathbf{t}_3^{(0)} + \mathbf{t}_1^{(0)} \mathbf{t}_3^{(0)})]_C | \Phi \rangle$ term obtained in the CCSDT calculation within the active space to the CCSD equations projected on internal double excitations and correct the CCSD equations projected on singles by adding the $\langle \Phi_i^a | (H_N \mathbf{t}_3^{(0)})_C | \Phi \rangle$ term, represents the best and the most efficient way of incorporating the internal T_3 components. On the other hand, as mentioned earlier, it might be easier to develop analytic derivatives within the CCSD t' scheme, in which internal T_3 components are iterated with all T_1 and T_2 clusters.

The best results for the cc-pVTZ model of H_2O are provided by the CCSD t method including internal as well as semi-internal triexcited clusters. We must emphasize that the present CCSD t calculations for the cc-pVTZ model of H_2O are the first calculations of this kind for a fairly large basis set and active spaces containing as many as twenty unoccupied orbitals in the active block. The CCSD t results listed in Table II look very promising. As in the DZP case, it is entirely sufficient if we use the minimum active space corresponding to a valence shell of H_2O . Indeed, the difference between the CCSD t (3,3) and CCSDT energies is only $2.727mE_h$, which is less than 10% of the total T_3 effect. When larger active spaces are employed, the CCSD t and CCSDT energies become virtually identical. For example, the error in the CCSD t (3,14) result relative to the CCSDT energy is only $0.426mE_h$ and there is a negligible, $0.111mE_h$ difference between the CCSD t (4,20) and CCSDT energies.

It is important to realize that the CCSD t approach offers a tremendous savings in computer effort compared to the full CCSDT method. The $n_o^3 n_u^5$ scaling of the full CCSDT method reduces to $N_o N_u n_o^2 n_u^4$, when the CCSD t approach is employed, and the number of T_3 cluster amplitudes that are considered in the CCSD t scheme is very small compared to a complete CCSDT problem. For example, the number of all t_{abc}^{ijk} amplitudes for the cc-pVTZ model of H_2O is $\sim 2\,400\,000$ (assuming the nonorthogonally spin-adapted or spin-free description and making no use of the spatial sym-

TABLE III. Correlation energies (in mE_h) for the pVDZ+ model of C_2^a ($n_o=4$, $n_u=30$). The equilibrium internuclear distance of $2.348 a_0$ is assumed throughout. Numbers in parentheses represent correlation energies obtained in CCSDT or CCSDTQ calculations using active orbitals only.

Method	Active space (N_o, N_u)				
	(2,4)	(4,4)	(2,12)	(4,12)	(4,19)
CCSD{ t' }	-312.648 (-15.822)	-313.584 (-78.436)	-312.738 (-60.226)	-317.438 (-180.782)	-328.826 (-261.543)
CCSD{ t }	-312.648 (-15.822)	-313.558 (-78.436)	-312.758 (-60.226)	-317.346 (-180.782)	-328.924 (-261.543)
CCSD t'	-312.648	-313.165	-312.732	-316.246	-327.323
CCSD t -1	-331.525	-333.049	-338.424	-340.081	-341.438
CCSD t	-330.099	-331.578	-336.033	-337.654	-338.861
CCSD{ $t'q'$ }	-312.658 (-15.862)	-313.806 (-78.727)	-313.208 (-61.023)	-319.792 (-183.395)	-330.728 (-263.529)
CCSD $t'q'$	-312.652	-313.370	-312.934	-318.968	-329.911
CCSD tq	-331.515	-333.206	-338.153	-340.026	-341.456
CCSD		-312.648			
CCSDT-1		-341.554			
CCSDT		-338.972			
CCSDTQ		-341.623			
FCI ^a		-342.245			

^aThe basis set, geometry, and FCI energy were taken from Ref. 66. The pVDZ+ basis set used here and in Ref. 66 was obtained by eliminating diffuse d functions from the aug-cc-pVDZ basis set of Ref. 65. In all correlated calculations, the lowest two orbitals, $1\sigma_g$ and $1\sigma_u$, were kept frozen.

metry of the Hamiltonian). The number of spin-free t_{abc}^{ijk} amplitudes characterizing the CCSD t (3,3) calculation is only 382 032 (if we do not take into account the spatial symmetry of the Hamiltonian). It is, therefore, remarkable that with 16% of all t_{abc}^{ijk} coefficients we can reproduce more than 90% of the total T_3 effect. Clearly, the CCSD{ t }, CCSD{ t' }, and CCSD t' approaches including the internal T_3 components only use even smaller numbers of t_{abc}^{ijk} amplitudes. The number of all t_{ABC}^{IJK} coefficients (assuming again the spin-free description and no symmetry) characterizing the CCSD{ t }, CCSD{ t' }, and CCSD t' calculations based on the active space containing four occupied and fourteen unoccupied orbitals is as little as $\sim 44\,000$. The CCSD{ t }, CCSD{ t' }, and CCSD t' approaches based on the active space containing four occupied and twenty unoccupied orbitals need as little as 128 000 spin-free t_{ABC}^{IJK} coefficients, which is 5% of all t_{abc}^{ijk} amplitudes. With these very few t_{ABC}^{IJK} coefficients, the CCSD{ t }, CCSD{ t' }, and CCSD t' approaches reproduce $\sim 60\%$ of the entire T_3 effect without risking the failure associated with the use of perturbative approximations. This is certainly encouraging.

As in the DZP case, the CCSD t -1 method, which uses inexpensive n^5 steps in the calculation of perturbative T_3 component, is capable of reproducing the complete CCSDT-1 result. The difference between CCSD t -1(3,3) and CCSDT-1 energies is only $2.876mE_h$ and for larger active spaces the CCSD t -1 and CCSDT-1 energies become virtually identical (differences between CCSD t -1 and CCSDT-1 energies are less than $0.5mE_h$).

C. The pVDZ+ model of C_2

The results for the pVDZ+ model of C_2 are collected in Table III. The C_2 molecule is known to represent a very

challenging system. The correlation effects in C_2 are largely nondynamic already at the equilibrium geometry ($R=R_e$). The quasidegenerate nature of the electronic ground state of C_2 at $R=R_e$ is reflected by large T_3 and T_4 contributions to the energy, which are 26.3 and $2.7mE_h$, respectively, when the pVDZ+ basis set of Ref. 66 is employed (cf. Table III). Higher-than-quadruply excited clusters play a much smaller role, even though the $0.6mE_h$ difference between the CCSDTQ and FCI energies is larger than a similar energy difference characterizing the DZP model of H_2O with $R=2R_e$. Another difference with the stretched water molecule is the fact that both T_3 and T_4 components lower the energy (the signs of T_3 and T_4 energy contributions are opposite in the H_2O case).

The advantage of studying the pVDZ+ model of C_2 is the availability of the FCI,⁶⁶ CCSDT,^{30,67} and CCSDTQ^{30,67} energies, which are important if we want to analyze the performance of various CCSD t and CCSD tq methods. Before we begin our discussion, a few words should be mentioned about possible choices of active spaces for CCSD t and CCSD tq calculations.

The RHF solution for the $R=R_e$ C_2 molecule has a somewhat unusual orbital structure. The energy ordering of the RHF orbital symmetry species (according to irreducible representations of the $D_{\infty h}$ point group) is as follows:

$$\Phi = |(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2(2\pi_u)^2| \times (3\sigma_g)^0(3\sigma_u)^0(1\pi_g)^0(2\pi_g)^0 \dots \quad (39)$$

There is a small energy difference between the highest occupied molecular orbital, $1\pi_u$, which correlates with a $2p$ shell of the carbon atom, and the $2\sigma_u$ orbital, which correlates with a $2s$ shell of C ($0.06E_h$ if the pVDZ+ basis set is

employed; this energy difference should be compared to $0.55E_h$ difference between energies of $2\sigma_g$ and $2\sigma_u$ orbitals). The significant lowering of the energies of $1\pi_u$ and $2\pi_u$ orbitals causes C_2 to sometimes be regarded as a triple-bond species. Formally, however, the C_2 molecule is a double-bond species, so we decided to see if we can obtain any information about T_3 and T_4 effects by using active spaces containing only two occupied orbitals (the $1\pi_u$ and $2\pi_u$ orbitals). Clearly, a much better choice is offered if all four occupied orbitals corresponding to valence shells of carbon atoms, i.e., $2\sigma_g$, $2\sigma_u$, $1\pi_u$, and $2\pi_u$, are included in the active space. Both choices ($N_o=2$ and 4) are considered in this study. The smallest N_u value which makes chemical sense is 4 . This value of N_u corresponds to a situation in which all four unoccupied orbitals, which correlate with valence shells of both carbon atoms, i.e., $3\sigma_g$, $3\sigma_u$, $1\pi_g$, and $2\pi_g$, are included in the active space. We could try to use smaller values of N_u , since the lowest unoccupied molecular orbital ($3\sigma_g$) is separated from the next $3\sigma_u$ valence orbital by $0.19E_h$ (which should be compared to $0.03E_h$ difference between energies of $3\sigma_u$ and $1,2\pi_g$ orbitals), but we have *not* done anything like that since all unoccupied valence orbitals have fairly close energies. Along with $N_u=4$, we also consider two other cases, $N_u=12$ and $N_u=19$. The $N_u=12$ case corresponds to adding the entire ($3s,3p$) shell of each carbon atom to the active space. The choice $N_u=19$ is justified by a rather large energy difference between the nineteenth and twentieth unoccupied orbitals ($0.17E_h$) and the fact that the twentieth unoccupied orbital is the lowest δ orbital in the pVDZ+ basis set, which we do not want to include in our calculation. The total number of unoccupied orbitals is thirty, so that the $N_u=19$ case corresponds to inclusion of 63% of the unoccupied orbitals in the active space.

Let us begin our discussion with the smallest active space, $(N_o, N_u)=(2,4)$. In this case, the CCSD $\{t'\}$, CCSD $\{t\}$, and CCSD t' methods give energies which are identical to the CCSD energy. This is a consequence of the fact that none of the t_{ABC}^{JK} amplitudes corresponding to $(N_o, N_u)=(2,4)$ is totally symmetric. As a result, there is no internal T_3 contribution to the ground-state problem if the active space consists of $1\pi_u$ and $2\pi_u$ occupied orbitals and $3\sigma_g$, $3\sigma_u$, $1\pi_g$, and $2\pi_g$ unoccupied orbitals. In fact, there are very few totally symmetric t_{ABCD}^{JKL} amplitudes in this case, so that there is only a very small, $0.01mE_h$ or less, difference between the CCSD $\{t'q'\}(2,4)$ and CCSD $t'q'(2,4)$ energies and the energy obtained in the CCSD calculation. Clearly, we cannot rely on the CCSD $\{t'\}$, CCSD $\{t\}$, CCSD t' , CCSD $\{t'q'\}$, CCSD $\{tq\}$, and CCSD $t'q'$ methods, which include only internal T_3 and T_4 components, if the active space is too small to support rich tri- and tetraexcited manifolds. In fact, the symmetry of the C_2 molecule is so high that we cannot introduce many t_{ABC}^{JK} and t_{ABCD}^{JKL} amplitudes if we continue to use active spaces with $N_o=2$. Indeed, the CCSD $\{t'\}$, CCSD $\{t\}$, CCSD t' , CCSD $\{t'q'\}$, CCSD $\{tq\}$, and CCSD $t'q'$ methods using $(N_o, N_u)=(2,12)$ give us practically no information about the T_3 and T_4 clusters. In fact, both active spaces with $N_o=2$ [$(N_o, N_u)=(2,4)$ and $(N_o, N_u)=(2,12)$] are so small that we cannot even describe a significant portion of the correlation energy by performing

the CCSDT or CCSDTQ calculations in these spaces. The CCSDT and CCSDTQ calculations using two occupied and four unoccupied orbitals reproduce only 5% of the FCI correlation energy. A somewhat larger portion of the correlation energy is reproduced if the CCSDT and CCSDTQ calculations use two occupied and twelve unoccupied orbitals (18% of the FCI correlation energy is reproduced in this case), but then practically no information about T_3 components and little information about T_4 components result from such calculations. Indeed, the CCSDT and CCSDTQ correlation energies obtained using two occupied and twelve unoccupied orbitals are -60.226 and $-61.023mE_h$, respectively (cf. Table III). The corresponding CCSD energy obtained using the same orbital space is $-59.966mE_h$. Our CCSD $\{t'\}$, CCSD $\{t\}$, CCSD t' , CCSD $\{t'q'\}$, CCSD $\{tq\}$, and CCSD $t'q'$ results corresponding to $(N_o, N_u)=(2,4)$ and $(2,12)$ imply that it is very likely that almost no information about T_3 and T_4 components would be provided by the CASSCF-corrected CCSD calculations using these particular values of N_o and N_u .

The situation changes dramatically when we include semi-internal T_3 and T_4 components in the calculations. In spite of the fact that for $N_o=2$ the internal triexcited component, T_3^{int} , vanishes or is almost zero, the CCSD $t(2,4)$ and CCSD $t(2,12)$ approaches reproduce most of the T_3 effect [66% and 89%, respectively; these percentages were obtained by forming the ratios of the following energy differences, CCSD $t(N_o, N_u)$ –CCSD and CCSDT–CCSD, for $(N_o, N_u)=(2,4), (2,12)$]. The CCSD $tq(2,4)$ and CCSD $tq(2,12)$ calculations reproduce most of the T_4 effect [53% and 80%, respectively; these percentages were obtained by forming the ratios of the following energy differences, CCSD $tq(N_o, N_u)$ –CCSD $t(N_o, N_u)$ and CCSDTQ–CCSDT, for $(N_o, N_u)=(2,4), (2,12)$]. As a result, there is good agreement between the CCSD $t(2,4)$, CCSD $t(2,12)$, CCSD $tq(2,4)$, and CCSD $tq(2,12)$ energies and FCI results. The errors in the calculated CCSD $t(2,4)$, CCSD $t(2,12)$, CCSD $tq(2,4)$, and CCSD $tq(2,12)$ energies, relative to FCI, are 12.146 , 6.212 , 10.730 , and $4.092mE_h$, respectively. This should be compared to 29.597 , 3.273 , and $0.622mE_h$ errors obtained with the CCSD, CCSDT, and CCSDTQ methods, respectively. Excellent performance of CCSD t and CCSD tq methods employing small active spaces and the poor performance of the CCSD $\{t'\}$, CCSD $\{t\}$, CCSD t' , CCSD $\{t'q'\}$, CCSD $\{tq\}$, and CCSD $t'q'$ methods employing small active spaces indicates that semi-internal triples and quadruples are the *dominant* types of T_3 and T_4 clusters. This makes a lot of sense in view of the quasidegenerate nature of the ground state of C_2 .

The fact that the CCSD t and CCSD tq methods employing internal and semi-internal T_3 and T_4 clusters and small active spaces are capable of providing good results for C_2 agrees with the earlier SSCSD(T) and SSCSD(TQ) calculations for this molecule using a DZ basis set and active spaces consisting of two or three occupied and two or three unoccupied orbitals.⁵⁶ The results presented in Table III indicate that very good CCSD t and CCSD tq energies can also be obtained when a basis set is significantly larger, which is an important finding since larger basis sets enhance the role

of T_3 and T_4 clusters, making their description somewhat more difficult.

As expected, the performance of the CCSD t and CCSD tq methods including internal as well as semi-internal triples and quadruples can be further improved by employing larger active spaces. For example, the energy resulting from the largest CCSD t calculation reported in this paper, in which we included four occupied and nineteen unoccupied orbitals, is virtually identical with the CCSDT energy (the difference between both energies is $\sim 0.1mE_h$). A similar observation applies to the largest CCSD tq calculation reported here [the CCSD $tq(4,19)$ calculation]. The CCSD $t(4,12)$ and CCSD $tq(4,12)$ results are excellent as well [the corresponding differences between CCSD $t(4,12)$ and CCSD $tq(4,12)$ energies and their CCSDT and CCSDTQ analogs are 1.318 and $1.597mE_h$, respectively]. The CCSD $t(4,12)$ and CCSD $tq(4,12)$ calculations reproduce 95% and 89% of T_3 and T_4 effects, respectively.

As in the case of H₂O, the CCSD t -1 method using perturbative internal and semi-internal triples can be regarded as a reasonable alternative to a more complete and thus significantly more expensive CCSDT-1 approach. Indeed, the CCSD t -1(4,12) and CCSD t -1(4,19) energies are practically identical to the CCSDT-1 energy, which is impressive since the CCSD t -1(4,12) and CCSD t -1(4,19) calculations do not use the n^7 steps of the CCSDT-1 procedure. In fact, the relationship between CCSDT-1 and CCSD t -1 results is very similar to the relationship between full CCSDT and CCSD t results. For example, the difference between CCSD t -1(4,12) and CCSDT-1 energies is $1.473mE_h$, which should be compared to the $1.318mE_h$ difference between CCSD $t(4,12)$ and CCSDT energies. For smaller active spaces, such as (2,4), we obtain $10.029mE_h$ for the difference between CCSD t -1(2,4) and CCSDT-1 energies and $8.873mE_h$ for the difference between CCSD $t(2,4)$ and CCSDT energies. This confirms our earlier observation that T_3 clusters are largely semi-internal in nature. Our CCSD t -1 results clearly demonstrate that the semi-internal nature of T_3 components is preserved at the CCSDT-1 level.

Let us now turn our attention to the CCSD t and CCSD tq calculations employing large active spaces and internal T_3 and T_4 components only. As the results in Table III clearly indicate, in the CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, CCSD $\{t'q'\}$, CCSD t' , and CCSD $t'q'$ calculations for C₂, the use of larger active spaces is a necessity, at least as long as we insist upon RHF virtual orbitals. Various kinds of frozen natural or improved virtual orbitals⁷⁰⁻⁷² may offer improvements in CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, CCSD $\{t'q'\}$, CCSD t' , and CCSD $t'q'$ results and we plan to return to this issue in future publications.

We cannot obtain a great deal of information about T_3 and T_4 components if the CCSDT or CCSDTQ calculations using active orbitals only do not reproduce a significant portion of the FCI correlation energy. In case of C₂, very good CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, CCSD $\{t'q'\}$, CCSD t' , and CCSD $t'q'$ results are obtained only if $N_o=4$ and $N_u=19$. In this case, the CCSDT and CCSDTQ calculations using four occupied and nineteen unoccupied orbitals reproduce 76% and 77% of the FCI correlation energy, respec-

TABLE IV. CPU timings for some CC calculations performed for the C₂ molecule. Except for the CCSDT calculation, the convergence threshold for the energy was set to $10^{-11}E_h$. The convergence threshold for the CCSDT calculation was set to $10^{-7}E_h$. All calculations were performed on IBM R6000 model 590 assuming C₁ symmetry.

Method	CPU time (s)
CCSD	167
CCSD $\{t'\}$ (4,12)	219
CCSD $\{t'\}$ (4,19)	415
CCSDT-1	513
CCSDT	1869

tively. In consequence, the CCSD $\{t'\}$ (4,19) calculation reproduces 61% of the total T_3 contribution to the energy (the difference between CCSD $\{t'\}$ (4,19) and CCSDT energies is $10.146mE_h$, which should be compared to $26.324mE_h$ of the total T_3 contribution). The CCSD $\{t'q'\}$ (4,19) calculation is quite successful too as it recovers 71% of the total T_4 contribution [the difference between CCSD $\{t'q'\}$ (4,19) and CCSD $\{t'\}$ (4,19) energies is $1.902mE_h$, which should be compared to $2.651mE_h$ of the total T_4 effect]. Other CCSD t and CCSD tq approaches based on internal T_3 and T_4 clusters behave in a similar way (which again implies that the simplest CCSD $\{t'\}$ and CCSD $\{t'q'\}$ approaches give us all the information about internal T_3 and T_4 contributions that one can possibly obtain with methods of this type). A lot of information about T_3 clusters is lost already when we replace the active space (4,19) by the active space (4,12). Indeed, the CCSD $\{t'\}$ (4,12) calculation recovers only 18% of the total T_3 contribution, which confirms our earlier observation that a very good description of T_3 cluster components in C₂ requires an explicit inclusion of semi-internal excitations involving high-lying virtual orbitals. On the other hand, the CCSD $\{t'\}$ (4,12) and CCSD $\{t'q'\}$ (4,12) calculations can be used to estimate the magnitude of T_4 energy contribution. The difference between the CCSD $\{t'q'\}$ (4,12) and CCSD $\{t'\}$ (4,12) energies is $2.354mE_h$, which is quite close to a total T_4 contribution to energy of $2.651mE_h$. A very similar observation applies to the CCSD t' and CCSD $t'q'$ methods, in which unlike in the CCSD $\{t'\}$ and CCSD $\{t'q'\}$ approaches, the internal T_3 and T_4 clusters are iterated together with all t_a^i and t_{ab}^{ij} amplitudes.

The fact that a fairly large active space must be employed to describe T_3 and T_4 effects in C₂ does not diminish the usefulness of the CCSD t and CCSD tq approaches using only internal T_3 and T_4 components. First of all, unlike the perturbative CCSDT and CCSDTQ methods, the CCSD t and CCSD tq approaches using internal T_3 and T_4 components never overshoot T_3 and T_4 contributions to the energy. Moreover, all CCSD t and CCSD tq approaches using internal T_3 and T_4 components offer tremendous savings compared to full CCSDT and CCSDTQ calculations. In Sec. IV B we showed that the number of t_{ABC}^{IJK} clusters carrying only active orbital indices drops very fast with decreasing values of N_o and N_u . In consequence, we never have to deal with many t_{ABC}^{IJK} (and t_{ABCD}^{IJKL}) amplitudes, even when the active space contains 50%–60% of all virtual orbitals. A significant reduction in computer effort is also observed if we

TABLE V. Total energies $E+100.0$ (in E_h , all signs reversed) for the DZP model of HF^a ($n_o=4$, $n_u=15$) at various internuclear separations R . The equilibrium internuclear distance R_e equals $1.733 a_0$.

R	CCSD	CCSD(T)	CCSDT-1	CCSDT	FCI ^a	CCSD $\{t'\}$ ^b	CCSD $\{t\}$ ^b	CCSD t' ^b	CCSD $t-1$ ^c	CCSD $t-1$ ^b	CCSD t^c	CCSD t^b
$1.0R_e$	0.247 963	0.250 572	0.250 800	0.250 704	0.250 969	0.249 560	0.249 415	0.249 223	0.248 833	0.250 777	0.248 808	0.250 680
$1.5R_e$	0.155 296	0.159 508	0.159 906	0.159 749	0.160 393	0.157 544	0.157 477	0.157 255	0.158 307	0.159 875	0.158 207	0.159 717
$2.0R_e$	0.070 927	0.080 850	0.080 886	0.079 982	0.081 108	0.074 861	0.074 850	0.074 461	0.079 432	0.080 849	0.078 446	0.079 941
$3.0R_e$	0.021 495	0.070 375	0.052 413	0.041 827		0.029 204	0.029 089	0.028 509	0.051 006	0.052 373	0.039 912	0.041 774
$3.5R_e$	0.017 962	0.087 312	0.056 293	0.040 531		0.026 190	0.026 043	0.025 515	0.054 880	0.056 253	0.038 494	0.040 475
$4.0R_e$	0.016 844	0.098 061	0.059 147	0.040 380		0.025 234	0.025 082	0.024 588	0.057 731	0.059 107	0.038 287	0.040 324

^aThe basis set and FCI energies were taken from Ref. 68. In all correlated calculations, the lowest 1σ orbital was kept frozen.

^bActive space (3,9).

^cActive space (3,1).

look at CPU timings. This is demonstrated in Table IV. The CCSD $\{t'\}$ (4,12) calculation for the pVDZ+ model of C_2 is only 31% more expensive than the standard CCSD calculation. The CCSD $\{t'\}$ (4,19) calculation is 2.5 times more expensive than the CCSD calculation, while recovering 61% of the T_3 effect for a very difficult case of C_2 . The CASSCF-corrected CCSD calculation of the type discussed in Refs. 39–41 with $N_o=4$ and $N_u=19$ would be much more expensive than the CCSD and CCSD $\{t'\}$ (4,19) calculations without giving a lot more information about T_3 clusters than the CCSD $\{t'\}$ (4,19) calculation, since the important semi-internal T_3 components, which are largely responsible for the remaining $\sim 40\%$ of the T_3 effect, cannot be included in the CASSCF-corrected CCSD method using $N_o=4$ and $N_u=19$. The CCSD $\{t'\}$ (4,19) calculation with the convergence threshold for the energy set to $10^{-11}E_h$ is almost five times faster than the CCSDT calculation converged to seven decimal places. If we compare the CPU timings corresponding to the same convergence threshold (seven decimal places), the CCSDT calculation is seven times slower than the CCSD $\{t'\}$ (4,19) calculation. The CPU time saving resulting from switching from CCSDT to the CCSD $\{t'\}$ approach would be even larger if we increased the size of the basis set, since the number of unoccupied active orbitals that we must include to get good CCSD $\{t'\}$ results grows slower with the size of the basis set than the total number of unoccupied orbitals. One might argue, of course, using timings listed in Table III, that at least for the pVDZP+ model of C_2 with $R=R_e$, a better alternative is provided by one of the perturbative approaches, such as CCSDT-1. Indeed, the CCSDT-1 calculation is in this case only 24% longer than the CCSD $\{t'\}$ (4,19) calculation and the CCSDT-1 and CCSDT energies differ only by $2.582mE_h$. However, we should also notice that the CCSDT-1 method overestimates the T_3 contribution (the CCSDT-1 energy is too negative), whereas the CCSD $\{t'\}$ (4,19) energy is inevitably between the CCSD and CCSDT energies. For larger internuclear distances R , the CCSDT-1 energies would overestimate the T_3 contribution even more and we would finally end up with a completely unphysical shape of the potential energy curve resulting from the CCSDT-1 calculations. An example of unphysical behavior of the CCSDT-1 approach at large internuclear distances is presented in Sec. IV D.

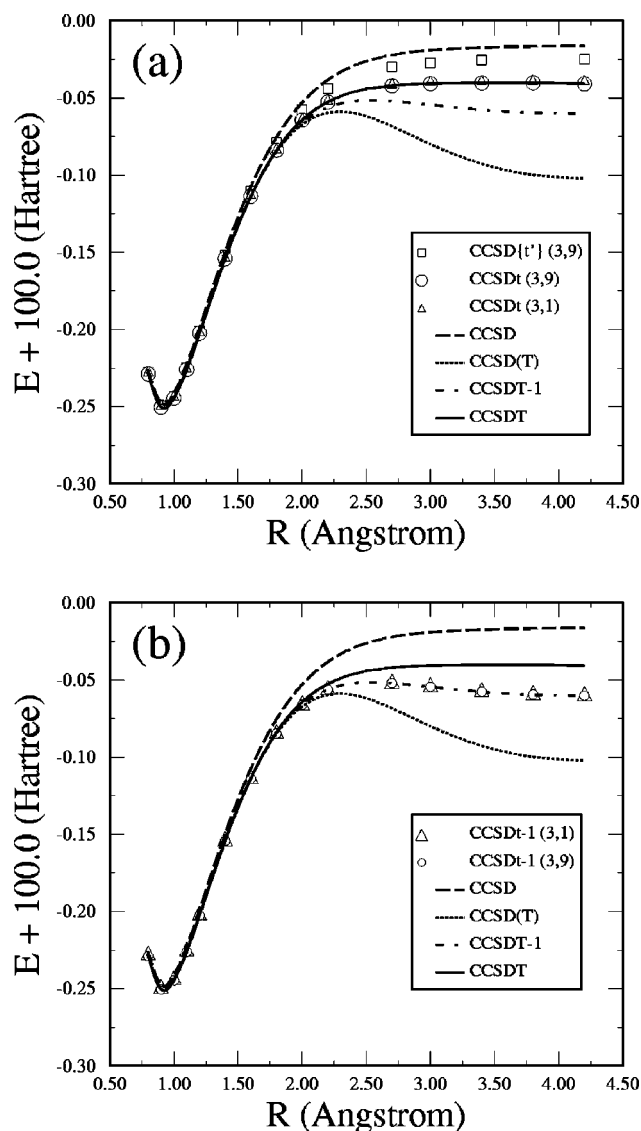


FIG. 1. Potential energy curves for the DZP model of HF. (a) A comparison of the CCSD $\{t'\}$ (3,9), CCSD t (3,1), and CCSD t (3,9) results (open squares, open triangles, and open circles, respectively) with the results of CCSD, CCSD(T), CCSDT-1, and full CCSDT calculations (designated by dashed, dotted, dashed-dotted, and solid lines, respectively). (b) A comparison of the results obtained with perturbative CCSD $t-1$ (3,1) and CCSD $t-1$ (3,9) schemes (open triangles and open circles, respectively) with the CCSD, CCSD(T), CCSDT-1, and full CCSDT results [line textures the same as in (a)].

D. The DZP model of HF

The results for the DZP model of HF are given in Table V and Fig. 1. In this case, we studied the entire potential energy curve (the internuclear separation R was varied between 0.8 and 4.2 Å; recall that the equilibrium bond length R_e equals 0.917 Å or $1.733a_0$). Our aim was to investigate the ability of various CCSD t schemes to describe the breaking of a single chemical bond. In particular, we focused on the ability of various CCSD t methods to reproduce the T_3 cluster components, which become increasingly large as the H–F bond breaks. The T_3 contribution to the energy, as measured by a difference between CCSD t and CCSD energies, increases from $2.7mE_h$ at $R=R_e$ to $23.5mE_h$ at $R=4R_e$. In fact, the magnitude of the T_3 effect is large already for $R=2R_e$. In this case, the T_3 contribution to the energy equals $9.1mE_h$.

Another reason for focusing on various CCSD t schemes in our calculations for HF was the fact that the full CCSD t method provides almost exact (FCI) results in this case (which are available for $R=R_e$, $1.5R_e$, and $2R_e$ ⁶⁸). The role of T_4 and higher-than-quadruply excited clusters is very small. Indeed, differences between the exact FCI energies and their CCSD t analogs are $0.263mE_h$ at $R=R_e$, $0.642mE_h$ at $R=1.5R_e$, and $1.123mE_h$ at $R=2R_e$. We can thus assume that the potential energy curve resulting from CCSD t calculations is practically identical to the exact, FCI curve. We use our CCSD t energies as a representation of FCI energies, even for geometries for which FCI results are not available. The fact that the CCSD t method is capable of describing the bond breaking in HF is an immediate consequence of the nature of the H–F bond, which is essentially a single bond involving two valence electrons and two molecular orbitals (the highest occupied and the lowest unoccupied σ orbitals). In fact, the qualitatively correct description of the bond breaking in HF is provided by the much simpler CCSD method (cf. Fig. 1). The only problem with the CCSD description is the lack of important T_3 contributions, which lower the CCSD energy by more than $20mE_h$ upon dissociation.

At the equilibrium geometry and for geometries near the equilibrium one, the energy ordering of the RHF orbital symmetry species (according to irreducible representations of the $C_{\infty v}$ point group) is as follows:

$$\Phi = |(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^2(2\pi)^2| \times (4\sigma)^0(5\sigma)^0(3\pi)^0(4\pi)^0(6\sigma)^0 \dots \quad (40)$$

In this region of nuclear geometries, the RHF configuration is a dominant configuration in the FCI expansion of the ground-state wave function. If we were only interested in describing the equilibrium region, the choice of active space for various CCSD t calculations would not be a critical issue, since even the basic CCSD approach provides an excellent description for $R \approx R_e$. The choice of active space becomes important, however, if we want to study geometries far from the equilibrium one. Indeed, at large internuclear separations R , the ground-state RHF configuration

$$\Phi = |(1\sigma)^2(2\sigma)^2(1\pi)^2(2\pi)^2(3\sigma)^2| \times (4\sigma)^0(5\sigma)^0(3\pi)^0(4\pi)^0(6\sigma)^0 \dots, \quad (41)$$

becomes almost degenerate with the configuration corresponding to the $(3\sigma)^2 \rightarrow (4\sigma)^2$ double excitation. The $3\sigma \rightarrow 4\sigma$ monoexcitation becomes important as well. This means that the most natural choice of the active space, which should allow us to incorporate the most essential nondynamic correlation effects characterizing the region of large R values into various CCSD t wave function expansions, is the one including the 3σ and 4σ orbitals. The orbital energy ordering for $R \approx R_e$ suggests, however, that a better description of the $R \approx R_e$ region should be obtained if we added the 1π and 2π orbitals to the active space [cf. Eq. (40)]. This implies that the smallest, chemically meaningful, active space that should allow us to correctly describe the entire potential energy curve for HF in the $X^1\Sigma^+$ state is the one containing the entire valence shell (the occupied 1π , 2π , and 3σ orbitals and the unoccupied 4σ orbital). For this reason, we choose the active space with $N_o=3$ and $N_u=1$ as a primary space for our considerations. We can expect, however (on the basis of our calculations reported in Secs. IV A–IV C), that an active space consisting of only three occupied orbitals and too few unoccupied orbitals may be too small for the CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' calculations (as a matter of fact, the internal T_3 component is zero if $N_o=3$ and $N_u=1$). For this reason, we consider another, yet physically meaningful active space consisting of three occupied and nine unoccupied orbitals. This space is almost equivalent to a space corresponding to $1s$, $2s$, and $2p$ shells of the H atom and $2p$, $3s$, $3p$, and $4s$ shells of the F atom [we decided to exclude the tenth unoccupied (9σ) orbital of HF, since the energy separation between the tenth and ninth unoccupied orbitals is very large, $1.38E_h$ at $R=R_e$ and $2.37E_h$ at $R=4R_e$].

The results presented in Table V and in Fig. 1 (a) clearly demonstrate that the best description of the potential energy curve for HF is provided by the CCSD t method employing internal as well as semi-internal T_3 clusters. The CCSD t and CCSD t' curves shown in Fig. 1 (a) are practically indistinguishable, particularly when the active space (3,9) is employed. The CCSD $t(3,9)$ calculations reproduce 99%–100% of the total T_3 effect (99% for $R < 2R_e$ and 100% for $R \geq 2R_e$), so that the differences between the CCSD $t(3,9)$ and CCSD t energies are almost zero for all values of R ($0.024mE_h$ for $R=R_e$, $0.042mE_h$ for $R=2R_e$, $0.065mE_h$ for $R=3R_e$, and $0.056mE_h$ for $R=4R_e$). The CCSD t results obtained using small, yet a chemically meaningful active space consisting of only the three highest occupied orbitals and a single, lowest energy unoccupied orbital are excellent as well. For $R \geq 3R_e$, the CCSD $t(3,1)$ calculations reproduce 91% of the total T_3 contribution. A somewhat worse description of the T_3 effect is obtained only when $R \approx R_e$. For $R=R_e$, the CCSD $t(3,1)$ calculation gives 31% of the T_3 contribution to the energy, compared to 99% obtained in the CCSD $t(3,9)$ calculation. Although this might be viewed as a failure of the CCSD t approach at shorter distances R , this poorer description of T_3 cluster components for $R \approx R_e$ is actually a useful and important feature, as it

helps the potential energy curve resulting from CCSD t (3,1) calculations to remain almost parallel to the CCSDT curve (it is important to remember that all CCSD t curves always lie between the CCSD and CCSDT curves). Indeed, for large internuclear separations ($R \geq 3R_e$), the difference between the CCSD t (3,1) and CCSDT energies is $\sim 2mE_h$ ($1.915mE_h$ for $R=3R_e$, $2.093mE_h$ for $R=4R_e$), which should be compared to more than $20mE_h$ error relative to CCSDT results obtained with the standard CCSD method. If the CCSD t (3,1) calculation reproduced 91% of the T_3 contribution at $R=R_e$, as it does for $R \geq 3R_e$, the difference between the CCSD t (3,1) and CCSDT energies for $R=R_e$ would be $0.247mE_h$, which is only 12% of the similar energy difference characterizing large internuclear separations ($R \geq 3R_e$). The resulting CCSD t (3,1) curve would not be parallel to the CCSDT curve, as the difference between such CCSD t (3,1) energies and their CCSDT counterparts would increase from $0.2mE_h$ at $R=R_e$ to $2.1mE_h$ at $R=4R_e$. Fortunately, the CCSD t (3,1) calculation reproduces only 31% of the T_3 effect at $R=R_e$. This increases the difference between CCSD t (3,1) and CCSDT energies at $R=R_e$ to $1.896mE_h$ and makes the CCSD t (3,1) curve almost parallel to the CCSDT curve. We can thus expect that various properties of HF related to the shape of the potential energy curve, such as vibrational term values and the dissociation energy resulting from the CCSD t (3,1) calculations, will closely resemble the CCSDT values. For example, the dissociation energy D_e , defined as an energy difference $E(R=4R_e) - E(R=R_e)$, gives 5.729 eV using the CCSD t (3,1) results, 5.723 eV using the CCSDT results, and 6.289 eV using the CCSD results. In this case, the CCSD t (3,1) approach reproduces the CCSDT value of D_e to within 0.01 eV. Clearly, the CCSD t (3,9) and CCSDT vibrational term values and dissociation energies should be virtually identical. Indeed, if we calculate the CCSD t (3,9) value of D_e using the CCSD t (3,9) energies for $R=4R_e$ and $R=R_e$, we obtain $D_e^{\text{CCSD}t(3,9)} = 5.724$ eV, which differs from the CCSDT value of D_e only by 0.001 eV.

An excellent performance of the CCSD t method is related to the presence of the semi-internal T_3 clusters defined by Eq. (24) in the CCSD t calculations. A similar behavior of the CCSD t =SSCCSD(T) procedure was observed earlier,⁴⁶ even though the choice $(N_o, N_u) = (3,9)$ was not considered in Ref. 46. This choice of active space is important for us, since we want to compare the performance of the CCSD t method using semi-internal and internal T_3 clusters with much simpler CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' methods, which use internal T_3 components only. The latter three approaches require that larger active spaces be employed. As mentioned earlier, we would not gain anything by applying active spaces containing, for example, a single unoccupied orbital.

Let us therefore discuss the performance of the CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' approaches. We restrict our discussion to only one active space, which contains three occupied and nine unoccupied orbitals. Let us first emphasize that although there are only fifteen unoccupied orbitals in the DZP basis set, the CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' calculations using $(N_o, N_u) = (3,9)$ are many times faster

than the corresponding CCSDT calculations. This is related to $n_o^3 n_u^5$ scaling of the CCSDT method (as explained in Sec. II, the CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' approaches scale as $\sim n_o^2 n_u^4 + N_o^3 N_u^5$). In fact, our CPU timings indicate that the CCSD $\{t\}$ (3,9), CCSD $\{t'\}$ (3,9), and CCSD t' (3,9) calculations for the DZP model of HF are only twice as slow as the standard CCSD calculations (for geometries near the equilibrium, the factor is even less than two) and as twice as fast as the CCSDT-1 calculations, which provide unphysical results at large distances R (cf. Fig. 1 and the discussion below). We should also point out that the fact that we use $\frac{9}{15} = 60\%$ of all unoccupied orbitals as active orbitals in calculations employing a DZP basis set does not necessarily mean that we must always use 60% of all unoccupied orbitals in CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' calculations employing larger basis sets in order to obtain a reasonable description of T_3 contributions. As mentioned earlier, the number of active orbitals that leads to reproduction of a given fraction of T_3 contributions to the energy by CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' methods grows significantly slower than the size of the basis set. This means that CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' calculations become less and less expensive, when compared to CCSDT or even CCSDT-1 calculations, once larger and larger basis sets are employed. Asymptotically, i.e., for very large basis sets, the cost of CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' calculations giving 50% or more of the total T_3 contribution to the energy would be similar to the cost of CCSD calculations, since $N_o^3 N_u^5$ steps related to CCSDT calculations within the active space become significantly less expensive than $n_o^2 n_u^4$ steps of the CCSD procedure.

The CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' results for HF are most encouraging, particularly if we take into account the small computer effort involved. With only three occupied and nine unoccupied orbitals in the active space, the simplest CCSD $\{t'\}$ method reproduces as much as 58% of the total T_3 contribution at $R=R_e$, 43% of T_3 contribution at $R=2R_e$, 38% of T_3 contribution at $R=3R_e$, and 36% of T_3 contribution upon dissociation (for $R \geq 4R_e$). In consequence, the potential energy curve obtained in CCSD $\{t'\}$ (3,9) calculations represents a significant improvement in comparison to the CCSD curve [cf. Fig. 1 (a)].

The performance of the CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' approaches becomes particularly impressive if we realize that the perturbative CCSDT-1 calculations, which are more expensive than the CCSD $\{t\}$ (3,9), CCSD $\{t'\}$ (3,9), and CCSD t' (3,9) calculations, give a completely unphysical shape of the potential energy curve for HF. Indeed, the CCSDT-1 curve lies below the CCSDT (or FCI) curve and has an unphysical hump for intermediate values of R (see Fig. 1). For larger internuclear separations, the CCSDT-1 method overestimates the T_3 effect, so that the errors in the CCSDT-1 results relative to CCSDT increase from acceptable $0.903mE_h$ at $R=2R_e$ to totally unacceptable $18.767mE_h$ at $R=4R_e$. The situation becomes even worse, if we employ the popular CCSD(T) method. The errors in the CCSD(T) results relative to CCSDT increase from $0.848mE_h$ at $R=2R_e$ to $28.451mE_h$ at $R=3R_e$ and $57.645mE_h$ at $R=4R_e$. The hump in the CCSD(T) curve is

more pronounced than in the CCSDT-1 case. In addition, unlike the iterative CCSDT-1 approach, the noniterative CCSD(T) method underestimates the T_3 contribution at $R \approx R_e$, while grossly overestimating the T_3 effects at large internuclear separations, which shows that it is even difficult to predict if the CCSD(T) energies are above or below their CCSDT counterparts. The more accurate CCSDT-1 approach overestimates the T_3 contribution to the energy for all geometries.

None of the problems encountered in perturbative CCSDT-1 and CCSD(T) calculations shows up in the CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' calculations. The CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' methods provide an inexpensive and systematic improvement of the CCSD results and a correct description of the bond breaking. The magnitude of this improvement depends on the size of the active space employed. Moreover, it is somewhat easier to converge the CCSD equations at larger internuclear separations once the corrections due to internal T_3 components are properly incorporated into the CCSD scheme, as is, for example, done in the CCSD $\{t'\}$ method. This can be easily understood if we realize that t_a^i and t_{ab}^{ij} amplitudes iterated in the absence of higher-order clusters (the standard CCSD approach) are not as meaningful as the values of these amplitudes obtained by iterating T_1 and T_2 clusters in the presence of T_3 or T_3 and T_4 components. The same has been observed in the CASSCF-corrected CCSD calculations.⁴¹

As in all other cases examined in this paper, the difference between CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' results is very small. The difference between the CCSD $\{t\}$ (3,9) and CCSD $\{t'\}$ (3,9) energies does not exceed $0.15mE_h$ for all geometries examined by us, which confirms our earlier observation that there is no need to iterate the T_1 clusters in the $T_1t_3^{(0)}$ contribution to Eq. (13). It is sufficient to replace T_1 in the $T_1t_3^{(0)}$ contribution to Eq. (13) by the T_1 component resulting from the CCSDT calculations within the active space [cf. Eq. (16); for similar remarks about CASSCF-corrected CCSD calculations, see Ref. 41]. As explained in Sec. II A, this simplifies the CCSD $\{t'\}$ scheme tremendously. The differences between the CCSD t' (3,9) and CCSD $\{t'\}$ (3,9) energies are somewhat larger ($0.3\text{--}0.7mE_h$), but still far too small to conclude that there is any need to invoke the completely iterative CCSD t' approximation, in which internal T_3 components are iterated in the presence of all (not just internal) t_a^i and t_{ab}^{ij} cluster amplitudes. The simplest CCSD $\{t'\}$ scheme provides a satisfactory treatment of internal T_3 components.

Finally, it is interesting to observe the performance of the CCSD t -1 approach based on internal and semi-internal perturbative triples. The n^5 treatment of triexcited clusters, which is a major characteristic of the CCSD t -1 approach, is entirely sufficient to reproduce the entire CCSDT-1 curve [see Fig. 1(b)], in spite of the fact that the CCSD t -1 method is significantly less expensive than the CCSDT-1 approach (CCSDT-1 is an n^7 procedure). The differences between CCSD t -1(3,1) and CCSDT-1 energies are only $1.968mE_h$ at $R=R_e$, $1.453mE_h$ at $R=2R_e$, $1.412mE_h$ at $R=3R_e$, and $1.416mE_h$ at $R=4R_e$. With three occupied and nine unoccupied orbitals in the active space, the CCSD t -1 energies

become virtually identical to their CCSDT-1 counterparts [differences between CCSD t -1(3,9) and CCSDT-1 energies do not exceed $0.04mE_h$ for all geometries considered]. It is true that the CCSDT-1 scheme fails at large internuclear separations and that the same applies to the CCSD t -1 method due to the perturbative treatment of triples in both approaches. We must realize, however, that a large portion of the potential energy curve for HF (the entire $R \leq 2R_e$ region) is very well described by the CCSDT-1 approach. It is thus fascinating to learn that we can obtain the CCSDT-1 results employing inexpensive n^5 steps of the CCSD t -1 procedure.

V. SUMMARY

In this paper, we introduce a hierarchy of approximations to standard CCSDT and CCSDTQ approaches, in which the dominant T_3 and T_4 contributions are evaluated via the concept of active orbitals. We demonstrate that the resulting approaches, which we commonly label as the CCSD t and CCSD tq schemes, enable us to successfully describe the single and multiple bond breaking and quasidegenerate electronic states without using expensive n^8 and n^{10} steps of full CCSDT and CCSDTQ procedures. By restricting T_3 and T_4 clusters to internal or internal and semi-internal components only, we describe the dynamic as well as nondynamic correlation effects dynamically. This enables us to achieve an effectively multireference description, while retaining the simplicity of the SRCC theory.

All CCSD t and CCSD tq methods studied in this paper are essentially $n_o^2n_u^4$ procedures. The computer costs associated with the use of the CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, CCSD $\{t'q'\}$, CCSD t' , and CCSD $t'q'$ schemes, which require that we only evaluate the internal T_3 and T_4 components, are comparable to costs of standard CCSD calculations. The costs of the CCSD t and CCSD tq calculations employing internal as well as semi-internal T_3 and T_4 clusters are comparable to costs of standard MRCISD calculations. Even if we use fairly large active spaces, the CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' methods remain less expensive than the perturbative CCSDT-1 approach. This is an important observation, since perturbative CC approaches fail to describe bond breaking, whereas all nonperturbative CCSD t and CCSD tq approaches (including CCSD $\{t\}$, CCSD $\{t'\}$, and CCSD t' schemes) provide a correct description of the bond breaking process.

In order to test various CCSD t and CCSD tq methods, we studied three systems: The stretched water molecule, C_2 at the equilibrium geometry, and HF (the entire potential energy curve). Investigation of the stretched water molecule and C_2 was useful since these systems are characterized by large T_3 and T_4 contributions. Investigation of the potential energy curve for HF allowed us to see what happens to various methods when we go from a nondegenerate regime corresponding to the equilibrium geometry to a quasidegenerate regime characterizing the broken H-F bond.

Our immediate observations can be summarized as follows. All newly proposed methods improve the CCSD results and give the correct signs of the T_3 and T_4 energy contributions. Improvement in all CCSD t and CCSD tq re-

sults is proportional to size of the active space. None of the newly proposed CCSD t and CCSD tq methods (with an exception of the perturbative CCSD $t-1$ approach) overestimates the T_3 and T_4 contributions to the energy. In consequence, all nonperturbative CCSD t and CCSD tq methods provide a correct description of bond breaking and a very good description of dominant T_3 and T_4 effects. In all nonperturbative CCSD t and CCSD tq calculations for ground singlet states, it is sufficient to use ordinary RHF orbitals, in spite of the fact that the RHF method itself is a very poor reference at large internuclear distances. This means that we can adapt the CCSD t and CCSD tq methods to spin and spatial symmetries of the Hamiltonian (in fact, we used closed-shell codes in all our calculations).

The best results were obtained with the CCSD t and CCSD tq approaches employing internal as well as semi-internal triples and quadruples. We clearly demonstrated that there is no need to use large active spaces in this case. Our calculations indicate that the CCSD t and CCSD tq approaches, which are the well-defined and rigorously size-extensive CC analogs of the well-known MRCISD scheme, provide by far the best description of bond breaking and difficult quasidegenerate situations, so that they are ideally suited for reaction dynamics and various spectroscopic studies. The CCSD t and CCSD tq methods employing internal as well as semi-internal triples and quadruples are capable of reproducing nearly 100% of the total T_3 and T_4 contributions at a significantly lower cost compared to the full CCSDT and CCSDTQ schemes. With very small active spaces and for geometries near the equilibrium one, the CCSD t approach may reproduce less than 100% of the T_3 contributions, but that actually helps to improve the parabolic nature of the CCSD t and CCSDT potential energy curves, as we demonstrated for HF.

The CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, and CCSD $\{t'q'\}$ methods as well as their CCSD t' and CCSD $t'q'$ counterparts employing small active spaces are not capable of reproducing a large portion of T_3 and T_4 contributions, since none of these approaches describes the important T_3 and T_4 components of the semi-internal type. On the other hand, the CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, CCSD $\{t'q'\}$, CCSD t' , and CCSD $t'q'$ methods are not much more expensive than the CCSD scheme, even when large active spaces are employed, and they always improve the CCSD results. In fact, with judicious choice of the active space and by incorporating sufficiently many unoccupied orbitals in the active space, we can reproduce a significant portion of the T_3 and T_4 contributions using these approaches, in spite of the fact that the CCSD $\{t\}$, CCSD $\{tq\}$, CCSD $\{t'\}$, CCSD $\{t'q'\}$, CCSD t' and CCSD $t'q'$ methods use only internal T_3 and T_4 components. We can also consider various kinds of frozen natural or improved virtual orbitals^{70,71} to improve upon a description of the internal T_3 and T_4 clusters. A possibility for estimating the perturbative triples correction by considering a reduced space of virtual orbitals have been discussed in Refs. 70, 71, and 73. Other ways of handling active spaces in CC theory are considered by Krylov *et al.*⁷⁴

Interestingly enough, simple CCSD $\{t'\}$ and CCSD $\{t'q'\}$ methods, which do not require the storage of

internal t_{ABC}^{IJK} and t_{ABCD}^{IJKL} amplitudes and which are based on a straightforward modification of the subset of standard CCSD equations, which corresponds to equations projected on internal singly and doubly excited configurations, are as good as or actually even somewhat more accurate than the CCSD $\{t\}$ and CCSD $\{tq\}$ or CCSD t' and CCSD $t'q'$ approaches. We thus recommend using the CCSD $\{t'\}$ and CCSD $\{t'q'\}$ schemes in CCSD t and CCSD tq calculations employing internal T_3 and T_4 clusters only.

Finally, the CCSD $t-1$ method employing perturbative triples of the internal and semi-internal types gives results which are virtually identical to CCSDT-1 results. This is true even when small active spaces are employed. We can thus use the CCSD $t-1$ approach instead of the CCSDT-1 method without sacrificing the accuracy of the CCSDT-1 method.

The cost of CCSD $t-1$ calculations is very small compared to standard CCSDT-1 calculations. In fact, the cost of CCSD $t-1$ calculations is practically identical to the cost of ordinary CCSD calculations (the n^7 steps of the CCSDT-1 procedure are replaced by inexpensive n^5 steps if the CCSD $t-1$ method is employed). Although the CCSDT-1 method fails at large internuclear separations, it is still capable of giving very good results for a wide range of nuclear geometries. As we demonstrated in this paper, the same observation applies to the much less expensive CCSD $t-1$ approach. This indicates that we can mix perturbative and active space concepts and propose an entire hierarchy of perturbative CC methods employing selected classes of tri- and tetraexcited clusters defined through active orbitals. We are currently working on the implementation of the CCSD(t) method, which is a noniterative analog of the CCSD $t-1$ approach and an active-space analog of the popular CCSD(T) method. The only difference between CCSD(t) and CCSD(T) methods is the fact the former approach uses only internal and semi-internal triples in defining the noniterative correction due to T_3 , whereas the latter approach needs all triply excited configurations in defining the analogous correction. The CCSD(t) scheme that we hereby propose should be as accurate as the CCSD(T) method. At the same time, the cost of the calculation of triples correction reduces in the CCSD(t) scheme from noniterative, but still rather expensive n^7 steps, to noniterative and inexpensive n^5 steps. The CCSD(t) results will be presented as soon as the method is fully implemented.

ACKNOWLEDGMENT

This work has been supported by the United States Air Force Office of Scientific Research under Grant No. AFOSR-F49620-95-1-0130.

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