



High-order coupled-cluster calculations through connected octuple excitations

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Abstract

By exploiting a determinantal full configuration interaction (FCI) algorithm, we compute the correlation energies of molecules at any arbitrary order of coupled-cluster (CC) theory as well as high orders of configuration interaction (CI) and many-body perturbation theory (MBPT). This general-order CC program requires memory storage for three arrays of length N_{det} (the number of determinants) and a modest amount of disk storage. We perform the CC calculations including all connected n -fold excitations up to $n = 8$ for H_2O , FH, and F^- . © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Configuration interaction (CI) theory [1,2], many-body perturbation theory (MBPT) [3–6], and coupled-cluster (CC) theory [6–10] offer systematic routes to improving the wavefunctions and energies of atoms and molecules in their ground electronic state. The CI method [1,2], which is conceptually the simplest among them, allows the reference configuration to mix with single, double, etc. excitation configurations and determines the mixing coefficients (the CI coefficients) variationally. A serious deficiency of this method is that the wavefunctions and energies obtained in this way are not size-extensive [6,10] unless all possible excitation configurations are included. When all configurations are included, the method becomes full configuration interaction (FCI), and several results have been reported

[11–17]. Despite its very limited applicability, FCI is recognized as an indispensable computational method for benchmarks, as it provides the best possible wavefunction and energy of a system within a given one-particle basis set.

The MBPT method [3–6] treats electron correlation as a perturbation to the independent particle reference. The MBPT method truncated at any perturbation order is size-extensive and the MBPT calculations through fourth order [18,19] employing the Møller–Plesset partitioning scheme are routine. MBPT has also been implemented at MBPT(5) [20] and MBPT(6) in a general MBPT program [21,22]. The FCI method also makes it possible to compute the MBPT energies order by order and to study the convergence of the perturbation series, provided a FCI calculation is possible as demonstrated by Laidig et al. [23] and by others [24,25]. The convergence of the perturbation series is slow and oscillatory in many cases, and Olsen and co-workers [25,26] find that certain situations lead to divergent behavior in

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perturbation series even for systems having wavefunctions dominated by a Hartree–Fock (HF) determinant. Resummation techniques like Padé approximants, however, attest to the fact that the series can be made to converge [23,26].

A generalization of MBPT is CC theory [6–10], which combines the size-extensivity of MBPT with the infinite summation of CI. The key idea of the CC method is the use of an exponential wavefunction, which permits the inclusion of a greatly increased number of excited configurations relative to the number of unknown coefficients (t -amplitudes) and hence sums the correlation contributions from these configurations in a very efficient way. The exponential wavefunction ansatz also ensures the extensivity of the CC method. It has been shown [10] that the CC energies converge rapidly to the FCI energies as the CC order increases, i.e., as more and more independent t -amplitudes are included in the calculations. Unlike MBPT, whose correlation energies are formally obtained by a single evaluation of a closed expression, the CC method requires an iterative procedure to solve algebraic equations to determine the t -amplitudes which in turn give the CC energies. Each iteration of this procedure gives rise to certain terms in the MBPT energy expressions [10], which might imply that the convergence of the perturbation series is closely related to the convergence of the CC iterations. However, CC theory is an infinite-order perturbation method, and, unlike MBPT, is independent of the choice of the unperturbed Hamiltonian H_0 . This added flexibility makes it possible for the CC iterations to converge even when the corresponding MBPT series is apparently divergent.

In this Letter, we present a method to compute the wavefunctions and energies at any arbitrary order of the CC method. The calculations of the t -amplitudes and energies proceed by forming an exponential wavefunction explicitly and by substituting it into the Schrödinger equation. The procedure is, therefore, straightforward and general at the cost of applicability, and the extension of the method to less common reference wavefunctions or orbitals, or the use of other CC ansatz will be straightforward. The implementation of the method is based on a determinantal FCI algorithm, and the program is also capable of generating the wavefunctions and energies at high orders of the CI and MBPT methods. We report

demonstrative calculations for H₂O, FH, and F⁻ with the CC and CI methods through FCI and with the MBPT method through 20th order. In particular, we address the convergence of the CC energies with respect to the CC order and the correlation between the convergence of the perturbation series and the CC iterations.

2. Method

The CC method uses an exponential wavefunction $|\Psi\rangle$ written as [6–10]

$$|\Psi\rangle = \exp(T)|\Phi_0\rangle \\ = (1 + T + T^2/2! + T^3/3! + \dots)|\Phi_0\rangle, \quad (1)$$

where the independent particle reference $|\Phi_0\rangle$ is the HF wavefunction composed of n occupied (labeled by i, j, k, \dots) and $N - n$ unoccupied (a, b, c, \dots) spinorbitals. It is legitimate (and already routine with the ACES II program) to use other choices of reference in the CC method and such an extension will be straightforward for this program. The operator T is a sum of the excitation operators of different types such as single excitations T_1 , double excitations T_2 , and triple excitations T_3 . We may truncate the summation at m -tuple excitations T_m ,

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

defining the m -tuple excitation CC method as CC(m). The notations commonly used for the CC(2), CC(3), and CC(4) methods are CCSD [9], CCSDT [27], and CCSDTQ [28], respectively. If m equals the maximum allowed number of excitations, CC(m) becomes identical to FCI. The excitation operators are defined by the respective t -amplitudes ($t_i^a, t_{ij}^{ab}, t_{ijk}^{abc}$, etc.) and creation p^\dagger and annihilation p operators of electrons, e.g.,

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

$$T_2 = \sum_{i>j}^{\text{occ.}} \sum_{a>b}^{\text{virt.}} t_{ij}^{ab} a^\dagger i b^\dagger j, \quad (4)$$

$$T_3 = \sum_{i>j>k}^{\text{occ.}} \sum_{a>b>c}^{\text{virt.}} t_{ijk}^{abc} a^\dagger i b^\dagger j c^\dagger k, \quad (5)$$

where the order of the operators is meaningful, and we must keep proper track of the signs of the t -amplitudes due to the interchanges of the operators.

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

$$\langle \Phi_0 | H | \Psi \rangle = E, \quad (6)$$

$$\langle \Phi_i^a | H | \Psi \rangle = E \langle \Phi_i^a | \Psi \rangle, \quad (7)$$

$$\langle \Phi_{ij}^{ab} | H | \Psi \rangle = E \langle \Phi_{ij}^{ab} | \Psi \rangle, \quad (8)$$

$$\langle \Phi_{ijk}^{abc} | H | \Psi \rangle = E \langle \Phi_{ijk}^{abc} | \Psi \rangle, \quad (9)$$

etc. Here, Φ_{ij}^{ab} , for example, represents a double excitation configuration defined as

$$\begin{aligned} |\Phi_{ij}^{ab}\rangle &= |1_1 1_2 \cdots 0_j \cdots 0_i \cdots 1_n \\ &\quad \times 0_{n+1} \cdots 1_b \cdots 1_a \cdots 0_N\rangle \\ &= \kappa_{ij}^{ab} a^\dagger i b^\dagger j |\Phi_0\rangle, \end{aligned} \quad (10)$$

which may differ from $a^\dagger i b^\dagger j |\Phi_0\rangle$ by the sign designated as κ_{ij}^{ab} . The Hamiltonian H can be written as

$$H = \sum_{p,q} h_{pq} p^\dagger q + \frac{1}{2} \sum_{p,q,r,s} \langle pq|rs\rangle p^\dagger q^\dagger sr, \quad (11)$$

where h_{pq} is the one-electron part of the Fock matrix elements and $\langle pq|rs\rangle$ is the two-electron integrals, relative to any orthogonal orbital choice.

The general-order CC program determines the t -amplitudes and energy of closed-shell systems by literally following the above procedure using a determinant-based algorithm. We first generate all possible configurations for α electrons that occupy $n/2$ orbitals out of $N/2$ orbitals and similarly for β electrons. The α and β configurations may be compactly stored in memory as strings of bits with each bit representing the occupancy of an orbital [12]. Any determinant can be addressed by a pair of α - and β -strings (denoted as I^α and J^β , respectively), and we associate each of these α - and β -strings with an address ($A[I^\alpha]$ or $A[J^\beta]$) in a consecutive lexical order. Accordingly, any wavefunction can be represented by an array \mathbf{C} of length N_{det} (the number of determinants), each element of which, $C[A[I^\alpha], A[J^\beta]]$, stores the CI coefficients of the

corresponding determinant. Likewise each t -amplitude can be addressed by a pair of α - and β -strings, and hence all the t -amplitudes are conveniently packed into an array \mathbf{t} , which has the same structure as \mathbf{C} .

As in the regular CC method, the present CC method requires an iterative procedure. We assume that an initial guess of the t -amplitudes is available and is stored in memory as an array \mathbf{t} . The converged t -amplitude array obtained from a lower-order CC calculation is a preferable initial guess, but one can also start from the HF determinant. The former choice leads to substantially reduced numbers of CC iterations relative to the latter case, particularly for high-order CC calculations. In each CC iteration, we first form the exponential wavefunction by operating with T on $|\Phi_0\rangle$ recursively and by accumulating $T^k|\Phi_0\rangle/k!$. This process may be accomplished in the scheme described in Fig. 1. In our implementation, we have in memory two arrays \mathbf{C}_1 and \mathbf{C}_2 that accommodate the wavefunctions $T^{k-1}|\Phi_0\rangle$ and $T^k|\Phi_0\rangle$, respectively, in addition to the one \mathbf{t} that stores the t -amplitudes. The wavefunctions and t -amplitudes being associated with the α - and β -strings, we can operate with T on any wavefunction (steps 9 and 10 in Fig. 1) straightforwardly by applying explicitly the basic rules of creation and annihilation operators to the α - and β -strings. As we form $T^k|\Phi_0\rangle$, we add the corresponding contribution to the exponential wavefunction that is stored in an array \mathbf{C}_3 on disk. The summation over k is formally an infinite summation, but it can be truncated at the maximum allowed number of excitations due to the finite number of basis functions.

We then operate on the exponential wavefunction with the Hamiltonian and examine whether the CC iterations converge to within a preset tolerance. This process is common to the implementations of FCI, and efficient algorithms to compute the product of the Hamiltonian matrix and any vector are available [12,14,15]. We define a residual vector for Eqs. (7)–(9) by its elements

$$\Delta_i^\alpha = \langle \Phi_i^a | H | \Psi \rangle - E \langle \Phi_i^a | \Psi \rangle, \quad (12)$$

$$\Delta_{ij}^{ab} = \langle \Phi_{ij}^{ab} | H | \Psi \rangle - E \langle \Phi_{ij}^{ab} | \Psi \rangle, \quad (13)$$

$$\Delta_{ijk}^{abc} = \langle \Phi_{ijk}^{abc} | H | \Psi \rangle - E \langle \Phi_{ijk}^{abc} | \Psi \rangle, \quad (14)$$

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1 Initialize  $\mathbf{C}_1$  with  $\Phi_0$ 
2 Initialize  $\mathbf{C}_3$  with  $\Phi_0$ 
3 Loop over  $k = 1, 2, \dots, K$ 
4   Zero scratch  $\mathbf{C}_2$ 
5   Loop over  $A[I_1^\alpha]$ 
6     Loop over  $A[J_1^\beta]$ 
7       Loop over  $A[I_2^\alpha]$ 
8         Loop over  $A[J_2^\beta]$ 
9            $I_3^\alpha \leftarrow T^\alpha I_2^\alpha$ 
10           $J_3^\beta \leftarrow T^\beta J_2^\beta$ 
11           $C_2(A[I_3^\alpha], A[J_3^\beta]) \leftarrow \pm t(A[I_1^\alpha], A[J_1^\beta]) C_1(A[I_2^\alpha], A[J_2^\beta])$ 
13        End loop
14      End loop
15    End loop
16  End loop
17   $\mathbf{C}_3 \leftarrow + \mathbf{C}_2/k!$ 
18   $\mathbf{C}_1 \leftarrow \mathbf{C}_2$ 
19 End loop

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Fig. 1. Loop structures for the procedure of forming an exponential wavefunction for a given set of t -amplitudes. Arrays \mathbf{C}_1 and \mathbf{C}_2 accommodate in memory the wavefunctions $T^{k-1}|\Phi_0\rangle$ and $T^k|\Phi_0\rangle$, respectively, in the k -th cycle of the outermost loop, and array \mathbf{t} stores the t -amplitudes. The summation over k can be truncated at the maximum allowed number of excitations K by virtue of the finite number of basis functions used. The α - and β -strings I_1^α and J_1^β specify the α - and β -part of the excitation operator, T^α and T^β , respectively, while I_2^α , J_2^β , I_3^α , and J_3^β refer to the determinants, of which $T^{k-1}|\Phi_0\rangle$ and $T^k|\Phi_0\rangle$ consist. The exponential wavefunction is obtained as an array \mathbf{C}_3 on disk.

etc., where the energy is given by Eq. (6). We consider that the convergence is achieved when the norm of the residual vector (excluding those elements involving excitations higher than the CC order) becomes less than 10^{-6} . This criterion normally yields the energies converged to within 10^{-7} hartree.

If the convergence criterion is not met, we upgrade the t -amplitudes with the aid of the residual vector and repeat the above-mentioned procedures. Eqs. (7)–(9) might suggest that one natural way of improving the t -amplitudes is to increment them with the residuals divided by E multiplied by the signs κ . For the double excitation t -amplitudes, one may write this scheme as

$$t_{ij}^{ab} \leftarrow t_{ij}^{ab} + \kappa_{ij}^{ab} \Delta_{ij}^{ab} / E. \quad (15)$$

This relaxation scheme leads to the converged t -amplitudes and energy, but after a large number of iterations. The slow convergence is due to the too small increments (too large a denominator E) to the t -amplitudes given in each iteration. The regular CC amplitude equations [6,10] suggest a more practical

way of upgrading the t -amplitudes that amounts to using the energy differences of canonical HF orbitals $\{\epsilon_p\}$ as the denominators, e.g.,

$$t_{ij}^{ab} \leftarrow t_{ij}^{ab} + \kappa_{ij}^{ab} \Delta_{ij}^{ab} / (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b). \quad (16)$$

If we start from the HF determinant, the first iteration gives the first-order many-body perturbation wavefunction corrections (with signs) as an initial approximation to t_{ij}^{ab} and null correlation energy, and the second iteration gives the MBPT(2) correlation energy, regardless of the CC order [6,10]. By using this relaxation scheme and the converged t -amplitudes of the lower-order CC calculations, the t -amplitudes and energies converge, typically within a few tens of iterations for systems with wavefunctions dominated by a HF determinant (see below for exceptions). We can further accelerate the convergence by using RLE (reduced linear equation) [29] or DIIS (direct inversion in the iterative subspace) extrapolation [30] (both variants of conjugate gradient methods) or Padé approximants [23]. The process of forming the exponential wavefunctions from the

t -amplitudes becomes more and more expensive as the CC order becomes higher, and the cpu time usage of this process exceeds that of the matrix multiplication process.

3. Demonstrative calculations

The general-order CC method outlined above is implemented in the POLYMER program [31]. A determinantal FCI program which can compute the electron correlation energies at any order of truncated CI [32] and at high orders of MBPT [23,24] is also written in the POLYMER program. The total energies are calculated with the CC and CI method through FCI and the MBPT method through 20th order for H₂O and FH using the 6-31G basis set at the equilibrium bond length R_e and with bonds stretched to $1.5R_e$ and $2.0R_e$, and for F⁻ using the 6-31 + G basis set. The 1s core electrons of the O and F atoms are kept frozen in the correlation treatment. The results of these calculations are given in Tables 1–3. Although the molecules and the basis sets studied here are much smaller than those used for real chemical problems, several observations can be made which will occur in those more realistic applications as well.

Due to the variational character of the CI method, the total energies decrease uniformly as the CI order increases. However, the incremental contribution to the correlation energy from each order of CI does not decay uniformly with the CI order. The configurations with even numbers of excitations are more important than the ones with odd numbers of excitations, and the correlation energies incremented at CI(4) and CI(6) are frequently more negative than those at CI(3) and CI(5), respectively. This is primarily because the configurations with even numbers of excitations include the disconnected terms such as $T_2^2/2!$ and $T_2^3/3!$, which generally have larger contributions to correlation energies than the connected terms such as T_3 and T_5 . For all the systems studied here, the convergence of Davidson's algorithm is rapid and no more than a few tens of trial vectors are needed to form the converged ground-state wavefunctions. Since the truncated CI method is not size-extensive, the performance of the method will degrade as molecules become larger.

The incremental contributions to the correlation energies made from each order of MBPT may be negative or positive. The perturbation expansion must be carried out through more than tenth order to achieve converged correlation energies to within a micro hartree accuracy even for systems with a dominant HF determinant contribution. As bonds are stretched to $1.5R_e$ and $2.0R_e$, the restricted HF reference offers a particularly poor description and, accordingly, the convergence of the MBPT series becomes significantly slower. The anion of the F atom is a typical example in which the MBPT series does not converge when diffuse functions are included in the basis set [25,26]. Christiansen et al. [26] have identified the origin of this divergent behavior as back-door intruder states. In our example using the 6-31 + G basis set, the divergent behavior of the MBPT series manifests itself when the perturbation order reaches six. Even for this pathological case, the CI method using Davidson's algorithm is robust and achieves converged correlation energies within a few tens of iterations. This observation suggests that, by using the MBPT wavefunctions of different orders as trial vectors of the FCI procedure, we may reproduce the major part of the FCI correlation energies. This procedure (the variational perturbation method [33]), as well as Davidson's algorithm itself [32], is a variant of the reduced partitioning scheme proposed some years ago [34], and previously applied for MBPT and CI [23]. The total energies obtained from the procedure are given in Table 3. This procedure, which amounts to a variationally optimal resummation scheme of the MBPT series, yields a series of correlation energies of F⁻ rapidly converging to the FCI limit even though the underlying MBPT series is divergent. The correlation energies obtained in this way are variational upper bounds of the FCI limit, but they are no longer size-extensive unless the FCI limit of the energies is achieved. In contrast, Padé approximant resummations are not upper bounds of the FCI limit, but can be size-extensive [23]. As can be seen in the table, both the $[N, N-1]$ and $[N, N]$ Padé approximants (the procedure is described explicitly in Ref. [23]) can also make the MBPT series converge at $N \approx 5$.

The energies computed by CC theory rapidly converge to the FCI limit as the CC order increases. The absolute values of the correlation energies incre-

Table 1

Differences (in hartree) between the FCI energies and the energies obtained from the CI, MBPT, and CC theory series. The calculations are carried out for FH using the 6-31G basis set within the frozen core approximation at three selected bond lengths: $r_{\text{FH}} = R_e = 0.917 \text{ \AA}$; $r_{\text{FH}} = 1.5R_e$; $r_{\text{FH}} = 2.0R_e$. The FCI energies are $-100.114807H (R_e)$, $-100.048131H (1.5R_e)$, and $-99.979758H (2.0R_e)$. The number of determinants for FCI is 44100

Theory	R_e	$1.5R_e$	$2.0R_e$	Annotation ^a
CI(1)	0.131398	0.160174	0.202857	HF
CI(2)	0.005266	0.009677	0.019372	CISD
CI(3)	0.004701	0.007889	0.013932	CISDT
CI(4)	0.000114	0.000245	0.000531	CISDTQ
CI(5)	0.000065	0.000123	0.000210	
CI(6)	0.000001	0.000003	0.000005	
CI(7)	0.000000	0.000001	0.000000	
CI(8)	0.000000	0.000000	0.000000	FCI
MBPT(1)	0.131398	0.160174	0.202857	HF
MBPT(2)	0.003723	0.008782	0.024608	MP2
MBPT(3)	0.004932	0.011734	0.026523	MP3
MBPT(4)	0.000622	0.002446	0.007018	MP4
MBPT(5)	0.000422	0.001846	0.004885	
MBPT(6)	0.000050	0.000444	0.000113	
MBPT(7)	0.000055	0.000341	-0.000150	
MBPT(8)	0.000004	0.000053	-0.001066	
MBPT(9)	0.000007	0.000043	-0.000743	
MBPT(10)	0.000000	-0.000004	-0.000618	
MBPT(11)	0.000001	-0.000002	-0.000331	
MBPT(12)	0.000000	-0.000005	-0.000140	
MBPT(13)	0.000000	-0.000003	-0.000018	
MBPT(14)	0.000000	-0.000002	0.000054	
MBPT(15)	0.000000	-0.000001	0.000067	
MBPT(16)	0.000000	0.000000	0.000064	
MBPT(17)	0.000000	0.000000	0.000043	
MBPT(18)	0.000000	0.000000	0.000025	
MBPT(19)	0.000000	0.000000	0.000009	
MBPT(20)	0.000000	0.000000	-0.000001	
CC(1)	0.131398	0.160174	0.202857	HF
CC(2)	0.001032	0.002634	0.006007	CCSD
CC(3)	0.000350	0.000626	0.000970	CCSDT
CC(4)	0.000008	0.000020	0.000038	CCSDTQ
CC(5)	0.000002	0.000004	0.000005	
CC(6)	0.000000	0.000001	0.000000	
CC(7)	0.000000	0.000000	0.000000	
CC(8)	0.000000	0.000000	0.000000	FCI

^a Commonly used notations of the theoretical models. The CI(1), MBPT(1), and CC(1) total energies are the same as the HF energy.

mented at each order decrease monotonically by virtue of the proper inclusion of the disconnected terms. For the systems studied here, the total energies obtained from CC(4) are within a few micro hartree of the FCI limit, the connected T_5 and higher contributions being negligible. It should be noted, however, that for larger basis sets, the connected T_5

contributions are not necessarily negligible [35]. These tables clearly demonstrate the effectiveness of the exponential wavefunctions as approximations to the FCI wavefunctions. Because of the incorrect separation of the restricted HF reference, the errors are the greatest at $2.0R_e$. However, the increase in the errors upon the stretch of bonds is much less

Table 2

Differences (in hartree) between the FCI energies and the energies obtained from the CI, MBPT, and CC theory series. The calculations are carried out for H₂O using the 6-31G basis set within the frozen core approximation at three selected geometries: $r_{\text{OH}} = R_e = 0.967 \text{ \AA}$ and $a_{\text{HOH}} = 107.6^\circ$; $r_{\text{OH}} = 1.5R_e$ and $a_{\text{HOH}} = 107.6^\circ$; $r_{\text{OH}} = 2.0R_e$ and $a_{\text{HOH}} = 107.6^\circ$. The FCI energies are $-76.121174\text{H} (R_e)$, $-75.985789\text{H} (1.5R_e)$, and $-75.876474\text{H} (2.0R_e)$. The number of determinants for FCI is 245025

Theory	R_e	$1.5R_e$	$2.0R_e$	Annotation ^a
CI(1)	0.136671	0.197556	0.295881	HF
CI(2)	0.006858	0.020319	0.055476	CISD
CI(3)	0.005854	0.016243	0.045535	CISDT
CI(4)	0.000175	0.000929	0.003742	CISDTQ
CI(5)	0.000103	0.000409	0.001522	
CI(6)	0.000001	0.000010	0.000039	
CI(7)	0.000000	0.000002	0.000006	
CI(8)	0.000000	0.000000	0.000000	FCI
MBPT(1)	0.136671	0.197556	0.295881	HF
MBPT(2)	0.008215	0.020051	0.048894	MP2
MBPT(3)	0.006577	0.024159	0.066947	MP3
MBPT(4)	0.001300	0.005758	0.015235	MP4
MBPT(5)	0.000583	0.004446	0.014639	
MBPT(6)	0.000178	0.001762	0.004233	
MBPT(7)	0.000085	0.000845	-0.000270	
MBPT(8)	0.000022	0.000430	-0.000174	
MBPT(9)	0.000014	0.000156	-0.002020	
MBPT(10)	0.000003	0.000075	-0.001226	
MBPT(11)	0.000002	0.000022	-0.001001	
MBPT(12)	0.000000	0.000003	-0.000836	
MBPT(13)	0.000000	-0.000002	-0.000303	
MBPT(14)	0.000000	-0.000005	-0.000297	
MBPT(15)	0.000000	-0.000004	-0.000098	
MBPT(16)	0.000000	-0.000003	-0.000053	
MBPT(17)	0.000000	-0.000002	-0.000063	
MBPT(18)	0.000000	-0.000002	-0.000018	
MBPT(19)	0.000000	-0.000001	-0.000043	
MBPT(20)	0.000000	-0.000001	-0.000025	
CC(1)	0.136671	0.197556	0.295881	HF
CC(2)	0.001545	0.005710	0.009846	CCSD
CC(3)	0.000449	0.001200	-0.001965	CCSDT
CC(4)	0.000012	0.000097	0.000102	CCSDTQ
CC(5)	0.000003	0.000015	0.000023	
CC(6)	0.000000	0.000001	0.000001	
CC(7)	0.000000	0.000000	0.000000	
CC(8)	0.000000	0.000000	0.000000	FCI

^a Commonly used notations of the theoretical models. The CI(1), MBPT(1), and CC(1) total energies are the same as the HF energy.

acute for CC theory than for MBPT. We find that the convergence of the CC iterations based on Eq. (16) is reasonably rapid for H₂O and FH at their equilibrium geometries, but distinctly slower for H₂O and FH at $1.5R_e$ and $2.0R_e$ and for F⁻. For F⁻, the iterations for fifth and higher orders of CC theory can be divergent and the convergence of the CC(4)

iterations is extremely slow, if Eq. (16) alone is used to upgrade the t -amplitudes. There is obviously a correlation between the convergence of the CC iterations and the convergence of the MBPT series, since the latter largely defines the iterative algorithm of the former. The absolute values of the MBPT correlation contributions of F⁻ start to increase at

Table 3

Differences (in hartree) between the FCI energy and the energies obtained from the CI, MBPT, and CC theory series. The calculations are carried out for F^- with the 6-31 + G basis set within the frozen core approximation. The results obtained from the resummation of the MBPT series based on the variational perturbation method (VPCI) and Padé approximants are also given. The FCI energy is $-99.569174H$. The number of determinants for FCI is 245025

n	CI(n)	MBPT(n)	VPCI(n)	Padé[$N, N-1$]	Padé[N, N]	CC(n)
1 ^a	0.151798	0.151798	0.151798			0.151798
2	0.009614	-0.000415	0.016774			0.003662
3	0.007507	0.012780	0.003572	0.011727		0.000290
4	0.000442	-0.004349	0.000509		0.005326	-0.000040 ^b
5	0.000132	0.006661	0.000094	0.002144		-0.000005 ^b
6	0.000007	-0.006350	0.000011		-0.006088	0.000000 ^b
7	0.000001	0.007430	0.000002	0.000158		0.000000 ^b
8	0.000000 ^c	-0.008565	0.000000		-0.000087	0.000000 ^{b,c}
9		0.010318		0.000010		
10		-0.012676			0.000000	
11		0.015885		0.000000		
12		-0.020201			0.000000	
13		0.026007		-0.000001		
14		-0.033808			0.000000	
15		0.044301		0.000000		
16		-0.058422			0.000000	
17		0.077448		0.000001		
18		-0.103103			0.000000	
19		0.137726		0.000000		
20		-0.184484			0.000000	

^a The CI(1), MBPT(1), VPCI(1), and CC(1) total energies are the same as the HF energy.

^b The CC iterations are either very slowly convergent or divergent when Eq. (16) alone is used to upgrade the t -amplitudes. The energies given in the table are obtained by using the DIIS extrapolation in combination with Eq. (16), which makes the CC iterations converge within a few tens of iterations. Padé approximant resummations can also make the CC iterations converge (see text).

^c The CI(8) and CC(8) methods are identical to FCI.

MBPT(6). Interestingly, the divergent behavior of the CC iterations manifests itself at CC(4), which is correct through MBPT(6). The CC(2) and CC(3) methods, which are correct through MBPT(3) and MBPT(4), respectively, do not have any difficulty in achieving convergence with Eq. (16).

The divergence in the CC iterations encountered here, however, does not imply any intrinsic flaw in CC theory, but is pertinent to the particular scheme for upgrading the t -amplitudes. Unlike MBPT, CC theory is formally independent of the choice of the unperturbed Hamiltonian H_0 , so many alternative schemes to converge the results can be considered. Two such schemes are the RLE and DIIS extrapolation [29,30], which can make the CC iterations converge within a few tens of cycles even when the underlying CC iterations based on Eq. (16) are divergent. The CC(4) through CC(8) energies given in Table 3 are obtained with the DIIS scheme. Another

convergence acceleration scheme is provided by Padé approximants. We find that both $[N, N-1]$ and $[N, N]$ Padé approximants can make the CC iterations converge reasonably rapidly. Here we define $[N, N-1]$ and $[N, N]$ Padé approximants by Eqs. (12) to (17) of Ref. [23] and $E(n)$ appearing in these equations is understood to represent the increment in the CC energy obtained from the n -th CC iteration based on Eq. (16) of this paper. For example, $[5,4]$ and $[5,5]$ Padé approximants extrapolate the CC(4) total energy to be -99.569214 hartree and $[11,10]$ and $[11,11]$ Padé approximants extrapolate the CC(6) total energy to be -99.569175 hartree, which agree with the corresponding CC energies obtained from the DIIS extrapolation. The advantage of Padé approximants over the RLE/DIIS scheme is that Padé approximants use only the series of CC energies, while the latter requires the t -amplitudes and the residual vectors used in several previous CC itera-

tions, which have to be stored externally. The RLE/DIIS scheme, on the other hand, extrapolates the t -amplitudes rather than the CC energies and we can confirm that the wavefunction obtained with the extrapolated t -amplitudes satisfy the proper convergence criteria (in this case, the norm of the residual vector is less than the preset tolerance).

Note added in proof

A related FCI to CC method was reported by J. Olsen at the Strasbourg meeting in Poland, September 1999.

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