Theor Chem Acc (1997) 98:75–84

Theoretical
Chemistry Accounts

CCSD(T) expectation value calculations of first-order properties

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Received: 15 May 1997 / Accepted: 5 June 1997

Abstract. An expectation value approach to calculations of first-order properties using the non-iterative, triple-excitation amplitudes in the coupled cluster wave function is exploited. Three methods are suggested and analysed using the many body perturbation theory (MBPT) expansion arguments. The first method, in which non-iterative triple-excitation amplitudes are used in the expression for the expectation values, makes the wave function accurate through the second order of MBPT. In the second method, which is an extension of the first, effects of triple-excitation amplitudes are coupled with single- and double-excitation amplitudes. The correlated density matrix equivalent through the fourth order to that obtained when CCSDT-la amplitudes are used is employed in the third method. The suggested methods are tested on dipole moment and polarizability calculations for several diatomic closed-shell molecules and are compared to other related approaches.

Key words: CCSD(T) expectation value calculations – First-order properties

1 Introduction

Since the advent of quantum chemistry there have been many attempts to describe electric and magnetic properties of atoms and molecules. Although nowadays we can perform calculations of higher-order properties, the question of inexpensive and accurate calculations of first-order properties still remains. There are two traditional ways to attack this problem. The first is based on a definition of the first-order properties as a differentiation of the total energy of a molecule with respect to an external field. The second uses the wave function of the system in expectation value calculations. Differentiation of the energy can be performed either numerically or analytically. However, in the case of the numerical differentiation (FPT method) we need to perform at least two very accurate high-level energy calculations for the first-order property which is often time consuming. It is usually more convenient to differentiate analytically, but this also places high demands on computer time and memory. A very general formulation of analytical energy derivatives within the couple cluster (CC) theory is presented in [1–3]. Calculations based on the perturbation theory also belong to this category. At the correlation level we distinguish a double-perturbation approach with the perturbation involving the correlation term and the term corresponding to an external field. This method is equivalent to calculation of correlation corrections made to the results of Dalgarno's uncoupled Hartree-Fock perturbation scheme [4, 5]. Another perturbative approach is based on the evaluation of correlation effects to coupled perturbed Hartree-Fock (CPHF) theory [4–6].

In the framework of the CC method [7], alternative approaches to the energy derivative calculations have been suggested following the philosophy of the linear response theory pioneered by Monkhorst [8]. These were expanded upon by Salter et al. [9], Arponen [10] and the Danish group [11]. The orthogonally spin-adapted linear response CC theory was recently developed by Kondo, Paldus et al. [12]. Their approach also allows calculation of higher-order properties. Closely related to the present work are the papers published by Pal and his group [13] and more recently by Ghose [14]. In general, one can consider the response theory approaches as an alternative formulation of the CC theory, mostly oriented towards the energy functionals from which CC amplitudes and/or derivative amplitudes are calculated from the stationary principle. A series of functionals was introduced and carefully analysed by Kutzelnigg [15] and Bartlett et al. [16]. A thorough comparison and analysis of the linear response approaches from the perturbative viewpoint was recently published by Nooijen and Snijders [17].

In this paper we have focused on calculations of the first-order properties as expectation values of one-electron operators associated with specific properties. In comparison to both numerical and analytical derivative

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methods, the expectation value approach is presumably less time-consuming, since it only requires one energy (and related wave function) calculation followed by the construction of a density matrix. What we need in this case is a sufficiently accurate wave function (or density matrix) describing a molecule in a specific state. According to the Hellman-Feynman theorem, the definitions of first-order properties as a differentiation of the energy and as the expectation value of the operator of this property are only equivalent for fully variational wave functions and exact eigenfunctions of the Hamiltonian. Since the former definition is physically closer to experimental techniques, we first try to find an appropriate level of calculation for the energy differentiation. Then, in the expectation value calculation we construct a density matrix from the corresponding wave function, calculate the expectation value, and analyse the difference between both values. If our trial function approximates the eigenfunction of the Hamiltonian accurately enough the difference should be negligible.

Noga and Urban [18] investigated the possibility of using CC wave function in the expression for the expectation value of a first-order property. They assessed the accuracy of wave functions at different levels of the CC method by comparing their results with those obtained by FPT calculations. They concluded that the CCSD method leads to qualitatively satisfactory estimations, but there are many cases where the inclusion of triple excitations is unavoidable. The price to pay in the case of iterative versions of CCSDT is a higher computational demand. Therefore, non-iterative approaches – CCSD+T(CCSD) and CCSD(T) [19, 20] that approximate the effects of triple excitations have been suggested. These mostly provide accurate energies, but the wave function cannot be uniquely defined.

This work investigates substituting converged triple-excitation amplitudes with the non-iterative T_3 amplitudes in the expression for the expectation value of a first-order property, as well as addressing some remarks on the accuracy of the wave function. This can be quite successfully assessed by its ability to provide reliable molecular properties.

2 Theory

2.1 CC method

The CC theory has been nicely presented in recent reviews by Paldus [21] and Bartlett [22]. For the purpose of our analysis we will briefly summarize the basic principles. A common feature of all CC methods is the exponential expansion of the wave function

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

where $|\Phi\rangle$ is a reference state and $\mathbf{T}$ is the cluster operator for N electrons

$$\mathbf{T} = T_1 + T_2 + \cdots + T_N = \sum_{\alpha=1}^{N} T_\alpha \ , \tag{2}$$

$$T_\alpha = \frac{1}{(\alpha!)^2}\sum_{\substack{ij\ldots\\ ab\ldots}} t^{ab\ldots}_{ij\ldots}\left\{a^+ ib^+ j\ldots\right\} \ . \tag{3}$$

The sum runs over the various α-tuple excitations; $t^{ab\ldots}_{ij\ldots}$ are anti-symmetrized cluster amplitudes and the symbol $\{\}$ represents a normal product of creation and annihilation operators. The indices $i, j, \ldots$ denote spin orbitals which are occupied in the reference function and the indices $a, b, \ldots$ correspond to the virtual spin orbitals.

This exponential formulation guarantees the size extensivity of the CC methods even with a truncated cluster operator, and inclusion of higher excitations gives the CC theories on advantage over traditional approximate CI methods.

Considering the intermediate normalization ($\langle\Phi|\Psi\rangle = 1$) the correlation energy for the standard CC methods is given as:

$$\Delta\mathbf{E}_{\mathrm{CC}} = \left\langle\Phi\middle|\mathbf{e^{-T}H}_N\mathbf{e^T}\middle|\Phi\right\rangle = \left\langle\Phi\middle|\left(\mathbf{H}_N\mathbf{e^T}\right)_C\middle|\Phi\right\rangle \ , \tag{4}$$

where $\mathbf{H}_N$ is a normal-ordered second quantized Hamiltonian and index C indicates that only connected terms are to be taken into account within the diagrammatic representation. Cluster amplitudes are determined by solving CC equations:

$$\langle\Phi^{ab\ldots}_{ij\ldots}|(\mathbf{H}_N\mathbf{e^T})_C|\Phi\rangle = 0 \ , \tag{5}$$

where $\langle\Phi^{ab\ldots}_{ij\ldots}|$ is a Hermitian conjugated bra-state to the excited determinant

$$|\Phi^{ab\ldots}_{ij\ldots}\rangle = a^+ ib^+ j\ldots|\Phi\rangle \ . \tag{6}$$

A disadvantage of the standard truncated CC methods is that they are not variational. It means that the $\mathbf{T}$ amplitudes being solutions of CC Eqs. (4) and (5) do not minimize the expectation value energy functional

$$\Delta\mathbf{E}_X = \frac{\langle\Phi|\mathbf{e^{T^+}}\mathbf{H}_N\mathbf{e^T}|\Phi\rangle}{\langle\Phi|\mathbf{e^{T^+}}\mathbf{e^T}|\Phi\rangle} \ . \tag{7}$$

If the cluster operator $\mathbf{T}$ is complete, Eqs. (4) and (5) give the *exact* result equivalent to a full CI result. In fact we construct the expectation value functional in Eq. (7) for the truncated cluster operator $\mathbf{T}$ with amplitudes obeying Eq. (5), but then the energy eigenvalue differs from the expectation value of energy. The difference is due to excitations, which are not considered in $\mathbf{T}$ and do not satisfy Eq. (5) and can be expressed as follows [8]:

$$\Delta\mathbf{E}_X - \Delta\mathbf{E}_{\mathrm{CC}} = {\sum_a}' \frac{\left\langle\Phi\middle|\mathbf{e^{T^+}}\mathbf{e^T}\middle|\Phi^a\right\rangle\left\langle\Phi^a\middle|\mathbf{e^{-T}H}_N\mathbf{e^T}\middle|\Phi\right\rangle}{\langle\Phi|\mathbf{e^{T^+}}\mathbf{e^T}|\Phi\rangle} \ , \tag{8}$$

where the sum runs over all excitations for which Eq. (5) is not satisfied. If we compare the expectation-value calculations of properties with energy-derivative calculations, we have to keep in mind that we differentiate the CC energy from Eq. (4) which, in general, is not the expectation value for the energy.

2.2 CC methods with non-iterative triples

According to the truncation of the $\mathbf{T}$ operator one distinguishes the different levels of the CC methods. Although the CCSD method [23] which corresponds to $\mathbf{T} = T_1 + T_2$ has been shown to be an accurate method for a wide spectrum of correlation problems, there are many cases where the inclusion of triple excitations effects is necessary. Since the full CCSDT [24] is extremely computationally demanding, simpler versions based on a restriction of the exponential expansion of the wave operator $\mathbf{e}^{\mathbf{T}}$ have been suggested first [19, 25, 26]. However, even the simplest version of CCSDT, i.e. CCSDT-1 [25], requires $\sim \mathbf{n}_{\mathrm{occ}}^3 \mathbf{n}_{\mathrm{virt}}^4$ operations in each iteration. Therefore, using the philosophy of the MBPT, non-iterative methods to treat the effects of triple excitations have been introduced. In CCSD + T(CCSD) [19] the T(CCSD) correction formally corresponds to fourth-order MBPT energy due to triple excitations:

$$\mathbf{E}_{\mathbf{T}}^{(4)} = -\langle\Phi|T_3^{+}\mathbf{F}_N T_3|\Phi\rangle \tag{9a}$$

$$-(\mathbf{F}_N T_3)_C|\Phi\rangle = (\mathbf{W}_N T_2)|\Phi\rangle \tag{9b}$$

where $\mathbf{F}_N$ is the normal-ordered Fock operator and $\mathbf{W}_N = \mathbf{H}_N - \mathbf{F}_N$. Unlike in MBPT(4), T_2 amplitudes in Eq. (9b) are not of the first order, but the result from the solution of CCSD. Since from numerical experience it follows that T(CCSD) often overestimates the effects of triple excitations, a more established CCSD(T) method has been suggested [20] which formally includes all the fifth-order terms covered by CCSDT-1a. In addition to T(CCSD), the correction includes the fifth-order term

$$\mathbf{E}_{\mathrm{ST}}^{(5)} = -\langle\Phi|\left(T_1^{+}\mathbf{W}_N T_3\right)_C|\Phi\rangle \tag{9c}$$

where T_3 is again defined by Eq. (9b). Although in both methods we deal with a certain set of CC amplitudes, the final energy expression can be considered as a combination of the two approaches – CC and MBPT. This is the reason why the wave function is not precisely defined. What we can do, however, is to use the non-iterative T_3 amplitudes to construct a certain wave function or density matrix and test their accuracy say by comparing the expectation value of a first-order property with the CCSD(T) energy derivative. A small difference between the two is at least a plausible indication of the accuracy of such a constructed wave function.

2.3 CC calculations of first-order properties

2.3.1 Analytic derivative of energy

It is not the purpose of this paper to give a full description of analytical gradient methods in the frame of CC theory, but since there is a close relation between CCSD(T) formulation of λ-equations [1, 27, 28] and the construction of the non-relaxed CCSD(T) density matrix in the expectation value approach, we will briefly present a basic outline of the CCSD(T) gradient method. Derivative of the triple-excitation contribution in the CCSD(T) method for the case of canonical UHF orbitals is of the form:

$$\begin{aligned}\frac{\partial \mathbf{E}_{\mathbf{T}}}{\partial\chi} =& \sum_a \mathrm{D}_a \frac{\partial\varepsilon_a}{\partial\chi} + \sum_i \mathrm{D}_i \frac{\partial\varepsilon_i}{\partial\chi} + \sum_{ia} \mathrm{s}_i^a \frac{\partial \mathrm{t}_i^a}{\partial\chi} \\ &+ \frac{1}{4}\sum_{ijab} \mathrm{s}_{ij}^{ab} \frac{\partial \mathrm{t}_{ij}^{ab}}{\partial\chi} + \sum_{pqrs} \Gamma(pq,rs)\frac{\partial\langle pq\|rs\rangle}{\partial\chi} \ .\end{aligned} \tag{10}$$

For exact definitions of the one- and two-electron density matrices D and Γ see Watts et al. [27]. Quantities s_i^a and s_{ij}^{ab} are defined as follows:

$$\mathrm{s}_i^a = \frac{1}{4}\sum_{bcjk} \mathrm{t}(c)_{ijk}^{abc}\langle bc\|jk\rangle \ , \tag{11a}$$

$$\begin{aligned}\mathrm{s}_{ij}^{ab} = \frac{1}{2}\Bigg(&\sum_{efk} \mathbf{P}(ab)\langle bk\|ef\rangle\left[2\mathrm{t}(c)_{ijk}^{aef} + \mathrm{t}(d)_{ijk}^{aef}\right] \\ &- \sum_{mnc} \mathbf{P}(ij)\langle mn\|jc\rangle\left[2\mathrm{t}(c)_{imn}^{abc} + \mathrm{t}(d)_{imn}^{abc}\right]\Bigg) \ ,\end{aligned} \tag{11b}$$

where the connected and disconnected triple-excitation amplitudes are given respectively by

$$\begin{aligned}\widetilde{\mathrm{D}}_{ijk}^{abc}\mathrm{t}(c)_{ijk}^{abc} =& \sum_e \mathbf{P}(i/jk)\mathbf{P}(a/bc)\mathrm{t}_{jk}^{ae}\langle bc\|ei\rangle \\ &+ \sum_m \mathbf{P}(i/jk)\mathbf{P}(a/bc)\mathrm{t}_{mi}^{bc}\langle jk\|ma\rangle\end{aligned} \tag{12}$$

and

$$\widetilde{\mathrm{D}}_{ijk}^{abc}\mathrm{t}(d)_{ijk}^{abc} = \mathbf{P}(i/jk)\mathbf{P}(a/bc)\mathrm{t}_i^a\langle bc\|jk\rangle \ . \tag{13}$$

The permutation operators are defined by

$$\mathbf{P}(p/qr) = 1 - (pq) - (pr) \ , \tag{14}$$

where (pq) means permutation of indices p and q. $\widetilde{\mathrm{D}}_{ijk}^{abc}$ is given by

$$\widetilde{\mathrm{D}}_{ijk}^{abc} = \varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c \ , \tag{15}$$

where ε_p are the UHF orbital energies.

As for the amplitude derivatives in Eq. (10), their evaluation is not necessary. Instead, one has to solve a set of perturbation independent linear Λ-equations. Formally the Λ-equations for the CCSD method can be written as

$$F_1\left(\lambda_i^a, \lambda_{ij}^{ab}\right) = 0 \tag{16}$$

and

$$F_2\left(\lambda_i^a, \lambda_{ij}^{ab}\right) = 0 \ , \tag{17}$$

where the terms included in the functions F_1 and F_2 are defined in [1]. When triple excitations are added, they become

$$F_1\left(\lambda_i^a, \lambda_{ij}^{ab}\right) = \mathrm{s}_i^a \tag{18}$$

and

$$F_2\left(\lambda_i^a, \lambda_{ij}^{ab}\right) = \mathrm{s}_{ij}^{ab} \ . \tag{19}$$

As we can see, s_i^a and s_{ij}^{ab} represent the first approximations of the triple-excitation contributions to Λ-amplitudes. Through these quantities a coupling of non-iterative T_3 amplitudes with those of Λ_1 and Λ_2 is introduced. Thus, although in the expression for CCSD(T) energy no coupling of T_3 amplitudes with those of T_1 and T_2 is introduced by definition, the energy derivative does depend on such coupling.

Having the solutions of Eqs. (18) and (19) we add CCSD contributions to one- and two-electron density matrices. Then the expression for the CCSD(T) gradient has the form:

$$\frac{\partial \mathbf{E}}{\partial \chi} = \sum_a \mathrm{D}_a \frac{\partial \varepsilon_a}{\partial \chi} + \sum_i \mathrm{D}_i \frac{\partial \varepsilon_i}{\partial \chi} + \sum_{pqrs} \Gamma(pq, rs) \frac{\partial \langle pq \| rs \rangle}{\partial \chi} \quad . \tag{20}$$

MO integral and orbital-energy derivatives can be divided into AO and MO contributions. After eliminating CPHF coefficients by the *z*-vector method [29] we arrive at a final expression for the energy gradient which, for zero AO derivatives, has the following form:

$$\frac{\partial \mathbf{E}}{\partial \chi} = \sum_{pq} \mathrm{D}_{pq} \mathrm{h}^{\chi}_{pq} \quad , \tag{21}$$

where D_{pq} is the total relaxed density matrix given as the sum of amplitude and orbital-response contributions, and h^{χ}_{pq} is the Hamiltonian derivative matrix element in the MO basis.

2.3.2 Expectation value calculations

The general ideas presented in this section originate from the pioneering work of Čížek [30] and Monkhorst [8]. Let us have a system, which is exposed to an external field. For such a system the Hamiltonian can be written in the form:

$$\hat{\mathbf{H}}(\chi) = \hat{\mathbf{H}}(0) + \chi \hat{\mathbf{O}} \quad . \tag{22}$$

We can express the energy of this system as an expectation value for the externally perturbed wave function $\Psi(\chi)$:

$$\mathbf{E}(\chi) = \frac{\langle \Psi(\chi) | \mathbf{H}(\chi) | \Psi(\chi) \rangle}{\langle \Psi(\chi) | \Psi(\chi) \rangle} \quad . \tag{23}$$

Property corresponding to the operator $\hat{\mathbf{O}}$ can be obtained by differentiating Eq. (23) at $\chi = 0$:

$$\left. \frac{d\mathbf{E}}{d\chi} \right|_{\chi=0} = \frac{\langle \Psi(0) | \hat{\mathbf{O}} | \Psi(0) \rangle}{\langle \Psi(0) | \Psi(0) \rangle} + \frac{2}{S} \langle \Psi(0) | [\mathbf{H}(0) - \mathbf{E}(0)] \left| \frac{d\Psi(\chi)}{d\chi} \right\rangle \Bigg|_{\chi=0} \quad , \tag{24}$$

where (0) refers to the unperturbed system and S is the overlap:

$$S = \langle \Psi(0) | \Psi(0) \rangle \quad . \tag{25}$$

The first term in Eq. (24) represents the expectation value of the operator $\hat{\mathbf{O}}$. The second term, the so-called non-Hellmann-Feynman term (non-HF term), does not in general vanish for approximate non-variational wave functions. However, it can be negligible for highly accurate wave functions. Noga and Urban [18] have shown that for the CC wave functions with the truncated cluster operator **T** the non-HF term can be expressed as follows:

$$\langle \Psi(0) | [\mathbf{H}(0) - \mathbf{E}(0)] \left| \frac{d\Psi(\chi)}{d\chi} \right\rangle \Bigg|_{\chi=0} = \sum_a{}' c_a \langle \Phi(0)_a | \mathbf{e}^{-\mathbf{T}} \mathbf{H} \mathbf{e}^{\mathbf{T}} | \Phi(0) \rangle \quad , \tag{26}$$

where the sum runs over all excitations which are not included in **T**.

Let us now turn back to the expression for the expectation value of the operator $\hat{\mathbf{O}}$. For CC wave functions even with truncated **T** it can be expressed in terms of connected contributions only [30]:

$$\langle \hat{\mathbf{O}} \rangle = \frac{\langle \Phi | \mathbf{e}^{\mathbf{T}^+} \hat{\mathbf{O}} \mathbf{e}^{\mathbf{T}} | \Phi \rangle}{\langle \Phi | \mathbf{e}^{\mathbf{T}^+} \mathbf{e}^{\mathbf{T}} | \Phi \rangle} = \langle \Phi | \mathbf{e}^{\mathbf{T}^+} \hat{\mathbf{O}} \mathbf{e}^{\mathbf{T}} | \Phi \rangle_C \quad . \tag{27}$$

Equation (27) only holds for the complete (i.e. infinite) expansion. Nevertheless, we can choose a truncation that leads to errors which are of a higher order in the MBPT expansion than those introduced by the approximation of the wave function itself.

We can summarize the reasons why $\langle \hat{\mathbf{O}} \rangle$ deviates from the energy eigenvalue differentiation for CC wave functions with a truncated **T**-operator as follows:

1. The CC energy eigenvalue is not equal to the energy expectation value.
2. The non-HF term is non-zero.
3. Truncation of the infinite expansion in Eq. (27) is necessary.

To put the truncation of Eq. (27) on a reasonable base, Noga and Urban [18] suggested employing MBPT logic and decided to retain all second-order terms of the wave function (i.e. terms which are exact through the second order in MBPT expansion) on both sides of the operator $\hat{\mathbf{O}}$. We shall denote this approach as WF(2). For the CCSDT method and its approximations they obtained the following expression:

$$\langle \hat{\mathbf{O}} \rangle_{\mathrm{WF(2)}} = \langle \Phi | \left(1 + T_2^+ + \tfrac{1}{2} T_2^+ T_2^+ + T_1^+ + T_3^+\right) \times \hat{\mathbf{O}} \left(1 + T_2 + \tfrac{1}{2} T_2 T_2 + T_1 + T_3\right) | \Phi \rangle_C \quad . \tag{28}$$

In the context of the stationary CC response approach Pal and his group [13] and Ghose [14] used slightly different criterion for the truncation of the expectation value expression. They distinguish linear, quadratic and cubic truncation of the exponential expansion of the CC wave function.

With the aim to improve the accuracy of the correlated density matrix coming from Eq. (28), Urban et al. [31] later suggested adding another term:

$$\langle \Phi | T_2^+ \hat{\mathbf{O}} T_1 T_2 | \Phi \rangle_C + \text{Hermitian conjugated term} \quad . \tag{29}$$

The resulting density matrix is exact through the fourth order of the MBPT only if the amplitudes come from full CCSDT (or at least from CCSDT-4 [19]). Using lower versions of CCSDT, the density matrix constructed according to Eqs. (28) and (29) does not necessarily contain all the fourth-order MBPT density matrix terms. Thus, when assessing the accuracy of the density matrix, the accuracy of the amplitudes has to be taken into account. A comparison with MBPT calculations of electric properties as proposed by Caves and Karplus [6] is topical. Accuracy of the amplitudes is particularly important if non-iterative methods are used.

2.3.3 Expectation value calculations with non-iterative triples

Non-iterative triple-excitation amplitudes in CCSD(T) Eq. (9b) are equivalent through the second order of the MBPT to those obtained iteratively by any of the CCSDT-n variants lower than CCSDT-4. Seemingly, both WF(2)-CCSD(T) and WF(2)-CCSDT-n should provide qualitatively comparable results, while the former is computationally much cheaper. Unfortunately, as will be seen in Sect. 3, the WF(2)-CCSD(T) method often leads to only slight improvement of CCSD results and completely fails to describe the dependence of the dipole moment on interatomic distance, for example for the CO molecule.

The reason for this can be found by a more detailed analysis of the correlated density matrix constructed from the iterative and non-iterative CC wave functions. Let us consider the CCSDT-1 wave function. Such a function is "only" exact through the second order of MBPT, the resulting density matrix contains most of the third- and fourth-order terms, which are important but which are not included within the non-iterative approach. Unfortunately, to calculate a density matrix exactly through the fourth order requires N^8 processes (vide infra), which for realistic systems would be unbearable. Nevertheless, even if the CCSDT-1a density matrix is not exact through the fourth order, the expectation values are in a very good agreement with the corresponding energy derivatives. We deduce that the strength of the approximate iterative versions of the CCSDT method lies in the fact that they offer "balanced" wave functions. Consequently, we do not strictly follow particular orders of the wave function and/or density matrix, but rather take the MBPT order criterion as a starting-point followed by an attempt to find a balanced correlated density matrix.

The absence of the coupling of T_3 amplitudes with those of T_1 and T_2 is the most important difference between non-iterative and iterative approaches. One argument for inclusion of such coupling in constructing the correlated density matrix comes from the analysis of the CCSD(T) analytic gradient approach. The CCSD(T) energy does not directly depend on such coupling, in the case of gradient calculation the coupling of T_3 with Λ_1 and Λ_2 amplitudes is introduced. Taking the interaction of T_3 amplitudes with those of T_1 and T_2 into account plays an important role in obtaining more accurate approximation of the expression for the expectation value. Thus, to improve the WF(2)-CCSD(T) density matrix we decided to add all the third- and fourth-order terms, in which the coupling of the non-iterative T_3 amplitudes with T_1 as well as T_2 amplitudes occurs

$$\begin{aligned}\langle\hat{\mathbf{O}}\rangle^{\mathrm{CCSD(T)}}_{\mathrm{WF(3)}} = {} & \langle\hat{\mathbf{O}}\rangle^{\mathrm{CCSD(T)}}_{\mathrm{WF(2)}} + \left\langle\Phi|T_2^{+}\hat{\mathbf{O}}T_2^{(3)}|\Phi\right\rangle_C \\ & + \left\langle\Phi|\hat{\mathbf{O}}T_1^{(3)}|\Phi\right\rangle_C + \left\langle\Phi|T_2^{+}\hat{\mathbf{O}}T_1^{(3)}|\Phi\right\rangle_C \\ & + \left\langle\Phi|T_2^{+}T_1^{+}\hat{\mathbf{O}}T_2|\Phi\right\rangle_C \\ & + \text{Hermitian conjugate} \ , \end{aligned} \qquad (30)$$

where $\langle\hat{\mathbf{O}}\rangle^{\mathrm{CCSD(T)}}_{\mathrm{WF(2)}}$ corresponds to Eq. (28) if non-iterative T_3 amplitudes are used. T_1 and T_2 are converged CCSD amplitudes and $T_1^{(3)}$ and $T_2^{(3)}$ are defined as follows

$$-(\mathbf{F}_N T_1^{(3)})_C|\Phi\rangle = (\mathbf{W}_N T_3)_C|\Phi\rangle \ , \qquad (31a)$$

$$-(\mathbf{F}_N T_2^{(3)})_C|\Phi\rangle = (\mathbf{W}_N T_3)_C|\Phi\rangle \ . \qquad (31b)$$

The diagrammatic representation of the terms in Eq. (30) is shown in Fig. 1.

Our T_1 and T_2 amplitudes are now accurate through the third order. Correspondingly, we denote this extended CCSD(T) expectation value approach as WF(3)-CCSD(T). To get the wave function exactly through the third order we would have to project the term $|(\mathbf{H}_N T_3)_C|\Phi\rangle$ onto T_3 subspace which would mean per-

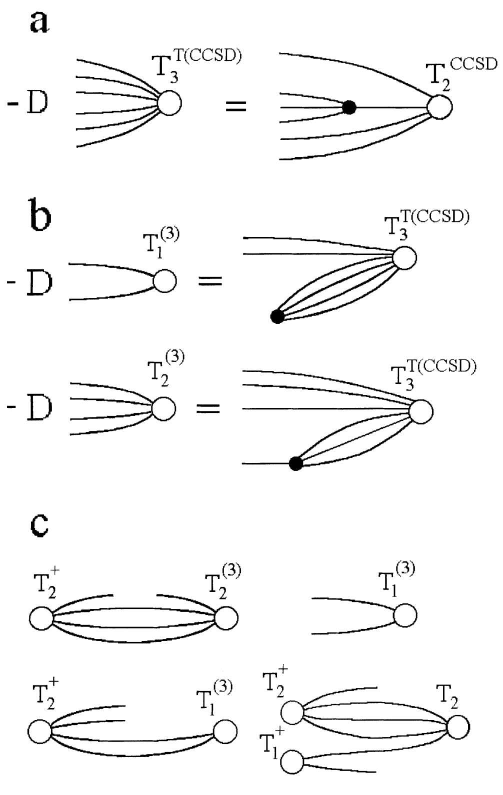

Fig. 1. a Schematic definition of the non-iterative $T_3^{\mathrm{T(CCSD)}}$ amplitudes. **b** Definition of the third-order contributions to the T_1 and T_2 amplitudes denoted as $T_1^{(3)}$ and $T_2^{(3)}$, respectively. **c** Diagrammatic representation of the third- and fourth-order correlation contributions to the WF(3)-CCSD(T) density matrix, which are added to the WF(2)-CCSD(T) density matrix terms coming directly from Eq. (28). The last diagram is the representation of Eq. (29). Diagrams of the Hermitian conjugates are not presented. *D* represents the denominator corresponding to the amplitude

forming N^8 operations. Such a projection, however, first appears in the CCSDT-4. Moreover, the analysis of the diagrammatic representation of the CCSD(T) analytical gradient method does not refer to such a contribution from T_3 amplitudes. These are the reasons why we do not consider this step essential in constructing the CCSD(T) correlated density matrix.

If we compare the definitions of $T_1^{(3)}$ and $T_2^{(3)}$ amplitudes (Fig. 1) with quantities s_i^a and s_{ij}^{ab} and (Eq. 11), we realize that the former represent that part of the latter, which comes from the connected T_3 amplitudes (Eq. 12). The second part, having its origin in the disconnected T_3 amplitudes, is already included in the converged CCSD T_2 amplitudes.

Within the non-iterative approaches we have also tried to use a density matrix equivalent through the fourth order to that obtained from CCSDT-1a. This requires addition of two more terms (which are easy to calculate) to the WF(3)-CCSD(T) density matrix (see Fig. 2):

$$\langle\hat{\mathbf{O}}\rangle^{\mathrm{CCSD(T)}}_{\mathrm{DM(4)}} = \langle\hat{\mathbf{O}}\rangle^{\mathrm{CCSD(T)}}_{\mathrm{WF(3)}} + \langle\Phi|\hat{\mathbf{O}}T_1^{(4a)}|\Phi\rangle_C + \langle\Phi|\hat{\mathbf{O}}T_1^{(4b)}|\Phi\rangle_C + \text{Hermitian conjugate} \ , \tag{32}$$

where $T_1^{(4a)}$ and $T_1^{(4b)}$ are defined as follows

$$-(\mathbf{F}_N T_1^{(4a)})_C|\Phi\rangle = (\mathbf{W}_N T_2^{(3)})_C|\Phi\rangle \ , \tag{33a}$$

$$-(\mathbf{F}_N T_1^{(4b)})_C|\Phi\rangle = (\mathbf{W}_N T_1^{(3)})_C|\Phi\rangle \ . \tag{33b}$$

This method is denoted as DM(4)-CCSD(T). Most likely due to the non-balanced accuracy of T_1 and T_2 amplitudes, the DM(4)-CCSD(T) method does not always give accurate results (see Sect. 3).

The main goal of developing CC expectation value calculations is to obtain a method less expensive than analytical or numerical derivative approaches, but still providing highly accurate results. Let us then summarize the computational demands of these methods. The most time-consuming step is calculation of the non-iterative T_3 amplitudes and the term $\langle\Phi|T_3^+\hat{\mathbf{O}}T_3|\Phi\rangle_C$ in all suggested methods. Both steps require N^7 operations. Moreover, WF(3)-CCSD(T) and DM(4)-CCSD(T) approaches require computation of $T_2^{(3)}$ amplitudes which is also a N^7 process. Thus, in comparison to the CCSD(T) analytic gradient approach the latter methods contain the same number of N^7 operations, but solving of modified CCSD Λ-equations iteratively is not necessary.

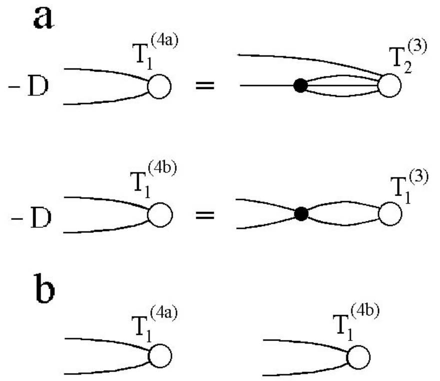

Fig. 2. a Definition of the fourth-order contributions to the T_1 amplitudes denoted as $T_1^{(4a)}$ and $T_1^{(4b)}$. **b** Diagrammatic representation of the fourth-order correlation contributions to the DM(4)-CCSD(T) density matrix. These have to be added to the WF(3)-CCSD(T) density matrix terms so as to obtain a density matrix equivalent, through the fourth order, to that of the CCSDT-1a method. Diagrams of the Hermitian conjugates are not presented

3 Numerical results and discussion

We have performed WF(2)-CCSD(T), WF(3)-CCSD(T), and DM(4)-CCSD(T) calculations of dipole moments and also calculations of dipole polarizabilities computed as first derivatives of the induced dipole moments. As our test examples we selected several diatomic closed-shell molecules and compared our results with those obtained by CCSD and CCSDT-1a expectation value methods and with numerical derivatives of CCSD, CCSD + T(CCSD), CCSD(T) and CCSDT-1a energies. It should be mentioned that the CCSD(T) method often gives better results than CCSDT-1a [32]. Wherever available, we compare the results with experimental values even if the difference between experimental and theoretical values is most likely affected by using restricted basis sets. All calculations were performed for equilibrium geometries.

In Table 1 we present the results of SCF- and CC-energy calculations for all the molecules investigated.

3.1 Dipole moment and polarizability of HF molecule

Tables 2 and 3 show the results of dipole-moment calculations in which Sadlej's [33] polarized basis set $[5s3p2d/3s2p]$ was used. It is seen that practically all computed values lie within the range of experimental

Table 1. SCF and CC energies. All calculations were performed at equilibrium geometries: HF molecule, $r = 1.733$ $[5s3p2d/3s2p]$ basis set; CO molecule, $r = 2.13161$ $[6s4p1d]$; BeO molecule, $r = 2.5149$, $[5s3p2d]$; HCN molecule, $r = 2.17885$ $[5s3p2d/3s2p]$. Atomic units are used and all electrons were correlated

Method	HF	CO	BeO	HCN
SCF	−100.053 464	−112.776 005	−89.429 153	−92.902 208
CCSD	−100.282 674	−113.122 003	−89.703 869	−93.241 138
CCSD + T(CCSD)	−100.287 318	−113.137 369	−89.718 657	−93.257 859
CCSD(T)	−100.286 571	−113.135 674	−89.714 158	−93.257 031
CCSDT-1a	−100.287 165	−113.137 309	−89.718 857	−93.257 813

data. Hence, we assess the accuracy of our proposed methods by comparison with CCSD(T) and CCSDT-1 energy derivatives.

First, let us note that there is a relatively large discrepancy between the numerical CCSD energy derivative and the expectation value for the dipole moment. This has been observed before [18], and implies that the CCSD wave function is “too far” from being exact. Let us stress that the CCSD wave function is only correct through the first order in the sense of MBPT. Inclusion of iterative triple excitations at the CCSDT-1a level leads to significant improvement of the results for both derivative- and expectation-value approaches. The difference between them is negligible.

Despite the fact that the WF(2)-CCSD(T) approach gives better results than the CCSD method, the improvement does not correspond to what we would have expected from the wave function through the second order. Much better results, practically comparable with CCSD(T) and CCSDT-1 numerical derivatives, can be obtained by the WF(3)-CCSD(T) approach. The DM(4)-CCSD(T) method also provides quite accurate results.

Table 2. Total values and some particular correlation contributions to the dipole moments calculated as the expectation value using SCF, CCSD and non-iterative CC density matrices. The geometries and basis sets as defined in Table 1 are used. All values are in a.u.

Method contribution	HF	CO	BeO	HCN
SCF	0.757	0.119	2.946	1.294
CCSD	0.688	−0.121	2.290	1.152
WF(2)-CCSD(T)	0.692	−0.097	2.321	1.162
$\langle\Phi\vert T_3^+\hat{O}T_3\vert\Phi\rangle_C$	−0.001	−0.007	−0.028	−0.003
$\Phi\vert T_2^+T_2^+\hat{O}T_3\vert\Phi\rangle_C + \langle\Phi\vert T_2^+\hat{O}T_3\vert\Phi\rangle_C + HC^{\mathrm{a}}$	0.006	0.031	0.060	0.013
WF(3)-CCSD(T)	0.703	−0.052	2.365	1.175
$\langle\Phi\vert T_2^+\hat{O}T_2^{(3)}\vert\Phi\rangle_C + HC^{\mathrm{a}}$	−0.003	−0.019	−0.084	−0.010
$\langle\Phi\vert\hat{O}T_1^{(3)}\ \vert\Phi\rangle_C + HC^{\mathrm{a}}$	0.018	0.082	0.179	0.020
$\langle\Phi\vert T_2^+\hat{O}T_1^{(3)}\vert\Phi\rangle_C + HC^{\mathrm{a}}$	−0.003	−0.018	−0.043	−0.004
$\langle\Phi\vert T_2^+T_1^+\hat{O}T_2\vert\Phi\rangle_C + HC^{\mathrm{a}}$	−0.001	0.000	−0.008	0.007
DM(4)-CCSD(T)	0.696	−0.099	2.226	1.159
$\langle\Phi\vert\hat{O}T_1^{(4a)}\vert\Phi\rangle_C + HC^{\mathrm{a}}$	−0.007	−0.047	−0.153	−0.019
$\langle\Phi\vert\hat{O}T_1^{(4b)}\vert\Phi\rangle_C + HC^{\mathrm{a}}$	0.000	0.001	0.014	0.003

[a] Hermitian conjugate

Table 3 also contains polarizabilities computed as the first derivatives of the induced dipole moment expectation values and the second derivatives of the total energy of a molecule with respect to the external field. This property is not so sensitive to the method chosen and all the correlated methods give similar results.

3.2 Dipole moment and polarizability of the CO molecule

It is well known that for the dipole moment of the CO molecule a correct description of the electron correlation is essential. Particularly, the proper description of its dipole-moment curve appears to be a very hard test of the accuracy of a method [34].

The [6*s*4*p*2*d*] basis set for CO was constructed from the [5*s*3*p*] set augmented by carbon and oxygen *d*-functions with exponents $\alpha_{d(\mathrm{C})} = 0.7$ and $\alpha_{d(\mathrm{O})} = 1.2$ and diffuse functions $\alpha_{s,p(\mathrm{C})} = 0.0438$ and $\alpha_{s,p(\mathrm{O})} = 0.0845$ [35].

Compared to HF, the dipole moment calculations of the CO molecule are much more sensitive to the inclusion of triple excitations. Although the CCSD method gives the correct sign of the dipole moment (in contrast to SCF), its value is still far from the experimental one as well as from the values obtained when the T_3 operator is taken into account. Again, as for HF, the difference between the CCSD energy derivative and the dipole moment expectation value is very large. Results of CCSD + T(CCSD), CCSD(T) and CCSDT-1a energy derivatives seem to be stable, and the WF(2)-CCSD(T) method only slightly improves the CCSD expectation value. Addition of other fourth-order terms in the DM(4)- CCSD(T) method does not lead to the expected results either. Much better results are obtained by using the WF(3)-CCSD(T) method.

In Table 4 computed values of polarizabilities are presented. Again, these do not appear to be very sensitive to a chosen correlation method. Even the CCSD

Table 3. HF molecule. Dipole moments and polarizabilities are calculated at $r = 1.733$ and [5*s*3*p*2*d*/3*s*2*p*] basis set. All values are in a.u.

Method	Dipole moment[a] $\langle\hat{\mathrm{O}}\rangle$	Dipole moment[b] $\mathrm{E}^{(1)}$	Polarizability[c] $\langle\hat{\mathrm{O}}\rangle^{(1)}$	Polarizability[d] $\mathrm{E}^{(2)}$
SCF	0.757	0.757	5.7	5.7
CCSD	0.688	0.707	6.6	6.3
CCSD + T(CCSD)	–	0.700	–	6.4
CCSD(T)	–	0.702	–	6.4
CCSDT-1a	0.701	0.700	6.4	6.4
WF(2)-CCSD(T)	0.692	–	6.5	–
WF(3)-CCSD(T)	0.703	–	6.4	–
DM(4)-CCSD(T)	0.696	–	6.5	–
Experiment[e]	–	0.68, 0.75	–	–

[a] The expectation values

[b] The first energy derivatives

[c] The first derivatives of the dipole moment expectation value

[d] The second energy derivatives

[e] Experimental values are taken from [41, 42]

Table 4. CO molecule. Dipole moments and polarizabilities are calculated at $r = 2.13161$ and $[6s4p1d]$ basis set. All values are in a.u. For notations see footnotes to Table 3

Method	Dipole moment $\langle\hat{O}\rangle$	Dipole moment $E^{(1)}$	Polarizability $\langle\hat{O}\rangle^{(1)}$	Polarizability $E^{(2)}$
SCF	0.119	0.119	14.5	14.5
CCSD	−0.121	−0.034	15.7	15.6
CCSD + T(CCSD)	–	−0.060	–	15.6
CCSD(T)	–	−0.056	–	15.6
CCSDT-1a	−0.054	−0.059	15.6	15.6
WF(2)-CCSD(T)	−0.097	–	15.6	–
WF(3)-CCSD(T)	−0.052	–	15.5	–
DM(4)-CCSD(T)	−0.099	–	15.7	–
Experiment[a]	–	−0.048	–	–

[a] The experimental value is taken from [43]

method gives accurate results in spite of its relative inability to provide accurate dipole moment. The comparatively better accuracy of the CCSD polarizability is quite understandable, if one realizes that it is only due to the change in electronic dipole moment, while the total dipole moment itself is the sum of electronic and nuclear parts which are both large and almost cancel each other. Although the contribution of triple excitations to the electronic dipole moment is relatively small, it becomes essential for the total dipole moment.

The dipole-moment curves calculated with several methods are shown in Figs. 3 and 4. In Fig. 3 the WF(2)-CCSD(T), WF(3)-CCSD(T) and DM(4)-CCSD(T) methods are compared with the CCSD(T) numerical-derivative approach. In Fig. 4 we present the non-iterative WF(3)-CCSD(T) results together with those obtained by the numerical differentiation with various CC methods. Trends observed already for single-point calculations at equilibrium geometry are preserved in the whole investigated interval of internuclear distances. Nevertheless, the differences are more pronounced with increasing internuclear distance. While WF(3)-CCSD(T) practically mimics the CCSD(T) and CCSDT-1a energy derivatives, DM(4)-CCSD(T) totally fails, which confirms that this approach uses an unbalanced density matrix.

3.3 Dipole moment and polarizability of the BeO molecule

The $X^1\Sigma_g^+$ state of BeO appears to be a challenge to ab initio calculations [36] not only because of the unknown experimental values of the dipole moment and polarizability. Scuseria and Lee's T_1 diagnostics [37] has led to the conclusion that non-dynamical correlation effects are very important and a multireference approach should be utilized. A comparison of CC calculations [32] with multireference results [38] has shown that the CCSDT method provides accurate results and although the magnitude of the triples corrections varies somewhat with method including triple excitations, the CCSD(T) method best approximates CCSDT. The sensitivity of individual corrections of the higher-level CC methods, including terms from connected quadruples, was demonstrated in calculations for the valence isoelectronic of BeS by Noga and Pluta [39].

Data for the BeO molecule computed with Sadlej's polarized basis set $[5s3p2d]$ are presented in Tables 2 and 5. We can see that the inclusion of triple-excitation effects is not as transparent as it was in the previous cases. The lowest iterative version of CCSDT seems to be somehow unbalanced. It gives results which are far from the full CCSDT value, and multireference methods [38] as well. In contrast, the CCSD(T) dipole moment and

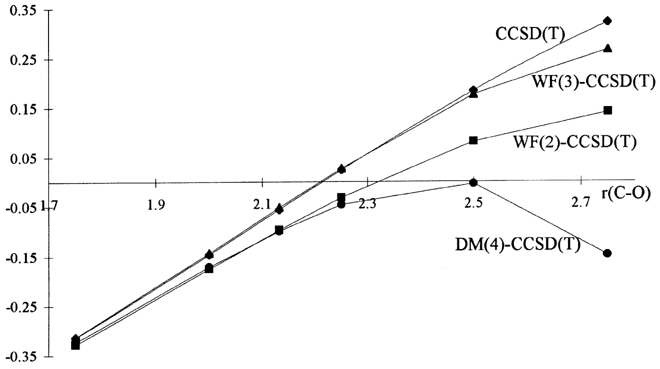

Fig. 3. Dipole-moment curves of the CO molecule. Three non-iterative CC methods suggested for calculation of the dipole moment as an expectation value are compared with the CCSD(T) numerical derivative approach. All values are in a.u.

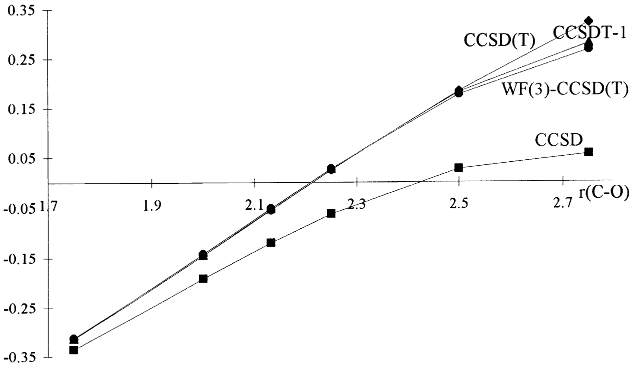

Fig. 4. Dipole-moment curves of the CO molecule. The WF(3)-CCSD(T) expectation value approach is compared with the CCSD, CCSD(T) and CCSDT-1a numerical derivatives. All values are in a.u.

Table 5. BeO molecule. Dipole moments and polarizabilities are calculated at $r = 2.5149$ and [$5s3p2d$] basis set. All values are in a.u.

Method	Dipole moment $\langle \hat{O} \rangle$	Dipole moment $E^{(1)}$	Polarizability $\langle \hat{O} \rangle^{(1)}$	Polarizability $E^{(2)}$
SCF	2.946	2.946	19.7	19.7
CCSD	2.290	2.558	39.1	28.8
CCSD + T(CCSD)	–	2.256	–	46.2
CCSD(T)	–	2.432	–	34.5
CCSDT-1a	2.226	2.256	53.8	48.5
CCSDT[a]	–	2.40	–	36.0
WF(2)-CCSD(T)	2.321	–	38.6	–
WF(3)-CCSD(T)	2.365	–	39.6	–
DM(4)-CCSD(T)	2.226	–	44.6	–

[a] CCSDT values are taken from [32]

Table 6. HCN molecule. Dipole moments and polarizabilities are calculated at $r(\mathrm{CH}) = 2.0126$, $r(\mathrm{CN}) = 2.1789$ and [$5s3p2d/3s2p$] ANO basis set. All values are in a.u.

Method	Dipole moment $\langle \hat{O} \rangle$	Dipole moment $E^{(1)}$	Polarizability $\langle \hat{O} \rangle^{(1)}$	Polarizability $E^{(2)}$
SCF	1.294	1.294	22.5	22.5
CCSD	1.152	1.190	21.8	22.2
CCSD + T(CCSD)	–	1.175	–	22.6
CCSD(T)	–	1.174	–	22.5
CCSDT-1a	1.169	1.175	22.6	22.6
WF(2)-CCSD(T)	1.162	–	22.0	–
WF(3)-CCSD(T)	1.175	–	22.4	–
DM(4)-CCSD(T)	1.159	–	22.3	–
Experiment[a]		1.163 ± 0.010		

[a] Experimental value is taken from [40]

polarizability values are close to those of the CCSDT method. As for non-iterative expectation value approaches, particularly the WF(3)-CCSD(T) method, they provide relatively accurate estimations of CCSD(T) numerical derivative results. Although the differences are slightly larger than in the cases of HF and CO molecules, they are still acceptable. We observed reasonably good agreement of WF(3)-CCSD(T) and full CCSDT values of dipole moment.

3.4 Dipole moment and polarizability of the HCN molecule

In calculations of HCN we used the [$5s3p2d/3s2p$] ANO basis set with equilibrium geometry taken from [40]. It can be seen from Tables 2 and 6 that all values of first as well as the second-order numerical derivatives of energy obtained by CC methods including triple excitations are in very good mutual agreement.

The non-iterative expectation value methods preserve the trends observed in previous cases. The WF(2)-CCSD(T) method produced a slight improvement over CCSD results, while the WF(3)-CCSD(T) approach gave dipole moment and polarizability values practically identical to those of CCSD(T) energy derivatives. With the DM(4)-CCSD(T) method we obtained results similar to those of WF(2)-CCSD(T).

4 Conclusion

In this study we have investigated the possibility of using expectation value calculations of first-order properties using the CC wave function in which non-iterative triple excitations are involved. The basic idea was to substitute iteratively obtained T_3 amplitudes with non-iterative ones in the truncated expression for the expectation value of the operator associated with a certain first-order property. Since they are equivalent through the second order of the MBPT expansion, the original criterion for truncation of the infinite expansion in Eq. (28) has remained preserved. We refer to this approach as WF(2)-CCSD(T). Its extension has been achieved by adding all third- and fourth-order terms to the correlated density matrix, which include T_1 and T_2 amplitudes obtained by projection of the term $\left|(\mathbf{H}_N T_3)_C\right|\Phi\rangle$ onto the subspaces of mono- and bi-excitations. Since the accuracy of T_1 and T_2 was improved through the third order of the MBPT expansion, we denote this approach as WF(3)-CCSD(T). Inclusion of some other fourth-order terms has led to the density matrix equivalent through the fourth-order of the MBPT expansion to that obtained if CCSDT-1 amplitudes were used in Eq. (28). We denote this approach as DM(4)-CCSD(T).

Suggested methods were tested by calculations of dipole-moment values and polarizabilities as the derivatives of induced dipole-moment values for several diatomic closed-shell molecules. Moreover, for the CO molecule we have calculated the dipole-moment curve. Our results were compared with those of numerical differentiation of energy for different versions of the standard CC theory and with experimental values where available.

While the WF(2)-CCSD(T) approach has usually led to only a slight improvement of CCSD results, the WF(3)-CCSD(T) method was able to reproduce the accuracy of the CCSD(T) energy derivative results in all cases investigated. Inclusion of additional terms in the DM(4)-CCSD(T) approach has often caused destabilization of the density matrix and the method provided worse results than WF(3)-CCSD(T). As to computational demands, in comparison with the analytical CCSD(T) energy derivative calculation, the WF(3)-CCSD(T) approach requires the same number of N^7 operations, but the iterative procedure of solving modified CCSD Λ-equations is in our case omitted.

Although theoretical derivation of the WF(3)-CCSD(T) method involves several approximations, this method provides results comparable in accuracy to those of the CCSD(T) energy derivative approach, and it is cheaper.

Acknowledgements. We thank the Slovak grant agency VEGA for support of this work (project no. 1/4227/97).

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