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On expectation value calculations of one-electron properties using the coupled cluster wave functions

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The ability of various approximate coupled cluster (CC) methods to provide accurate first-order one-electron properties calculated as expectation values is theoretically analysed and computationally examined for BH and CO. For actual calculations the infinite number of terms of the expectation value expansion ($\langle \mathcal{O} \rangle = \langle \phi | \exp(T^+) \mathcal{O} \exp(T) | \phi \rangle_c$) was truncated so that T_1, T_2, T_3, and $(1/2)T_2T_2$ clusters were retained on both sides of $\mathcal{O}$. The role of individual clusters is carefully discussed. Inclusion of T_1 is unavoidable, but if triples are essential in the energy evaluation, they may play an even more important role in the property expansion, as shown in the case of CO. It is shown that the CC wave function, which is exact to second order, effectively satisfies the Hellmann-Feynman theorem.

Key words: Coupled cluster method — One-electron properties — Expectation value

1. Introduction

Parallel to the development of many-body perturbation theory (MBPT) and coupled clusters (CC) computer programs for the calculation of correlation energy of molecules, attempts have also been made to calculate various molecular properties for which the SCF method is often unsatisfactory. The natural and at the same time the most convenient approach to solving the latter problem has been the finite field (or more precisely the finite perturbation) theory (FPT), which allows the utilization of existing MBPT/CC codes without any change. Also, as was suggested by Diercksen et al. [1], FPT should be taken as a "legitimate" approach, which leads to the proper definition of electric properties, e.g. the dipole moment, which are directly related to experimentally measurable quantities. FPT has been widely applied in calculations of various electric properties of small systems [1, 2]. Besides its convenience, FPT also has some disadvantages. First, since the routine FPT calculations are based on numerical differentiation of the energy with respect to an external perturbation, the accuracy of energy calculations should usually be much higher than is customary. Second, at least two (or more) separate SCF and correlation energy calculations must be performed for each property component, which is time consuming. Third, for some magnetic properties the method can be applied only with difficulty [3].

As an alternative to the numerical differentiation, first (or higher) order properties may be calculated using analytical derivatives of the external-perturbation-dependent energies (electric field strength, field gradients etc.). General theories, mostly used for molecular geometry calculations, can be applied to CI [4-7] as well as to MBPT/CC [6, 8-10]. Within the MBPT/CC framework we can also mention the theoretical work of Sadlej [11] and Monkhorst [12], or the variational CC treatment of Arponen [13] and Pal [14]. For static properties, Pal also analysed and compared various CC approaches, with $T \approx T_2$, in particular. Finally, the third possibility (adopted in this paper) is offered by calculating the expectation (average) value of the property operator ($\mathcal{O}$) using the pertinent wave function (ψ).

$$\langle \mathcal{O} \rangle = \langle \psi | \mathcal{O} | \psi \rangle / \langle \psi | \psi \rangle. \tag{1}$$

This is usually reduced to the task of evaluating the correlated density matrix, which can easily be contracted with the property integrals. Evaluation of the density matrix for the (standard) CI wave function restricted to single and double excitations is relatively easy, thanks to the finite number of terms in the wave function expansion and the need for handling only single- and double-excitation coefficients. Unlike variational CI, the CC wave function is an infinite expansion in which higher powers of non-variationally determined coefficients also take part. Obviously, the expectation value calculation from a CC wave function is therefore theoretically not so straigthforward as it is in the case of CI.

It is fair to note here that the energy differentiation and expectation value approaches do not, in general, lead to the same result for approximate wave functions, since the Hellmann-Feynman theorem, (HFT) is only valid for exact wave function or wave functions with complete variation in a complete functional space defined by the method (e.g. SCF, MCSCF, full CI, full CC). The thorough analysis of this problem in the case of limited CI was given a few years ago by Nerbrant et al. [15]. In the present paper we shall try to analyse this problem for the case of various versions of the CC method. We shall try to determine what may be a reasonable truncation of the infinite expansion (1) to provide us with results that are quite close to those obtained by differentiating the energy. Finally, the theoretical analysis is supported by numerical results for CO and BH as test cases.

2. Expectation values from approximate CC wave functions and the Hellmann–Feynman theorem

At the very beginning of this section, let us consider a system which is influenced by an external perturbation $\lambda\mathcal{O}$ (with the perturbation parameter λ). If only the first-order response is taken into account, the perturbed Hamiltonian of such a system can be expressed as:

$$H(\lambda)=H(0)+\lambda\mathcal{O}. \tag{2}$$

The externally perturbed energy

$$E(\lambda)=\frac{\langle\psi(\lambda)|H(\lambda)|\psi(\lambda)\rangle}{\langle\psi(\lambda)\,|\,\psi(\lambda)\rangle}. \tag{3}$$

can be expanded in a power series of λ as

$$E(\lambda)=E(0)+\lambda E^{(1)}+\frac{\lambda^2E^{(2)}}{2}\cdots \tag{4}$$

where $\psi(\lambda)$ is the wave function describing the pertinent externally perturbed system. Substituting from Eqs. (2) and (4) into Eq. (3) and subsequently differentiating at $\lambda=0$ we obtain the first-order perturbed energy ($E^{(1)}$), which is closely related to the corresponding property

$$\left.\frac{dE}{d\lambda}\right|_{\lambda=0}=E^{(\lambda)}=\frac{\langle\psi(0)|\mathcal{O}|\psi(0)\rangle}{\langle\psi(0)|\psi(0)\rangle}+\frac{2}{S}\langle\psi(0)|[H(0)-E(0)]\left|\frac{d\psi(\lambda)}{d\lambda}\right\rangle\Bigg|_{\lambda=0} \tag{5}$$

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

$$S=\langle\psi(0)|\psi(0)\rangle.$$

Obviously, the first term on the right-hand side of Eq. (5) represents the expectation value of the operator $\mathcal{O}$. The second term on the right-handside of Eq. (5) vanishes for "exact" wave functions in accord with the HFT. In general, this term (let us call it the non-HFT term) does not vanish for approximate wave functions and is responsible for non-validity of the HFT in such cases. Thus, to obtain the first-order property this term should be calculated together with the expectation value. Since the non-HFT term is usually much more complicated to calculate than the HFT term itself, its calculation is not a standard practice. Quite often it is simply neglected. However, its neglect should be based on careful analysis of its importance in the method used for the calculation of the expectation value. As mentioned above, Nerbrant et al. [15] analysed this term for the CI-SD case, and they have shown that it involves contributions from triple and higher excitations. Using similar consideration as applied by Nerbrant et al., we are able to analyse the non-HFT term for approximate CC methods, too.

In the single reference (UHF or closed shell RHF) CC method the wave function (ψ in general) is given by the action of an exponential cluster operator exp (T) onto an HF reference state ϕ.

$$|\psi\rangle=e^T|\phi\rangle \tag{6}$$

where T is the excitation operator given as the sum of its l-excitation components:

$$T=\sum_{l=1}^{N_e} T_l \tag{7}$$

$$T_l=\sum_{\substack{i>j>k\\a>b>c}} t_{ijk\cdots}^{abc\cdots}\, a^+ i\, b^+ j\, c^+ k \tag{8}$$

$t_{ijk\cdots}^{abc\cdots}$ are antisymmmetrized amplitudes of the operator T_l which are to be determined. Here (and throughout the paper) we use $i, j, k, \ldots$ and $a, b, c, \ldots$ to denote occupied and virtual orbitals, respectively. In practice, T is restricted to some types of excitations [2], usually to T_l with $1<l<3$. In addition, the expansion of $\exp(T)$ with a chosen set of T_l operators in Eq. (6) is not complete in some versions of the method (L-CCD, CCSDT-n etc.). The CC energy is obtained by projecting the Schrödinger equation onto the reference state, or equivalently by first multiplying it from the left by $\exp(-T)$ and by subsequent projection (cf. e.g. [12]):

$$\langle\phi|(H-E)e^T|\phi\rangle=\langle\phi|e^{-T}(H-E)e^T|\phi\rangle=0 \tag{9a}$$

(The $t_{ijk\ldots}^{abc\cdots}$ amplitudes can be obtained by projecting the Schrödinger equation onto the subspace of all possible excited states of the chosen types of excitations in T and by solving the corresponding system of coupled (in general) non-linear equations:

$$\langle\phi_{ijk\cdots}^{abc\cdots}|(H-E)e^T|\phi\rangle=\langle\phi_{ijk\cdots}^{abc\cdots}|e^{-T}He^T|\phi\rangle=0. \tag{9b}$$

Eqs (9a) and (9b) lead to a connected diagram expansion which ensures the size extension property of the method even in the case of truncated T[2]. Let us recall that Eqs. (6)-(9) are valid irrespective of the external perturbation. Then we can express the non-HFT term from Eq. (5) as (for simplicity we omit the constant $2/S$):

$$\begin{aligned}&\langle\psi(0)|(H(0)-E(0))\left|\frac{d\psi(\lambda)}{d\lambda}\right\rangle\Big|_{\lambda=0}\\&=\langle\psi(0)|(H(0)-E(0))e^{T(0)}\left|\frac{d\phi(\lambda)}{d\lambda}\right\rangle\Big|_{\lambda=0}\\&\quad+\langle\psi(0)|(H(0)-E(0))\frac{de^{T(\lambda)}}{d\lambda}|\phi(0)\rangle\Big|_{\lambda=0}.\end{aligned} \tag{10}$$

Using the coupled perturbed Hartree-Fock theory we arrive at [15]:

$$\left|\frac{d\phi(\lambda)}{d\lambda}\right\rangle\Big|_{\lambda=0}=\sum_{ia} x_{ia}a^+ i|\phi(0)\rangle \tag{11}$$

where x_{ia} is an expansion coefficient [15]. Substituting from Eqs. (7) and (11) into Eq. (10), and expanding $\exp(T(0))$ we get for the first term on the right-hand side

$$\begin{aligned}
&\langle\psi(0)|(H(0)-E(0))e^{T(0)}\left|\frac{d\phi(\lambda)}{d\lambda}\right\rangle\Bigg|_{\lambda=0}\\
&=\langle\psi(0)|(H(0)-E(0))(1+T+\tfrac{1}{2}T^2+\cdots)\sum_{ia}x_{ia}a^{+}i\,|\phi(0)\rangle\\
&=\sum_{ia}x_{ia}\langle\psi(0)|(H(0)-E(0))|\phi(0)_i^a\rangle\\
&\quad+\sum_{ijab}x_{ia}t_j^b\langle\psi(0)|(H(0)-E(0))|\phi(0)_{ij}^{ab}\rangle\\
&\quad+\sum_{\substack{ia\\ j>k\\ b>c}}x_{ia}(t_j^bt_k^c-t_j^ct_k^b+t_{jk}^{bc})\langle\psi(0)|(H(0)-E(0))|\phi(0)_{ijk}^{abc}\rangle+\cdots\\
&=\sum_l c_l\langle\psi(0)|(H(0)-E(0))|\phi(0)_l\rangle\\
&=\sum_l c_l\langle\phi(0)_l|e^{-T}He^{T}|\phi(0)\rangle
\end{aligned}\tag{12}$$

$\phi(0)_l$ is an excited state generated by the action of annihilation and creation operators on $\phi(0)$. c_l is an expansion coefficient related to this l-fold excited state. In the last equality we used Eq. (9b) (and the hermicity of the Hamiltonian) to show that this term is energy independent.

If we realize that $T(\lambda)$ can be expanded as a power series in λ [12]:

$$T(\lambda)=T(0)+\lambda T(0)^{(1)}+\frac{\lambda^2}{2}T(0)^{(2)}+\cdots\tag{13}$$

we can similarly express the second term of Eq. (10) as

$$\begin{aligned}
&\langle\psi(0)|(H(0)-E(0))\frac{de^{T(\lambda)}}{\lambda}|\phi(0)\rangle\Bigg|_{\lambda=0}\\
&=\langle\psi(0)|(H(0)-E(0))T(0)^{(1)}e^{T(0)}|\phi(0)\rangle\\
&=\sum_{ia}t_i^{a^{(1)}}\langle\psi(0)|(H(0)-E(0))|\phi(0)_i^a\rangle\\
&\quad+\sum_{\substack{ia\\ jb}}t_i^{a^{(1)}}t_j^b\langle\psi(0)|(H(0)-E(0))|\phi(0)_{ij}^{ab}\rangle\\
&\quad+\sum_{\substack{ia\\ j>k\\ b>c}}t_i^{a^{(1)}}(t_j^bt_k^c-t_j^ct_k^b+t_{jk}^{bc})\langle\psi(0)|(H(0)-E(0))|\phi(0)_{ijk}^{abc}\rangle+\cdots\\
&=\sum_l d_l\langle\psi(0)|(H(0)-E(0))|\phi(0)_l\rangle\\
&=\sum_l d_l\langle\phi(0)_l|e^{-T}He^{T}|\phi(0)\rangle
\end{aligned}\tag{14}$$

where d_l is an expansion coefficient. It is analogous but not equivalent to c_l. In Eqs. (12) and (14) we did not use any assumption on T. Obviously, if T is a complete excitation operator all terms in these equations vanish, since Eq. (9b) is valid for all excited determinants. Whenever T is incomplete, Eq. (9b) is valid only for those chosen l-fold excitation operators (and corresponding l-fold excited determinants) that are involved in the approximate T. As a consequence, many of the terms in Eqs. (12) and (14) remain in approximate CC methods, namely contributions from cluster operators which were not included in T. This resembles the situation with CI-SD [15], when configurations which are not involved in the incomplete functional space are responsible for the non-HFT term. It should be noted, however, that for CI-SD both the energy and the expectation values of property operators suffer from the size non-extensivity. In spite of this defect, CI-SD expectation values of first-order properties occasionally agree with the experiment very well, mainly due to the fortuitous cancellation of non-HFT contributions and unlinked contributions that cause size non-extensivity. This was discussed thoroughly by Diercksen et al. [1].

In contrast to restricted CI, for CC wave functions (even with truncated T) the expectation values can be expressed in terms of connected contributions only [16]

$$\langle \mathcal{O} \rangle = \frac{\langle \psi(0) | \mathcal{O} | \psi(0) \rangle}{\langle \psi(0) | \psi(0) \rangle} = \langle \phi | e^{T^+} \mathcal{O} e^{T} | \phi \rangle_c \tag{15}$$

where C indicates that only connected diagrams are to be considered in the diagrammatic representation of $\langle \mathcal{O} \rangle$. Unfortunately, Eq. (15) represents an infinite expansion which needs to be truncated in practice. Although the finite expansion of the CC wave function $\psi(0)$ in Eq. (15) does not guarantee a connected expression for $\langle \mathcal{O} \rangle$, we can choose a truncation that leads to errors which are of higher order than those introduced by the accuracy of the approximate wave function itself. We shall come back to the specific selection of the wave function in the forthcoming section.

Another point which should be mentioned here is that the energies from Eqs. (3) and Eq. (9a) are not equivalent for approximate CC wave functions. As Monkhorst has shown [12], the difference between these two quantities is due to contributions from other excitations than those involved in an approximate T. Since in actual calculations the CC energy is evaluated from Eq. (9a) (i.e. not as an expectation value but as an eigenvalue of H), one introduces a similar error either by FPT or by calculating the first-order property as an expectation value. For CCSDT (CC with singles, doubles and triples) the error is due to T_4 clusters which first appear in the fifth-order MBPT energy, or in the third-order MBPT wave function. Contributions from T_4 clusters are usually assumed negligible, though there are indications that they may play an important role in systems with high quasidegeneracy [17].

3. Computational implementation

In deciding to which terms the expansion (15) must be restricted, we used the logic of MBPT. We arrived at the conclusion that retention of all second-order-type terms of the wave function (i.e. terms which are exact up to the second order in the MBPT expansion) on both sides of $\mathcal{O}$ in Eq. (15) should be an adequate truncation, since we only introduce an error which is of the same order as the non-HFT term. Thus, for our most sophisticated approach, the CCSDT method and its variants [18–21] we restrict the Eq. (15) to the following terms

$$=\langle\phi(0)|(1+T_2^{+}+\tfrac{1}{2}T_2^{+}T_2^{+}+T_1^{+}+T_3^{+})\mathcal{O}(1+T_2+\tfrac{1}{2}T_2T_2+T_1+T_3)|\phi(0)\rangle_C. \quad (16)$$

For simpler CC methods, such as CCSD or CCD, $T_3=0$ and $T_1=T_3=0$, respectively. Let us recall that within a chosen method the T amplitudes are correctly determined by solving the Eq. (9b).

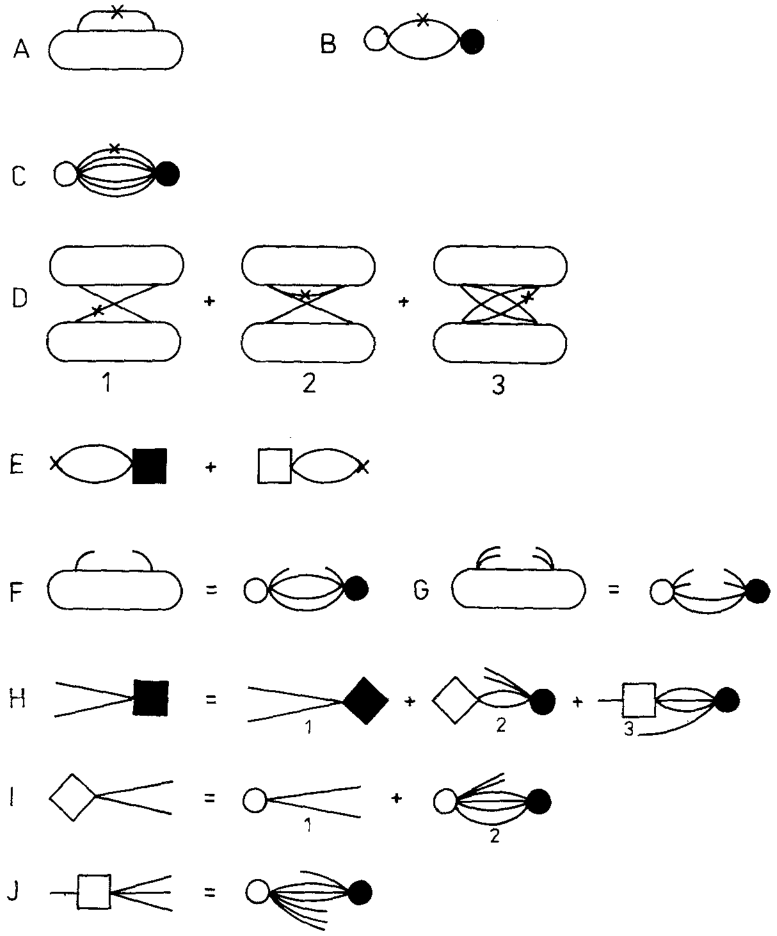

Fig. 1.A–I. All arrowless diagrams taken into account in the calculation of correlation contributions to first-order one-electron properties. For antisymmetrized (Hugenholtz) diagrams of T operator we use the notation introduced by Cizek [16]. By inserting diagrams F–I into A, D and E, and by drawing arrows all individual diagrams can be generated.—×—, vertex represents the property operator

Diagrams corresponding to Eq. (16) are depicted in Fig. 1, where the use of intermediate summation is applied. Thus, the true diagrams which contribute to the property are obtained by inserting intermediate "vertices" (diagrams F–I) into *A*, *D*, *E*. This is a standard practice in MBPT or CC, since in applying them one usually arrives at irreducible summations which are efficiently programmable, unlike true diagrams. When we take off the property operators from the diagrams *A*–*E*, the remaining "opened" diagrams correspond to the correlation contributions to the one-electron density matrix. The diagrams *F* and *H* may serve as an example of such "opened" diagrams; besides being intermediate interaction diagrams, they also represent the contributions to the density matrix from diagrams *A* and *E*. Let us denote these contributions ρ_{pq} where *p*, *q* are general indices for both occupied and virtual orbitals. The correlation contribution to a one-electron property is simply calculated as:

$$\langle \mathcal{O} \rangle^{\text{corr}} = \sum_{pq} \rho_{pq}^{\text{corr}} \langle p | \mathcal{O} | q \rangle \tag{17}$$

where $\langle p|\mathcal{O}|q\rangle$ are usual property matrix elements. They are the same as in SCF calculations, but run over all indices (not only over indices of occupied molecular orbitals as in regular SCF calculation of one-electron properties). Explicit formulae used in our computer program for calculating ρ_{pq}^{corr} are separately given in Table 1 for *p*, *q* being two occupied (i, j), two virtual (a, b) or a mixed pair (i, a) of orbitals. Since the structure of these formulae is analogous to that in fourth-order MBPT the computer program and the computational demands are also analogous to those in fourth-order MBPT. Again the most time-consuming

Table 1. Explicit formulae for correlated density matrix contributions

Contribution[a]	UHF reference (in spinorbitals)[b]	RHF reference (in orbitals)[c]
ρ_{ij}^{A}	$-\chi(i,j)$	$-\chi(i,j)$
ρ_{ab}^{A}	$-\chi(a,b)$	$-\chi(a,b)$
ρ_{ij}^{B}	$-\sum_{c} t_i^c t_j^c$	$-\sum_{c} t_i^c t_j^c$
ρ_{ab}^{B}	$\sum_{k} t_k^a t_k^b$	$\sum_{k} t_k^a t_k^b$
ρ_{ij}^{C}	$-\sum_{\substack{c>d>e \\ k>l}} t_{ikl}^{cde} t_{jkl}^{cde}$	$-\sum_{\substack{cde \\ k\geq l}} \left(1-\frac{\delta kl}{2}\right) t_{ikl}^{cde}[4t_{jkl}^{cde}+t_{jkl}^{dec}+t_{jkl}^{ecd}$ $-2(t_{jkl}^{dce}+t_{jkl}^{edc}+t_{jkl}^{ced})]$
ρ_{ab}^{C}	$\sum_{\substack{k>l>m \\ c>d}} t_{klm}^{acd} t_{klm}^{bcd}$	$\sum_{\substack{klm \\ c\geq d}} \left(1-\frac{\delta kl}{2}\right) t_{klm}^{acd}[4t_{klm}^{bcd}+t_{lmk}^{bcd}+t_{mkl}^{bcd}$ $-2(t_{lkm}^{bcd}+t_{mlk}^{bcd}+t_{kml}^{bcd})]$
ρ_{ij}^{D1}	$\sum_{k} \chi(i,k)\chi(j,k)$	$\sum_{k} \chi(i,k)\chi(j,k)$
ρ_{ab}^{D1}	$-\sum_{c} \chi(a,c)\chi(b,c)$	$-\sum_{c} \chi(a,c)\chi(b,c)$

Table 1 (continued)

Contribution[a]	UHF reference (in spinorbitals)[b]	RHF reference (in orbitals)[c]
ρ_{ij}^{D2}	$\sum_{cd} \chi(c,d)\chi(c,j,i,d)$	$\sum_{cd} \chi(c,d)[2\chi(c,j,d,i)+\chi(c,j,i,d)]$
	$+\sum_{kl} \chi(k,l)\chi(i,k,j,l)$	$+\sum_{kl} \chi(k,l)[2\chi(i,k,j,l)-\chi(k,i,j,l)]$
ρ_{ab}^{D2}	$-\sum_{kl} \chi(k,l)\chi(a,l,k,b)$	$-\sum_{kl} \chi(k,l)[2\chi(b,k,a,l)+\chi(b,k,l,a)]$
	$+\sum_{cd} \chi(c,d)\chi(a,c,b,d)$	$+\sum_{cd} \chi(c,d)[2\chi(a,c,b,d)-\chi(c,a,b,d)]$
ρ_{ij}^{D3}	$-\sum_{\substack{k>l\\m}} \chi(i,m,k,l)\chi(j,m,k,l)$	$-\sum_{klm} \chi(k,l,i,m)[2\chi(k,l,j,m)-\chi(l,k,j,m)]$
	$-\sum_{kcd} \chi(c,k,i,d)\ \chi(c,k,j,d)$	$-\sum_{kcd} (\chi(c,k,i,d)[2\chi(c,k,j,d)+\chi(c,k,d,j)]$
		$+\chi(c,k,d,i)[2\chi(c,k,d,j)+\chi(c,k,j,d)]\}$
ρ_{ab}^{D3}	$\sum_{\substack{c>d\\e}} \chi(a,e,c,d)\chi(b,e,c,d)$	$\sum_{cde} \chi(a,e,c,d)[2\chi(b,e,c,d)-x(b,e,d,c)]$
	$+\sum_{klc} \chi(a,k,l,c)\ \chi(b,k,l,c)$	$+\sum_{klc} \{\chi(a,k,l,c)[2\chi(b,k,l,c)+\chi(b,k,c,l)]$
		$+\chi(a,k,c,l)[2\chi(b,k,c,l)+\chi(b,k,l,c)]\}$
ρ_{ia}^{E}	$2\chi(i,a)$	$2\chi(i,a)$
$\chi(i,j)$	$\sum_{\substack{c>d\\k}} t_{ik}^{cd} t_{jk}^{cd}$	$\sum_{cdk} t_{ik}^{cd}(2t_{jk}^{cd}-t_{jk}^{dc})$
$\chi(a,b)$	$-\sum_{\substack{k>l\\c}} t_{kl}^{ac} t_{kl}^{bc}$	$-\sum_{klc} t_{kl}^{ac}(2t_{kl}^{bc}-t_{lk}^{bc})$
$\chi(i,j,k,l)$	$\sum_{c>d} t_{ij}^{cd} t_{kl}^{cd}$	$\sum_{cd} t_{ij}^{cd} t_{kl}^{cd}$
$\chi(a,b,c,d)$	$\sum_{k>l} t_{kl}^{ab} t_{kl}^{cd}$	$\sum_{kl} t_{kl}^{ab} t_{kl}^{cd}$
$\chi(a,j,i,b)$	$\sum_{ck} t_{ik}^{ac} t_{jk}^{bc}$	$\sum_{ck} (2t_{ik}^{ac}-t_{ki}^{ac})t_{jk}^{bc}-t_{ik}^{ac}t_{jk}^{cb}$
$\chi(a,j,b,i)$		$\sum_{kc} t_{ki}^{ac} t_{kj}^{bc}$
$\chi(i,a)$	$\tau(i,a)+\sum_{ck} \tau(k,c)t_{ik}^{ac}$	$\tau(i,a)+\sum_{ck} \tau(k,c)(2t_{ik}^{ac}-t_{ik}^{ca})$
	$-\sum_{\substack{k>l\\c}} \chi(c,i,k,l)t_{kl}^{ca}$	$-\sum_{klc} \chi(c,i,k,l)(2t_{kl}^{ca}-t_{kl}^{ac})$
$\tau(i,a)$	$t_i^a+\sum_{\substack{j>k\\b>c}} t_{ijk}^{abc} t_{jk}^{bc}$	$t_i^a+\sum_{\substack{j\geq k\\bc}} \left(1-\frac{\delta_{jk}}{2}\right)(2t_{jk}^{bc}-t_{jk}^{cb})(2t_{ijk}^{abc}-t_{ijk}^{cba}-t_{ijk}^{bac})$
$\chi(a,k,i,j)$	$\sum_{\substack{c>d\\l}} t_{kl}^{cd} t_{ijl}^{acd}$	$\sum_{cdl} t_{kl}^{cd}(2t_{ijl}^{acd}-t_{ijl}^{dca}-t_{ijl}^{adc})$

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[a] The superscript indicates from which diagram the contribution follows

[b] Formulae are presented in terms of antisymmetrized amplitudes

[c] The final contribution to the property is $2\rho_{pq}\langle p|\mathcal{O}|q\rangle$ due to the spin factor

step is the calculation of triples, with summations over seven indices. Moreover, it requires the storage of t_{ijk}^{abc} amplitudes.

The main advantage of the above-mentioned calculation of first-order properties follows from the fact that the correlation contributions to the density matrix do not depend on the external perturbation. This allows us to evaluate a series of properties just from a calculation of contributions which arise from a single correlated wave function. Recently, a relaxed correlation density matrix calculation based on low-order perturbation theory has been proposed by Bartlett's group [22].

Obviously, our computer code can be used without any modification for true second-order MBPT wave functions. The estimation of non-HFT term is, however, not so clear as in the case of CC. If we take into account that the second-order MBPT wave function is obtained within the first few iterations of the CC iterative solution [2], the above approach should be acceptable at least for well-convergent systems. The computer code of one-electron properties closely follows the logic of our program COMENIUS [23] for MBPT and CC calculations.

4. Sample calculations

To illustrate the techniques described in the previous section, we have calculated the CC dipole, quadrupole and octopole moments for boron hydride and carbon monoxide. Our primary goal was to examine the performance of coupled cluster methods at various levels of sophistication, rather than to get a perfect agreement with experiment. We also tried to demonstrate the relative importance of various cluster operators in the calculation of expectation values of several molecular properties.

In the CCSDT method we applied the CCSDT-1a approximation [18]. The single determinant restricted Hartree–Fock wave function was our starting point in all cases. Calculations were carried out at experimental geometries. In the BH calculation we used the $[4s3p1d/2s1p]$ basis set with exponents of boron d functions $\alpha_{d(B)} = 0.41$ and exponents of hydrogen p functions $\alpha_{p(H)} = 0.24$ optimized for the dipole moment of BH by Maurolis et al. [24]. The basis for CO was constructed from a $[5s3p]$ set augmented by carbon and oxygen d functions with exponents $\alpha_{d(C)} = 0.7$ and $\alpha_{d(O)} = 1.2$ and diffuse functions with exponents $\alpha_{s,p(C)} = 0.0438$ and $\alpha_{s,p(O)} = 0.0845$. This is the same basis as we used recently in the calculation of the $H_2CO \rightarrow H_2 + CO$ reaction energy [25].

4.1. *Multipole moments of BH*

Calculated electric moments of BH are presented in Table 2. We notice that correlation effects change the SCF dipole moment quite substantially - it contributes by about 34% to the total moment. The percentage contribution of electron correlation to quadrupole moments is smaller (about 16%), but octopole moments are very heavily influenced by electron correlation—their values

Table 2. SCF and CC energy, dipole moment, quadrupole moments[a] and octopole moments[a] of BH at $R = 2.336$. All values are in a.u.

Method (energy) contribution	FPT μ	$\langle\mu\rangle$	$\langle\theta_{zz}\rangle$	$\langle\theta_{xx}\rangle$	$\langle O_{zzz}\rangle$	$\langle O_{zxx}\rangle$
SCF(−25.124691)	0.658	0.658	−2.804	1.402	0.078	−0.039
CCD(−25.225894)	0.505	0.601	−2.641	1.320	−0.091	0.045
$\langle\phi\|T_2^+\mathcal{O}T_2\|\phi\rangle_c$		−0.061	0.177	−0.088	−0.179	0.090
$\langle\phi\|T_2^+T_2^+\mathcal{O}T_2T_2\|\phi\rangle_c$		0.005	−0.013	0.007	0.011	−0.005
CCSD (−25.226848)	0.502	0.505	−2.409	1.205	−0.463	0.231
$\langle\phi\|T_2^+\mathcal{O}T_2\|\phi\rangle_c$		−0.067	0.185	−0.092	−0.193	0.096
$\langle\phi\|T_2^+T_2^+\mathcal{O}T_2T_2\|\phi\rangle_c$		0.005	−0.014	0.007	0.012	−0.006
$\langle\phi\|T_1^+\mathcal{O}T_1\|\phi\rangle_c$		0.000	−0.007	0.003	0.008	−0.004
Mixed[b]		−0.092	0.231	−0.116	−0.368	0.184
CCSDT-1a (−25.228660)	0.494	0.491	−2.424	1.212	−0.535	0.267
$\langle\phi\|T_2^+\mathcal{O}T_2\|\phi\rangle_c$		−0.073	0.198	−0.099	−0.204	0.102
$\langle\phi\|T_2^+T_2^+\mathcal{O}T_2T_2\|\phi\rangle_c$		0.006	−0.016	0.008	0.014	−0.007
$\langle\phi\|T_1^+\mathcal{O}T_1\|\phi\rangle_c$		−0.000	−0.007	0.004	0.007	−0.004
$\langle\phi\|T_3^+\mathcal{O}T_3\|\phi\rangle_c$		−0.000	0.002	−0.001	0.001	−0.000
Mixed[c]		−0.100	0.204	−0.102	−0.430	−0.215
Experiment[d]	0.4497 ±0.0826					

[a] Related to the centre of mass, 0.199 a.u.

[b] Mixed contributions from Eq. (14), i.e. $\langle\phi|\mathcal{O}T_1|\phi\rangle_c$ and $\langle\phi|T_1^+\mathcal{O}T_2|\phi\rangle_c$. Only diagram $I1$ is included in I (see Fig. 1)

[c] Mixed contributions $\langle\phi|\mathcal{O}T_1|\phi\rangle_c$, $\langle\phi|T_1^+\mathcal{O}T_2|\phi\rangle_c$, $\langle\phi|T_2^+\mathcal{O}T_3|\phi\rangle_c$ and $\langle\phi|T_3^+\mathcal{O}T_2T_2|\phi\rangle_c$. All diagrams are included in I

[d] Taken from [24]

increased considerably and even changed the sign. Analogous trends were also found in other works [e.g. 26].

In order to verify the significance of non-HFT terms in the dipole moment, we compared the expectation value with the FPT results for individual approaches. In accord with the previous analysis of CI and CEPA approaches [27, 28], electron moments from a wave function which does not comprise single excitations are heavily affected by non-HFT contributions. This is fully confirmed by our CCD results, where the expectation value of the dipole moment is a factor of 1.2 too large compared with its FPT counterpart. The bad agreement of FPT and expectation value dipole moments with all methods which do not contain single excitation operators may be explained as a "self-consistency effect" which is connected with the adaptation of the wave function to the external field. With the CCD wave function the deviation of the expectation value dipole moment from its FPT value is easily understandable using the diagrammatic arguments. Single excitation operators omitted in CCD are unavoidable in the expectation value, since the lowest-order diagrams which contain contributions from T_1 operators, diagrams E with $H1$ and $I1$ insertions, are of the same order as the lowest-order contribution from T_2, diagram A (see Fig. 1). More specifically, T_2 operators whose amplitudes appear for the first time in the first-order wave function form altogether [i.e. from the left and the right side of the operator $\mathcal{O}$ in Eq. (15)] the second-order contribution to the $T_2^+\mathcal{O}T_2$ term (i.e. the same as the $\mathcal{O}T_1$ term with T_1 amplitudes appearing for the first time in the second-order wave function). In contrast to the CCD expectation value, single excitations are implicitly involved in the FPT approach through the numerical differentiation of the CCD energies, as follows from Sect. 2.

With CCSD and CCSDT methods the agreement of FPT and expectation values of the dipole moments is really very good. On grounds of diagrammatic arguments (vide infra) and analysis in Sect. 2, this may be expected for the very high quality CCSDT wave function. With CCSD, however, this agreement should not be generalized to other molecules, since triples are not so important for BH. Thus, CCSD mimics the CCSDT wave function very closely. More details will be given in the discussion of CO results.

Upon analysing individual contributions to correlation effects in the electric moments of BH, it is readily seen that with CCSD and CCSDT wave functions the most important contributions arise from mixed terms, followed by the $T_2^+\mathcal{O}T_2$ term. All other contributions are an order of magnitude smaller. Since terms from T_2 are strictly dominant in the CC correlation energy with canonical HF reference orbitals, one would intuitively expect the contribution from $T_2^+\mathcal{O}T_2$ to dominate in electric properties as well. The reason why contributions from $T_2^+\mathcal{O}T_2$ and $\mathcal{O}T_1$ are comparable simply follows from the fact that both are of the same order in electric properties. The energy is a completely different situation since first appearance of contributions from T_2 and T_1 differs by two orders.

We may observe that the magnitude of the contribution from $T_2^+\mathcal{O}T_2$ gradually increases from CCD to CCSDT electric moments. This is a consequence of the effect of T_1 and T_3 operators on T_2 amplitudes in the CCSD and CCSDT wave functions. Thus, although direct contributions from $T_1^+\mathcal{O}T_1$ and $T_3^+\mathcal{O}T_3$ (diagrams B and C) are negligible, T_1 and T_3 contribute significantly through their effects on T_2 amplitudes, in addition to their importance in the mixed term.

4.2. Multipole moments of CO

The dipole, quadrupole and octopole moments of CO are displayed in Table 3. We omitted CCD values, since we learned from BH results that this approach is not suitable for the expectation value calculations. Most noticeable is the huge effect of electron correlation on the dipole moment, which is positive at the SCF level but negative at the correlated level. This change in the sign of the dipole moment is very well known from many previous calculations (see e.g. [1, 2, 28]). Quadrupole and octopole moments are less sensitive to electron correlation, correlation contribution to these quantities being 2% and 26%, respectively.

Table 3. SCF and CC energy, dipole moment, quadrupole moments[a] and octopole moments[a] of CO at $R = 2.13161$ with the $[6s4p1d]$ basis set. Inner shell and corresponding highest virtual molecular orbitals are dropped in correlation calculations. All values are in a.u.

Method (energy) contribution	$\langle\mu\rangle$	$\langle\theta_{zz}\rangle$	$\langle\theta_{xx}\rangle$	$\langle O_{zzz}\rangle$	$\langle O_{zxx}\rangle$
SCF (−112.776146)	0.119	−1.707	0.854	−4.383	2.194
CCSD (−113.088261)	−0.120	−1.668	0.834	−3.481	1.741
$\langle\phi\|T_2^{+}\mathcal{O}T_2\|\phi\rangle_c$	−0.047	0.000	0.000	0.183	−0.092
$\langle\phi\|T_2^{+}T_2^{+}\mathcal{O}T_2T_2\|\phi\rangle_c$	0.001	−0.001	0.001	−0.009	0.004
$\langle\phi\|T_1^{+}\mathcal{O}T_1\|\phi\rangle_c$	−0.007	−0.008	0.004	−0.005	0.002
Mixed[b]	−0.186	0.049	−0.024	0.737	−0.368
CCSDT-1a (−113.103322)	−0.059	−1.671	0.835	−3.468	1.734
$\langle\phi\|T_2^{+}\mathcal{O}T_2\|\phi\rangle_c$	−0.098	−0.011	0.005	0.208	−0.104
$\langle\phi\|T_2^{+}T_2^{+}\mathcal{O}T_2T_2\|\phi\rangle_c$	0.002	−0.001	0.001	−0.012	0.006
$\langle\phi\|T_1^{+}\mathcal{O}T_1\|\phi\rangle_c$	−0.005	−0.004	0.002	0.000	0.000
$\langle\phi\|T_3^{+}\mathcal{O}T_3\|\phi\rangle_c$	−0.010	−0.006	0.003	0.001	−0.001
Mixed[c]	−0.067	0.058	−0.029	0.724	−0.362
Experiment[d]	−0.048	−1.44±0.03			

[a] Related to the centre of mass, 0.913547 a.u.
[b] See footnote b, Table 2
[c] See footnote c, Table 2
[d] Taken from [29]

As with BH, the most important correlation correction arises from the mixed term and from $T_2^{+}\mathcal{O}T_2$. Once again the T_2 amplitudes are significantly influenced by T_1 and T_3 clusters which cause the difference of $T_2^{+}\mathcal{O}T_2$ contributions in CCSD and CCSDT. Unlike BH, for CO, contributions from $T_1^{+}\mathcal{O}T_1$ and $T_3^{+}\mathcal{O}T_3$ are not negligible, especially when comparing the final value of the dipole moment.

Though our final dipole and quadrupole moments agree with experimental values quite well, there is something puzzling in the relation of the dipole moments from CCSD and CCSDT methods. Namely, the FPT results of Noga et al. [2, 29] show the CCSD dipole moment to be 0.021 a.u., which is less negative than the CCSDT dipole moment, which is −0.047 a.u. Our trend is quite opposite. Although our basis set is slightly less extended than the [7s5p2d] set used in [29], we could not explain this discrepancy simply by a basis set effect. Also Jaquet et al. [30] obtained a highly overestimated dipole moment of CO calculated as the expectation value from a CEPA wave function with singles and doubles. The inadequacy of the CEPA expectation values of dipole moments is also supported by other related calculations (see e.g. [31]). Because of the significant effect of triples, which in this case contribute to the non-HFT term, we suspected that the CCSD expectation value might be in disagreement with the FPT value. Unfortunately an FPT calculation with our $[6s4p1d]$ set was beyond the computer time available to us. Instead we were forced to verify the agreement of the expectation value and FPT dipole moments using a DZ basis set. The results in Table 4 confirm our suspicion. Unlike CCSD, with CCSDT-1a both quantities agree excellently,

Table 4. SCF and CC energy and dipole moment of CO with the DZ basis set. All values are in a.u. Inner shell and corresponding highest virtual molecular orbitals are dropped in correlation calculations

Method (energy) contribution	FPT μ	$\langle\mu\rangle$
SCF (−112.685038)	0.165	0.165
CCSD (−112.886100)	−0.031	−0.147
$\langle\phi\|T_2^+\mathcal{O}T\|\phi\rangle_c$		−0.052
$\langle\phi\|T_2^+T_2^+\mathcal{O}T_2T_2\|\phi\rangle_c$		0.000
$\langle\phi\|T_1^+\mathcal{O}T_1\|\phi\rangle_c$		−0.008
Mixed[a]		−0.251
CCSDT-1a (−112.895595)	−0.039	−0.033
$\langle\phi\|T_2^+\mathcal{O}T_2\|\phi\rangle_c$		−0.067
$\langle\phi\|T_2^+T_2^+\mathcal{O}T_2T_2\|\phi\rangle_c$		0.000
$\langle\phi\|T_1^+\mathcal{O}T_1\|\phi\rangle_c$		−0.003
$\langle\phi\|T_3^+\mathcal{O}T_3\|\phi\rangle_c$		−0.010
Mixed[b]		−0.116

[a] See footnote b, Table 2

[b] See footnote c, Table 2

which confirms the negligibility of non-HFT terms with our most accurate wave function.

Comparing individual contributions in Tables 3 and 4, it is easily seen that neither the direct contribution from $T_1^+\mathcal{O}T_1$ or $T_3^+\mathcal{O}T_3$ nor the influence of the T_3 operator on T_2 amplitudes (as measured by the difference in the magnitude of $T_2^+\mathcal{O}T_2$ in CCSD and CCSDT) is the source of the CCSD failure. The main reason is evidently the mixed term, which is too negative in CCSD. Using order by order analysis of the diagrams for the expectation value, we observe that the next order mixed contribution, after the lowest (i.e. second) order $\mathcal{O}T_1$ term, is the $T_1^+\mathcal{O}T_2$ term in CCSD and $T_1^+\mathcal{O}T_2$ and $T_2^+\mathcal{O}T_3$ terms in CCSDT. Thus, if we do not consider the $T_2^+\mathcal{O}T_3$ term in CCSD, which is of the same order as $T_1^+\mathcal{O}T_2$, which is considered [both are formed from the second- and first-order wave function contributions in Eqs. (15) and (16)], we are taking an incomplete third-order contribution in the diagrammatic expansion of the expectation value. With CCSDT, in contrast to CCSD, we are complete up to the fourth order. The fact that the amplitudes of T_1 and T_2 operators in CCSD are determined from the incomplete second-order-type wave function seems to be of lesser importance since the $T_2^+\mathcal{O}T_2$ terms in CCSD and CCSDT do not differ too dramatically. Moreover, this contribution is less negative in CCSD than in CCSDT. On the basis of our results for CO one might arrive at the conclusion that we have to prefer the FPT approach over the expectation value approach in CCSD. However, we do not think so. In fact, both FPT and expectation value CCSD dipole moments of CO are incorrect, simply because triples are unavoidable in this molecule. Where they are less important, as in BH, both approaches lead to similar results. We tend to believe, however, that the FPT approach can absorb to a limited extent some deficiencies of the wave function. This concerns, for example, the dipole moment functions [2, 29], where the single determinant wave function ceases to be a good starting point for largely distorted geometries.

Concerning CCSDT we wish to stress that all amplitudes of respective T_1, T_2, and T_3 operators are properly determined in CCSDT and that the CCSDT wave function is complete up to the second order. In this sense, the completeness of the determination of amplitudes resembles the completeness of the determination of variational SCF and MC-SCF coefficients, which both obey the HFT. The first non-HFT terms with CCSDT arise from the third-order wave function, that is, they are at least of the fifth order in the property expansion [see Eqs. (12)-(15) and the analysis in Sect. 2].

Conclusions

1. Our theoretical analysis and computational experience have shown that the expectation value calculation of one-electron properties is a very effective approach, since correlation contributions to a series of properties may be obtained in a single run using the correlated density matrix elements.

2. The effectiveness may even be enhanced by neglecting the $T_3^+\mathcal{O}T_3$ term, which is usually small and difficult to calculate.

3. In the computer code one can use algorithms developed for MBPT and CC energy calculations.

4. The first non-HFT terms arise from a wave function contribution which is one order higher than the last complete order of the wave function used in the determination of amplitudes. In CCSD it is the term from T_3, in CCSDT from T_4.

5. For BH we achieved very good agreement of expectation value dipole moments with CCSD and CCSDT wave functions, thanks to the fact that T_3 clusters are unimportant in this molecule. For CO, triples are unavoidable and thus the CCSDT method is recommended in this case. The need for highly accurate wave functions in similar calculations have been previously stressed, e.g. in [32].

6. The systematic dominance of mixed terms and $T_2^+\mathcal{O}T_2$ terms in all the calculated electric moments is demonstrated numerically and explained diagrammatically. The importance of the $\mathcal{O}T_1$ term is particularly stressed.

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