One-Electron Properties and Electrostatic Interaction Energies from the Expectation Value Expression and Wave Function of Singles and Doubles Coupled Cluster Theory

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Introduction

First-order molecular properties can be obtained either as first derivatives of the energy expression with respect to the perturbation, or as an expectation value of the perturbing operator. Coupled Cluster (CC) wave functions do not fulfill the Hellmann-Feynman theorem, therefore those two approaches applied to coupled cluster theory lead to different results.

Most practical progress has been made for the derivative method, which is naturally connected to the CC gradients (see e.g. Ref. [1]), although many theoretical works appeared, which deal with the expectation value approach and its extensions (see e.g. Ref. [2] for a critical review). In this contribution an efficient implementation of the first-order properties and one-electron density matrices is presented, which is based on the expectation value approach at the CCSD level of theory.

Theory

General equations

The average value of an operator X, in a state described by the wave function Ψ is given by the equation,

$$\bar{X} = \frac{\langle \Psi | X \Psi \rangle}{\langle \Psi | \Psi \rangle}. \tag{1}$$

In the case of coupled cluster theory one inserts in Eq. (1) the CC ansatz for the wave function, $\Psi = e^{T}\Phi$, which results in the following expression,

$$\bar{X} = \frac{\langle \Phi | e^{T^\dagger} X e^{T} \Phi \rangle}{\langle \Phi | e^{T^\dagger} e^{T} \Phi \rangle}. \tag{2}$$

The practical use of Eq. (2) has been hampered for a long time by the presence of powers of the deexcitation operator $T^\dagger$, which results in an infinite series of multiple commutators of T and $T^\dagger$, when the r.h.s. of Eq. (2) is written in an explicitly connected form.

A solution of the problem of the infinite series was proposed some time ago by Jeziorski and Moszynski [3]. This solution relies on the use of a new excitation operator S, defined through the equation,

$$e^{S}\Phi = \frac{e^{T^\dagger} e^{T} \Phi}{\langle \Phi | e^{T^\dagger} e^{T} \Phi \rangle}. \tag{3}$$

Eq. (3) contains mostly disconnected terms and it is not obvious that S is a connected operator. It can be shown, however, that S satisfies the following *linear* equation [3],

$$\langle \delta T |\, e^{-T}\, e^{-T^\dagger}\, \widetilde{S}\, e^{T^\dagger}\, e^{T}\, \rangle = \langle \delta T |\, \widetilde{T} - e^{-T}\, \widetilde{T}^\dagger\, e^{T} \rangle, \tag{4}$$

where $\widetilde{T} = T_1 + 2\,T_2 + 3\,T_3 + \ldots$ and $\widetilde{S} = S_1 + 2\,S_2 + 3\,S_3 + \ldots$, and $\langle A|B\rangle \doteq \langle A\Phi | B\Phi\rangle$. Both sides of Eq. (4) can be expressed as a finite series of nested commutators, which shows that S is connected, provided – of course – that T is connected itself.

With the operator S defined, the explicitly connected expansion of Eq. (2) can be written as follows [3]:

$$\bar{X} = \langle e^{S} | e^{-T} X e^{T} \rangle = \langle e^{S^\dagger} e^{-T} X e^{T} e^{-S^\dagger} \rangle. \tag{5}$$

CCSD equations

For a particular case of CCSD theory ($T = T_1 + T_2$) and a one-electron operator X the formula for the expectation value takes the following form,

$$\begin{aligned} \bar{X} &= \langle X \rangle + \langle S_1 | X \rangle + \langle X T_1 \rangle + \langle S_2 | [X, T_2] \rangle + \langle S_1 | [X, T_2] \rangle + \langle S_1 | [X, T_1] \rangle + \langle S_2 | [[X, T_1], T_2] \rangle \\ &+ \frac{1}{2} \langle S_1^2 | [X, T_2] \rangle + \frac{1}{2} \langle S_1 S_2 | [[X, T_2], T_2] \rangle + \frac{1}{2} \langle S_1 | [[X, T_1], T_1] \rangle + \frac{1}{2} \langle S_3 | [[X, T_2], T_2] \rangle \\ &+ \frac{1}{2} \langle S_1^2 | [[X, T_1], T_2] \rangle + \frac{1}{12} \langle S_1^3 | [[X, T_2], T_2] \rangle. \end{aligned} \tag{6}$$

Most of those terms contribute for the first time in a high W order (W denotes the HF fluctuation potential) and can be neglected.

The S operator can be expressed through the T and $T^\dagger$ operators using Eq. (4). The leading terms for S at the CCSD level of theory are [4],

$$\begin{aligned} S^{[1]} &= T, \\ S^{[2]} &= \widehat{\mathcal{P}}_1([T_1^\dagger, T_2]), \\ S^{[3]} &= \widehat{\mathcal{P}}_1(\frac{1}{2}[[T_1^\dagger, T_1], T_1] + [[T_2^\dagger, T_2], T_1]) + \widehat{\mathcal{P}}_2(\frac{1}{2}[[T_2^\dagger, T_2], T_2] + [[T_1^\dagger, T_2], T_1]) + \frac{1}{2}\widehat{\mathcal{P}}_3([[T_1^\dagger, T_2], T_2]). \end{aligned} \tag{7}$$

The formula (6) with the S operator truncated to terms of 3rd T order will be denoted as XCCSD[3]. It should be noted that this formula does not contain all $\mathcal{O}(W^3)$ terms (e.g. the contribution from $\langle S_2 | [X, T_3] \rangle$ is missing because of the T operator is truncated to double excitations). It can be shown that triples contributions of the $\mathcal{O}(W^3)$ order can be eliminated from Eq. (5). The resulting formula, rigorously correct through the $\mathcal{O}(W^3)$ order [3], is given below,

$$\bar{X}_{\mathrm{resp}}(3) = \langle X \rangle + \langle T_2 | [X, T_2] \rangle + 2\left(\langle T_2 | [W, C_1] \rangle + \langle T_2 | [[W, C_1], T_2] \rangle \right). \tag{8}$$

Here C_1 is the coupled Hartree-Fock (CHF) operator defined by the equation

$$\langle \delta T_1 | X + [H, C_1 - C_1^\dagger] \rangle = 0. \tag{9}$$

Technical details

The one-electron densities can be obtained from Eqs. (6) and (8) by replacing the X operator by the orbital substitution operator E_q^p. The orbital expressions for Eqs. (6), (7), and (8) were derived and programmed using the local automatic program and implemented into the MOLPRO package. The calculation of all commutators in Eqs. (6)–(8) can be effectively factorized, so that the most expensive contributions (in terms of the CPU time) scale as $\mathcal{O}(o^3v^3)$, therefore the calculation of first-order properties from XCCSD[3] and $\bar{X}_{\mathrm{resp}}(3)$ density matrices requires only a small additional computational effort (in the derivative method one also needs the Λ vector, with the cost $n_{\mathrm{iter}} \times \mathcal{O}(o^2v^4)$).

The electrostatic interaction energy of monomers A and B was calculated from the formula

$$E^{(1)}_{\mathrm{elst}} = \int \int \rho_{\mathrm{A}}(\mathbf{r}_1)\rho_{\mathrm{B}}(\mathbf{r}_2) v(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \tag{10}$$

where ρ_{A} and ρ_{B} are one-electron densities of monomers A and B and $v(\mathbf{r}_1, \mathbf{r}_2)$ is a generalized interaction potential,

$$v(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{r_{12}} - \frac{1}{N_A} \sum_{\alpha} \frac{Z_\alpha}{r_{\alpha 2}} - \frac{1}{N_B} \sum_{\beta} \frac{Z_\beta}{r_{\beta 1}} + \frac{1}{N_A N_B} \sum_{\alpha} \sum_{\beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}}. \tag{11}$$

Results

The new methods were tested by performing the calculations of dipole and quadrupole moments and electrostatic energies of various molecules. Details of calculations can be found in Ref. [5].

Table 1:

Dipole and quadrupole moments for HF and BH molecules. The results of approximate calculations are given as absolute errors in respect to FCI. All values in a.u.

	FCI	δ_{SCF}	$\delta_{\mathrm{XCCSD[3]}}$	$\delta_{\bar{X}_{\mathrm{resp}}(3)}$	$\delta^{\mathrm{nonrel}}_{\mathrm{CCSD}}$	$\delta^{\mathrm{rel}}_{\mathrm{CCSD}}$	$\delta^{\mathrm{nonrel}}_{\mathrm{CCSD(T)}}$	$\delta^{\mathrm{rel}}_{\mathrm{CCSD(T)}}$
HF, aug-cc-VDZ								
μ	–0.7025	–0.0573	0.0108	–0.0040	–0.0006	–0.0070	0.0013	–0.0009
Θ	1.6959	0.0387	–0.0026	0.0071	0.0040	0.0060	–0.0023	0.0006
BH, aug-cc-VTZ								
μ	0.543	0.143	0.017	–0.016	0.013	0.010	0.002	0.002
Θ	–2.334	–0.345	0.022	0.017	–0.005	–0.028	0.004	–0.007

FCI results for hydrogen fluoride were taken from A. Halkier *et al.*, *J. Chem. Phys.* **110**, 734 (1999).

Table 2:
Quadrupole moment of benzene (in a.u.) in several basis sets. The experimental quadrupole moment of benzene is equal to -6.31 ± 0.27 a.u.

Basis set	SCF	XCCSD[3]	$\bar{X}_{\mathrm{resp}}(3)$	CCSD$_{\mathrm{nonrel}}$	CCSD$_{\mathrm{rel}}$	CCSD(T)$_{\mathrm{nonrel}}$	CCSD(T)$_{\mathrm{rel}}$
aug-cc-pVDZ'	–6.857	–5.859	–5.713	–5.849	–5.854	–5.722	–5.739
aug-cc-pVDZ	–6.899	–5.916	–5.829	–5.932	–5.958	–5.816	–5.840
aug-cc-pVTZ	–6.645	–6.025	–5.864	–5.989	–5.983	–5.834	–5.855
aug-cc-pVQZ	–6.614	–6.065	–5.887	–6.017	-	-	-

Table 3:

Electrostatic energies of various van der Waals complexes calculated from one-electron densities originating from various post-HF approximations. In the first line the HF electrostatic energy is presented. For the post-HF methods we present the total correlation contribution $\epsilon^{(1)}_{\mathrm{elst}}$. Global minimum geometries were used in all cases but the azulene dimer. All values in cm^{-1}.

method/complex	Ar$_2$	(H$_2$O)$_2$	(CO)$_2$	He–H$_2$O	(Et)$_2$	(Bz)$_2$	(Az)$_2$
SCF	–42.70	–2334.12	–82.95	–7.71	–627.62	–865.78	–1833.01
MP2	–4.62	70.35	–50.75	–1.30	99.07	4.10	21.90
CCSD$_{\mathrm{nonrel}}$	–1.88	114.11	–34.63	–1.05	105.82	79.28	103.25
CCSD$_{\mathrm{rel}}$	–1.73	107.83	–29.88	–0.90	100.77	-	-
XCCSD[3]	–2.01	125.47	–42.09	–1.25	111.33	89.69	128.28
$\bar{X}_{\mathrm{resp}}(3)$	–1.62	111.36	–35.34	–0.92	117.00	143.31	226.77
SAPT	–2.32	102.26	–31.94	–0.63	89.60	-	-

Abbreviations used in Table: Et – ethyne, Bz – benzene, Az – azulene. Basis sets used: aug-cc-pV5Z/mb for Ar$_2$, aug-cc-pVTZ/mb for (H$_2$O)$_2$ and (CO)$_2$, aug-cc-pVTZ for (Et)$_2$, aug-cc-pVTZ' for (Bz)$_2$, aug-cc-pVDZ' for (Az)$_2$. (mb denotes midbond functions).

"SAPT" denotes the sum of corrections: $E^{(120)}_{\mathrm{elst,resp.}} + E^{(102)}_{\mathrm{elst,resp.}} + E^{(130)}_{\mathrm{elst,resp.}} + E^{(103)}_{\mathrm{elst,resp.}}$.

The $\epsilon^{(1)}_{\mathrm{elst}}$ correction for the benzene dimer changes sign for a distance close to the global minimum.

Summary

- New one-electron CCSD-type density matrices were derived and implemented into the MOLPRO suite of programs.
- Test calculations show that the XCCSD[3] and $\bar{X}_{\mathrm{resp}}(3)$ methods perform as well as derivative CCSD.
- From the theoretical point of view the $\bar{X}_{\mathrm{resp}}(3)$ method should be preferred, although XCCSD[3] performs surprisingly well.
- The computational cost of both new methods is two times smaller than the cost of derivative CCSD.
- Possible extensions of the expectation value method with the S operator:
  - Second-order properties were formulated in Ref. [4] and further investigated in Ref. [6].
  - The extension of the new method to include triples excitations, developed theoretically in Ref. [3], is planned in the near future.

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