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Size-extensive QCISDT – implementation and application

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Abstract

A size-extensive quadratic CI method with single (S), double (D), and triple (T) excitations, QCISDT, has been derived by appropriate cancellation of disconnected terms in the CISDT projection equations. Matrix elements of the new QCI method have been evaluated in terms of two-electron integrals and applied to a number of atoms and small molecules. While QCISDT results are of similar accuracy to CCSDT results, the new method is easier to implement, converges in many cases faster and, thereby, leads to advantages compared to CCSDT.

1. Introduction

Coupled cluster (CC) methods have become a primary tool for high-accuracy calculations of atomic and molecular properties [1–5]. In general, the results of CC calculations are better than those of configuration interaction (CI) or many-body perturbation theory (MBPT) calculations obtained with the same basis set and the same type of excitations (singles (S), doubles (D), triples (T), quadruples (Q), etc.). One of the most often used CC methods is quadratic CI (QCI) with S and D excitations (QCISD). Pople, Head-Gordon, and Raghavachari (PHR) [6] derived QCISD by adding quadratic terms to the CISD projection equations. In this way, QCISD becomes size-extensive at the cost of losing the variational character of a CI method. One can consider QCISD as a simplified CCSD method that does not contain cubic and quartic terms and, therefore, is somewhat easier to implement and to carry out than the CCSD method.

With QCISD, PHR introduced a new series of methods which they considered to be intermediate between CI and CC methods [6]. For the case that all excitations up to n-fold are included in the CI approach, the corresponding QCI method is obtained by adding just quadratic terms to the n and $n-1$ excitation equations. In this way, PHR expected to get a hierarchy of size-extensive QCI methods that provide computational advantages with regard to both CI and CC [6].

QCISD and its perturbational extension for T excitations, QCISD(T) [6], are widely used in ab initio investigations, which has to do with the fact that QCI programs were available since 1990 via the GAUSSIAN program series [7]. In addition, Gauss and Cremer developed analytical energy gradients for QCISD [8] and QCISD(T) [9], which allowed the routine calculation of response properties at the QCISD and QCISD(T) level of theory [10]. Many applications of QCISD and QCISD(T) have been published which show that QCI results are of similar accuracy to CCSD or CCSD(T) results in many cases, but sometimes are clearly worse, in particular when

T correlation corrections become important [10]. We have analyzed QCISD and QCISD(T) in terms of fifth, sixth, and infinite order perturbation theory and have shown that a major weakness of the two methods is the handling of T effects [11,12]. QCISD covers no T contributions at fourth or fifth order and only a few at sixth order MBPT and, therefore, often underestimates T effects while QCISD(T) lacks TT coupling terms and, accordingly, often overestimates T effects. Therefore, an extension of QCISD to QCISDT is needed.

The QCI concept has been criticized by various authors. For example, Paldus, Čížek, and Jeziorski [13] pointed out that QCISDT as suggested by PHR is no longer size-extensive even though the QCI methods were developed to restore size-extensiveness in CI. In a previous paper, we have analyzed the size-extensiveness problem of QCI and we have come to the following conclusions [14]:

(1) The original QCI concept introduced by PHR does not lead to a hierarchy of size-extensive methods. *There exists only one unique QCI method which is QCISD*, while QCID is identical with CCD, and QCISDT as suggested by PHR is not size-extensive and accordingly not useful for high-accuracy calculations.

(2) Improvement of the original QCI concept in such a way that it leads to size-extensive methods requires an iterative procedure for eliminating all disconnected terms in the CI projection equations. If one follows this procedure, one will obtain from CID CCD, from CISD QCISD, from CISDT a size-extensive method with several quadratic and one cubic term, which we have called ECISDT to distinguish it from the non-size-extensive QCISDT of PHR and from CISDT or CCSDT. We could show that size-extensivity corrections applied to the CI projection equations will always lead to the corresponding CC equations with the exception to QCISD and ECISDT. Hence, the QCI concept of PHR, even if properly applied, does not lead to a hierachy of independent CC methods [14].

We have also shown in the previous paper that the only way to preserve the QCI concept and to develop it to a hierarchy of independent size-extensive CC methods is to start from the CC projection equations rather than the CI equations (although formally one could also start from the latter) [14]. If one takes the

CC projection equations in their connected form and deletes all cluster operators but those required by the original QCI concept, then size-extensive QCI methods can be derived as counterparts for all possible CC methods. We have denoted these methods QCISDTc, QCISDTQc, etc. to distinguish them from the non-size-extensive QCISDT, QCISDTQ, etc. methods suggested by PHR. In this work, we develop the matrix elements of QCISDTc in terms of two-electron integrals, describe the implementation of QCISDTc, and report on the first results of its application. For reasons of simplicity, we use the acronym QCISDT for QCISDTc in the following.

2. Theory

We can write the projection equations of a truncated CI method with n-fold excitations in the following way:

$$E_{corr}^{CI} = \langle \Phi_0 | \bar{H}\hat{T}_2 | \Phi_0 \rangle , \tag{1}$$

$$\langle \Phi_p | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + ... + \hat{T}_n) | \Phi_0 \rangle = c_p E_{corr}^{CI}$$

$$(p = 1, 2, ..., n) , \tag{2}$$

or, alternatively, as

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = c_i^a E_{corr}^{CI} , \tag{3}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4) | \Phi_0 \rangle$$

$$= c_{ij}^{ab} E_{corr}^{CI} , \tag{4}$$

$$\langle \Phi_p | \bar{H}\left(\sum_{i=p-2}^{\min [p+2,n]} \hat{T}_i \right) | \Phi_0 \rangle = c_p E_{corr}^{CI}$$

$$(n \geqslant p \geqslant 3) . \tag{5}$$

In Eqs. (1)–(5), $| \Phi_i^a \rangle$ and $| \Phi_{ij}^{ab} \rangle$ are singly and doubly excited wavefunctions, while $| \Phi_p \rangle$ denotes any p-fold excited wavefunction. Subscripts $i, j, ...$ ($a, b, ...$) refer to occupied (virtual) spin orbitals, while subscripts $p, q, ...$ denote general orbitals. The reference function $| \Phi_0 \rangle$ is set equal to the Hartree–Fock (HF) wavefunction for reasons of simplicity. $\bar{H}$ denotes the normal-order Hamiltonian defined by

$$\bar{H} = \hat{H} - E(\text{HF}) = \bar{H}_0 + \hat{V} = \bar{H}_0 + \sum_{pq} \{\hat{b}_p^+ \hat{b}_q\}\langle p | \hat{F} | q \rangle$$

$$+ \tfrac{1}{4} \sum_{pqrs} \{\hat{b}_p^+ \hat{b}_q^+ \hat{b}_r \hat{b}_s\}\langle pq \| rs \rangle , \tag{6}$$

with $\hat{b}^+$ and $\hat{b}$ being creation and annihilation operators. The cluster operators $\hat{T}_1$ and $\hat{T}_2$ are given by

$$\hat{T}_1 = \sum_{ia} c_i^a \hat{b}_a^+ \hat{b}_i , \tag{7}$$

$$\hat{T}_2 = \tfrac{1}{4} \sum_{ij} \sum_{ab} c_{ij}^{ab} \hat{b}_a^+ \hat{b}_i \hat{b}_b^+ \hat{b}_j , \tag{8}$$

or, in general, by

$$\hat{T}_n = \frac{1}{n!} \sum_{ijk...} \sum_{abc...} c_{ijk...}^{abc...} \hat{b}_a^+ \hat{b}_i \hat{b}_b^+ \hat{b}_j \hat{b}_c^+ \hat{b}_k... . \tag{9}$$

In the following, we will use in the CI and QCI projection equations the same symbols for the cluster operators, but distinguish QCI amplitudes from CI coefficients by using $a_{ijk...}^{abc...}$ for the former.

Formally, the QCI projection equations can be derived from Eqs. (3)–(5) by adding or subtracting the following terms. (1) As for the S and D projection equations, it suffices to add $\hat{T}_1\hat{T}_2$ and $\tfrac{1}{2}\hat{T}_2^2$, respectively, in order to eliminate all disconnected terms from these equations. (2) For any excitation higher than D ($p \geqslant 3$), there appear just two disconnected terms, namely $\langle \Phi_p | \bar{H}\hat{T}_{p-2} | \Phi_0 \rangle$ ($= \langle ab \| ij \rangle c_{p-2}$) and $c_p E_{corr}^{CI}$ in the corresponding projection equation. Introducing $-\bar{H}\hat{T}_{p-2}$ and parts of the term $\bar{H}\hat{T}_2\hat{T}_p$, namely $(\bar{H}\hat{T}_2\hat{T}_p)_C$ and $(\hat{T}_p(\bar{H}\hat{T}_2)_C)_{\text{disconnected}}$, on the left side of Eq. (5) leads to cancellation of all disconnected terms and to the QCI equations in their general from [14],

$$E_{corr}^{QCI} = \langle \Phi_0 | \bar{H}\hat{T}_2 | \Phi_0 \rangle , \tag{10}$$

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3) \\ + (\bar{H}\hat{T}_1\hat{T}_2)_C | \Phi_0 \rangle = 0 , \tag{11}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4) \\ + \tfrac{1}{2}(\bar{H}\hat{T}_2^2)_C | \Phi_0 \rangle = 0 , \tag{12}$$

$$\langle \Phi_p | \bar{H}\left(\sum_{i=p-1}^{\min[p+2,n]} \hat{T}_i \right) + (\bar{H}\hat{T}_2\hat{T}_p)_C | \Phi_0 \rangle = 0 \\ (n \geqslant p \geqslant 3) . \tag{13}$$

Eqs. (10)–(13) establish a hierarchy of size-extensive QCI methods that also covers the original QCISD of PHR. Accordingly, it is straightforward to write down the projection equations of size-extensive QCISDT,

$$\langle \Phi_0 | \bar{H}\hat{T}_2 | \Phi_0 \rangle = E_{corr}^{QCISDT} , \tag{14}$$

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_2) | \Phi_0 \rangle_C = 0 , \tag{15}$$

$$(\Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \tfrac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle_C = 0 , \tag{16}$$

$$\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_2 + \hat{T}_3 + \hat{T}_2\hat{T}_3) | \Phi_0 \rangle_C = 0 . \tag{17}$$

Contrary to the non-size-extensive formulas of PHR [6], the S projection equation contains the cluster operators $\hat{T}_1\hat{T}_2$ to enforce size extensiveness.

The matrix elements of the QCISDT equations can be expressed in terms of two-electron integrals in order to obtain a form that can be implemented on a computer,

$$E_{corr}^{QCISDT} = \tfrac{1}{4} \sum_{ij,ab} \langle ij \| ab \rangle a_{ij}^{ab} , \tag{18}$$

$$(\epsilon_i - \epsilon_a) a_i^a = u_i^a + v_i^a \\ + \sum_{l<m} \sum_{d<e} \langle lm \| de \rangle a_{ilm}^{ade} , \tag{19}$$

$$(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) a_{ij}^{ab} = u_{ij}^{ab} + v_{ij}^{ab} \\ + \sum_{l,d<e} (\langle bl \| de \rangle a_{ijl}^{ade} + \langle al \| de \rangle a_{ijl}^{dbe}) \\ + \sum_{l<m,d} (\langle lm \| dj \rangle a_{ilm}^{abd} + \langle lm \| di \rangle a_{ljm}^{abd}) , \tag{20}$$

where u_i^a, v_i^a, u_{ij}^{ab} and v_{ij}^{ab} have already been defined to set up the QCISD equations [6], namely

$$u_i^a = - \sum_{ld} \langle la \| id \rangle a_i^d - \tfrac{1}{2} \sum_{lde} \langle la \| de \rangle a_{il}^{de} \\ - \tfrac{1}{2} \sum_{lmd} \langle lm \| id \rangle a_{lm}^{ad} , \tag{21}$$

$$u_{ij}^{ab} = \sum_d (\langle ab \| dj \rangle a_i^d - \langle ab \| di \rangle a_j^d) \\ + \sum_l (\langle la \| ij \rangle a_l^b - \langle lb \| ij \rangle a_l^a) \\ + \tfrac{1}{2} \sum_{de} \langle ab \| de \rangle a_{ij}^{de} + \tfrac{1}{2} \sum_{lm} \langle lm \| ij \rangle a_{lm}^{ab} \\ - \sum_{ld} \sum_p (-1)^p P(ij|ab) \langle lb \| jd \rangle a_{il}^{ad} , \tag{22}$$

$$v_i^a = \tfrac{1}{2} \sum_{lm} \sum_{de} \langle lm \| de \rangle (a_l^d a_{lm}^{ea} + a_l^a a_{im}^{ed} + 2a_l^d a_{im}^{ad}) , \tag{23}$$

$$v_{ij}^{ab} = \tfrac{1}{4} \sum_{lm} \sum_{de} \langle lm \| de \rangle [a_{ij}^{de} a_{lm}^{ab} \\ - 2(a_{ij}^{ad} a_{lm}^{be} + a_{ij}^{be} a_{lm}^{ad} + a_{il}^{ab} a_{jm}^{de} + a_{il}^{de} a_{jm}^{ab}) \\ + 4(a_{il}^{ad} a_{jm}^{be} + a_{il}^{be} a_{jm}^{ad})] . \tag{24}$$

From Eq. (17), the spin-independent formulation of the T equation is obtained as

$$(\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c)a_{ijk}^{abc}$$

$$= -\sum_p (-1)^P P(i/jk|a/bc)$$

$$\times \left(\sum_d X_1(i,d,b,c)a_{jk}^{ad} + \sum_l X_2(j,k,l,a)a_{il}^{bc} \right)$$

$$+ \sum_p (-1)^P P(a/bc) \left(\tfrac{1}{2}\sum_{ef} X_3(b,c,e,f)a_{ijk}^{aef} \right.$$

$$\left. + \sum_f Y_1(f,a)a_{ijk}^{fbc} \right) + \sum_p (-1)^P P(i/jk)$$

$$\times \left(\tfrac{1}{2}\sum_{mn} X_4(m,n,j,k)a_{imn}^{abc} + \sum_n Y_2(n,i)a_{njk}^{abc} \right)$$

$$- \sum_p (-1)^P P(i/jk|a/bc) \sum_{me} X_5(m,a,i,e)a_{jkm}^{bce} ,$$

$$(25)$$

where we make use of intermediate arrays X_n (see Table 1) to reduce computational work. The permutation symbol $\sum_p (-1)^P P(i/jk|a/bc)$ requires summation over the identity permutation and permutations that interchange orbital label i with j, k; and a with b, c without permutation of $j \leftrightarrow k$ or $b \leftrightarrow c$.

The QCISDT projection equations (Eqs. (19), (20), and (25)) are solved iteratively to get the QCISDT correlation energy E_{corr}^{QCISDT} (Eq. (18)). We

have programmed these equations and have inserted the corresponding computer code into the ab initio package COLOGNE [15]. In addition, we have written a CCSDT program in order to be able to compare QCISDT and CCSDT results.

Size extensiveness has been tested numerically by calculating dissociation energies of molecules such as N_2, CO, HCCH, etc. In all cases investigated, size extensiveness was fully confirmed.

In QCISDT calculations, the most time-consuming step is the evaluation of the third term in Eq. (25), which involves asymptotically $n_{occ}^3 n_{virt}^5$ operations. The computational effort per iteration cycle is for QCISDT similar to that for CCSDT, what becomes obvious when replacing in Eq. (25) QCISDT intermediate arrays by the corresponding CCSDT intermediate arrays also shown in Table 1. QCISDT has some advantages with regard to the number of $\mathcal{O}(M^6)$ steps (see Table 1), but the amount of computer time needed for these operations is only a fraction of the total QCISDT or CCSDT time. However, in many of the calculations presented in section 3 time savings (maximally 60%) result from the fact that QCISDT converges faster than CCSDT.

3. Numerical results and discussion

QCISDT has been applied to a set of atoms and molecules, for which Bauschlicher and co-workers

Table 1
Intermediate arrays used in the T amplitude equations for QCISDT and CCSDT [a]

Array	QCISDT	CCSDT
$X_1(i,d,b,c)$	$\langle id\|bc\rangle + \tfrac{1}{2}\sum_{mne}\langle mn\|ed\rangle a_{imn}^{ebc}$	$X_1^{QCISDT} - \sum_p (-1)^P P(bc)(\sum_{me}\langle mb\|ed\rangle a_{im}^{ce}$ $- \sum_m Z1(mb,id)a_m^c) + \sum_{m<n}(\langle mn\|id\rangle + \sum_e \langle mn\|ed\rangle a_i^f)\tau_{mn}^{bc}$ $+ \sum_e \langle bc\|ed\rangle a_i^f - \sum_{mn,e}(\langle mn\|ed\rangle a_m^a)a_{in}^{bc}$
$X_2(j,k,l,a)$	$\langle jk\|la\rangle + \tfrac{1}{2}\sum_{mef}\langle ml\|ef\rangle a_{mjk}^{aef}$	$X_2^{QCISDT} + \sum_p (-1)^P P(jk)(\sum_{me}\langle ml\|ej\rangle a_{km}^{ae} + \sum_e Z2(al,ej)a_k^e)$ $+ \sum_{e<f}(\langle la\|ef\rangle + \sum_m \langle ml\|ef\rangle a_m^a)\tau_{jk}^{ef} + \sum_m \langle ml\|jk\rangle a_m^a$
$X_3(b,c,e,f)$	$\langle bc\|ef\rangle + \tfrac{1}{2}\sum_{mn}\langle mn\|ef\rangle a_{mn}^{bc}$	$\langle bc\|ef\rangle + \tfrac{1}{2}\sum_{mn}\langle mn\|ef\rangle \tau_{mn}^{bc} + \sum_p (-1)^P P(bc)\sum_m \langle mb\|ef\rangle a_m^c$
$X_4(m,n,j,k)$	$\langle mn\|jk\rangle + \tfrac{1}{2}\sum_{ef}\langle mn\|ef\rangle a_{jk}^{ef}$	$\langle mn\|jk\rangle + \tfrac{1}{2}\sum_{ef}\langle mn\|ef\rangle \tau_{jk}^{ef} + \sum_p (-1)^P P(jk)\sum_e \langle mn\|ek\rangle a_j^e$
$X_5(m,a,i,e)$	$\langle ma\|ie\rangle - \sum_{nf}\langle mn\|ef\rangle a_{in}^{af}$	$\langle ma\|ie\rangle - \sum_{nf}\langle mn\|ef\rangle (a_{in}^{af} - a_n^a a_i^f) - \sum_f \langle ma\|ef\rangle a_i^f$ $- \sum_n \langle mn\|ie\rangle a_n^a$
$Y_1(f,a)$	$\tfrac{1}{2}\sum_{mne}\langle mn\|ef\rangle a_{mn}^{ae}$	$\tfrac{1}{2}\sum_{mne}\langle mn\|ef\rangle \tau_{mn}^{ae} + \sum_{me}\langle ma\|ef\rangle a_m^e$
$Y_2(n,i)$	$\tfrac{1}{2}\sum_{mef}\langle mn\|ef\rangle a_{im}^{ef}$	$\tfrac{1}{2}\sum_{mef}\langle mn\|ef\rangle \tau_{im}^{ef} + \sum_{me}\langle mn\|ie\rangle a_m^e$

[a] The arrays τ_{ij}^{ab}, $Z1(mb,id)$ and $Z2(al,ej)$ are defined by $\tau_{ij}^{ab} = a_{ij}^{ab} + a_i^a a_j^b - a_i^b a_j^a$, $Z1(mb,id) = \langle mb\|id\rangle + \sum_e \langle mb\|ed\rangle a_i^e + \sum_{ne}\langle mn\|ed\rangle a_{in}^a$, $Z2(al,ej) = \langle al\|ej\rangle - \sum_m \langle ml\|ej\rangle a_m^a + \sum_{mf}\langle ml\|ef\rangle a_{jm}^{af}$.

Table 2
Comparison of QCISDT energies with full-CI (FCI) and various other coupled cluster (CC) energies [a]

Molecule, state geom./ref./basis [a]	E(approx.) − E(FCI)					Absolute energies	
	MBPT(4)	QCISD	QCISD(T)	QCISDT	CCSDT	E(QCISDT)	E(FCI)
Ne							
R/4s2p1d	−0.873	+1.708	−0.155	−0.549	−0.066	−128.703011	−128.702462
R/6s4p1d	+2.562	+2.511	−0.040	−0.493	+0.119	−128.768382	−128.767889
F							
U/4s3p1d	+1.830	+1.463	−0.011	−0.475	−0.058	−99.547095	−99.546620
U/4s3p2d	+0.268	+2.250	−0.033	−0.585	−0.104	−99.567068	−99.566483
U/5s4p2d	+0.529	+3.097	+0.047	−0.478	−0.015	−99.595355	−99.594877
F⁻							
R/4s3p1d	−4.748	+2.232	+0.112	−2.538	+0.329	−99.655879	−99.653341
R/4s3p2d	−5.044	+3.533	+0.085	−2.410	+0.319	−99.680077	−99.677676
R/5s4p2d	−5.398	+5.935	−0.367	−2.633	+0.273	−99.709323	−99.706690
HF							
R_e/R/DZP	−1.263	+2.567	+0.242	−0.268	+0.266	−100.251237	−100.250969
1.5R_e/R/DZP	+0.769	+4.136	+0.664	−0.452	+0.645	−100.160845	−100.160393
2.0R_e/R/DZP	+4.841	+8.395	+1.383	−0.962	+1.125	−100.082070	−100.081108
H₂O							
R_e/R/DZP	+0.917	+3.879	+0.617	+0.030	+0.533	−76.256594	−76.256624
1.5R_e/R/DZP	+5.764	+9.365	+1.814	+0.021	+1.785	−76.071384	−76.071405
NH₂, ²B₁							
R_e/U/DZP	+1.900	+3.134	+0.510	−0.046	+0.216	−55.742666	−55.742620
1.5R_e/U/DZP	+39.230	+9.985	+3.609	+0.051	+1.226	−55.605158	−55.605209
2.0R_e/U/DZP	+18.790	+11.034	+7.393	+1.461	+2.277	−55.504063	−55.505524
NH₂, ²A₁							
R_e/U/DZP	+1.615	+2.908	+0.492	−0.023	+0.223	−55.688785	−55.688762
1.5R_e/U/DZP	+7.779	+7.276	+1.966	−0.059	+0.811	−55.517673	−55.517614
2.0R_e/U/DZP	+41.297	+19.926	+9.951	−0.197	b	−55.415330	−55.415133
CH₂							
³B₁/U/DZP		+2.054	+0.343	−0.107	+0.017	−39.046367	−39.046260
¹A₁/U/DZP		+3.522	+0.867	−0.024	+0.207	−39.027207	−39.027183
mean abs. dev. [c]	7.654	5.281	1.462	0.660	0.531		

[a] Energy differences in mE_h, absolute energies in E_h. Geometries, basis sets, and FCI energies are given in ref. [16]. MBPT(4), QCISD and QCISD(T) energies from ref. [6], CCSDT energies from ref. [17]. Restricted (RHF) reference denoted by R; unrestricted (UHF) reference denoted by U.
[b] Calculation did not converge. See ref. [17].
[c] Mean absolute deviation for 21 (QCISDT) and 20 (CCSDT) calculations.

[16] have reported full configuration interaction (FCI) calculations and which, therefore, have already been used as suitable test cases for QCISD and QCISD(T) by PHR [6]. Test cases comprise chemically interesting problems such as the determination of the electron affinity of F, the singlet–triplet separation in CH₂, and excited electronic states of NH₂. In Table 2, the energies from 21 QCISDT calculations are compared with the corresponding FCI ener-

gies. Energy differences E(approx.) − E(FCI) for fourth-order perturbation theory (MBPT(4)), QCISD, QCISD(T) [6] and CCSDT [17] calculations are also given in Table 2 for reasons of comparison.

All energies obtained at the QCISDT level of theory are lower than the corresponding CCSDT energies obtained with the same basis set at the same geometry. Differences vary from just 0.1 mE_h in the case

of CH_2 to 2.9 mE_h for the F^- anion. In general, QCISDT and CCSDT energies are closer for equilibrium geometries while energy differences increase for non-equilibrium geometries. Some of the CCSDT energies are lower than the FCI energies thus reflecting the non-variational character of CCSDT. Since QCISDT energies are lower than CCSDT energies, most of the former are also lower than the corresponding FCI energies. This reflects the fact that QCISDT is also non-variational, but shows in addition that positive energy contributions contained in CCSDT are not covered by QCISDT. For example, at fifth order perturbation theory both $E(\text{TS})$, $E(\text{TQ})$, and $E(\text{QT})$ are missing in QCISDT, of which $E(\text{TS}) \geqslant 0$ in most cases thus leading to $E(\text{QCISDT}) \leqslant E(\text{CCSDT})$ [14].

PHR have investigated whether QCISD and QCISD(T) energies come close to FCI results. In Table 2, the mean absolute deviation of calculated energies $E(\text{approx.})$ from FCI energies is compared for various correlation corrected methods. The mean deviation is 7.7 mE_h which is rather large in the case of MBPT(4), but drops to 5.2 mE_h for QCISD thus indicating the superiority of CC methods as compared to MBPT methods. The perturbational inclusion of T excitations at the QCISD level reduces the mean deviation to 1.5 mE_h, which reflects the importance of T excitations. When going from QCISD(T) to QCISDT, i.e. when introducing T excitations at the CC level of theory rather than the perturbation level, the mean deviation decreases to 0.7 mE_h, which means that results have essentially reached FCI quality. For CCSDT, the mean deviation is 0.5 mE_h which is slightly better than that for QCISDT, but basically both methods achieve the same level of accuracy.

Relative energies obtained by QCISDT or CCSDT do not differ much. The electron affinity of fluorine is 2.960, 3.075, and 3.101 eV at the QCISDT level white it is 2.894, 3.014, and 3.035 eV at the CCSDT level of theory (Table 2). The QCISDT singlet–triplet splitting of CH_2 (12.02 kcal/mol) is almost identical with the corresponding CCSDT value (12.09 kcal/mol). Similarly close are the excitation energies for NH_2 obtained at the two levels of theory (Table 2). We conclude that QCISDT fully reproduces CCSDT energies. However, in view of the fact that QCISDT is easier to implement than CCSDT and in view of time-savings because of faster convergence, QCISDT can represent an attractive alternative for

including T correlation effects at the CC level of theory.

Acknowledgement

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