Is coupled cluster singles and doubles (CCSD) more computationally intensive than quadratic configuration interaction (QCISD)?

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It is shown that the recently proposed QCI method including all single and double substitutions has essentially the same computational requirements as the more complete CCSD approach. If properly formulated, the CCSD equations contain at most quadratic terms in the excitation amplitudes.

INTRODUCTION

In a recent paper, Pople, Head-Gordon, and Raghavachari[1] introduced a new method, designated quadratic configuration interaction (QCI). Paldus, Čižek, and Jeziorski[2] have recently noted in a pedagogical paper that when limited to single and double substitutions, QCISD, is an approximation to the single reference coupled cluster single and double (CCSD) excitation model developed earlier.[3] Two approximate CC models, CPMET-C[4] and CCSD-1[5(a)] are quite similar to QCISD.[2] However, Pople *et al.* based their derivation on CI equations stressing the simplicity of the QCISD equations compared to CCSD and preferred to treat QCI as an intermediate approach between CC and CI.

It is the aim of this paper to demonstrate that if properly formulated, QCISD and CCSD have the same computational requirements at the m^6 level, m being proportional to the number of basis functions. In other words, all terms that need to be neglected in CCSD to obtain QCISD require only m^5 floating point operations (FPO) for their evaluation. Moreover, if appropriate intermediate products are defined, the algebraic equations of CCSD are not more complicated than those of QCISD.

To make our point, we first present in the Theory section the CCSD equations in the spin–orbital basis, using a set of intermediates leading to a very compact form. We prefer to work in the spin–orbital basis so that comparison with the spin–orbital QCISD expressions presented by Pople *et al.*[1] is straightforward. RHF closed-shell formulations of QCISD have not been presented in the literature yet. However, all of our present discussion and conclusions are easily extended to the closed-shell case. For the sake of comparison, we further assume that SCF spin–orbitals are employed (i.e., although not necesary we assume the Fock matrix to be diagonal). In the Discussion section the computational requirements of the two methods are investigated.

THEORY

In the following, letters i, j, k, l, (a, b, c, d) will indicate occupied (unoccupied) spin–orbitals in the reference SCF configuration.

In coupled cluster theory the correlation energy is obtained from

$$E_{\text{corr}} = \frac{1}{2}\sum_{\substack{ij\\ab}} \langle ij||ab\rangle \tau_{ij}^{ab}, \tag{1}$$

where

$$\langle ij||ab\rangle = \int\int \chi_i^*(1)\chi_j^*(2)(1/r_{12})[\chi_a(1)\chi_b(2) - \chi_b(1)\chi_a(2)]\,d\tau_1\,d\tau_2 \tag{2}$$

is an antisymmetrized two-electron Coulomb integral, and

$$\tau_{ij}^{ab} = \tfrac{1}{2}t_{ij}^{ab} + t_i^a t_j^b \tag{3}$$

is an "effective" double excitation amplitude.

The t_1 equation is

$$\sum_b h_b^a t_i^b - \sum_j h_i^j t_j^a + \sum_{jb} h_b^j (t_{ij}^{ab} + t_i^b t_j^a) + \sum_{jb}\langle ib||aj\rangle t_j^b - \sum_{jbc}\langle ja||bc\rangle \tau_{ij}^{bc} - \sum_{jkb}\langle jk||ib\rangle \tau_{jk}^{ab} = 0, \tag{4}$$

$$h_b^a = \epsilon_a \delta_{ab} - \sum_{jkc}\langle jk||bc\rangle \tau_{jk}^{ac}, \tag{5}$$

$$h_i^j = \epsilon_i \delta_{ij} + \sum_{kbc}\langle jk||bc\rangle \tau_{ik}^{bc}, \tag{6}$$

$$h_b^j = \sum_{kc}\langle jk||bc\rangle t_k^c, \tag{7}$$

and the t_2 equation is

$$\langle ij||ab\rangle + \sum_{kl} a_{ij}^{kl}\tau_{kl}^{ab} + \sum_{cd} b_{cd}^{ab}\tau_{ij}^{cd} + P_{ab}\left(\sum_c g_c^a t_{ij}^{cb} + \sum_k \langle ka||ij\rangle t_k^b\right) - P_{ij}\left(\sum_k g_i^k t_{kj}^{ab} - \sum_c \langle ab||ci\rangle t_i^c\right) + P_{ij}P_{ab}\left(\sum_{kc} h_{ic}^{ak} t_{jk}^{bc} - \sum_{kc}\langle ic||ak\rangle t_j^c t_k^b\right) = 0, \tag{8}$$

$$g_c^a = h_c^a + \sum_{kd}\langle ak||cd\rangle t_k^d, \tag{9}$$

$$g_i^k = h_i^k + \sum_{lc}\langle kl||ic\rangle t_l^c \tag{10}$$

$$a_{ij}^{kl} = \langle ij||kl\rangle + P_{ij}\sum_c \langle ic||kl\rangle t_j^c + \sum_{cd}\langle kl||cd\rangle \tau_{ij}^{cd}, \tag{11}$$

$$b_{cd}^{ab} = \langle ab||cd\rangle - P_{ab}\sum_k \langle ak||cd\rangle t_k^b, \tag{12}$$

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$$h_{ic}^{ak} = \langle ic||ak\rangle - \sum_l \langle ic||lk\rangle t_l^a + \sum_d \langle dc||ak\rangle t_i^d - \sum_{ld} \langle kl||cd\rangle \tau_{il}^{da}, \quad (13)$$

where P is a permutation operator ($P_{ab} g_c^a = g_c^a - g_c^b$, etc.).

The CCSD equations in the spin–orbital basis were first presented by Purvis and Bartlett back in 1982.[5(b)] Their set is of course equivalent to ours. However, in the present formulation t_2 has been "lumped together" with t_1^2 to the maximum possible extent through the use of τ [see Eq. (3)]. As a result we get a set of CCSD equations in which we need to evaluate at most *quadratic* terms in the t (or τ) amplitudes. Note that no cubic or quartic terms explicitly appear in this formulation. Of course, these terms are present in the model but they are all accounted for by τ t_2 and τ^2 terms. It is important to note that to the best of our knowledge this is the first time that this property of the CCSD model has been explicitly mentioned in the literature. We have therefore proven that the absence of cubic or quartic terms in the configuration amplitudes in QCISD is also a property of CCSD if the latter is formulated in terms of effective (τ) double excitation amplitudes and the right set of intermediate products is employed. We have shown in a recent paper[6] that the closed-shell CCSD model[7] may also be reformulated in this way with the aid of the unitary group approach.

To obtain QCISD from our CCSD equations, all quadratic terms in t_1 must be dropped. This is accomplished by replacing τ by $\frac{1}{2}t_2$ in all equations [i.e., the second term in Eq. (3) is not included]. Additionally, the $h_b^j t_i^b t_j^a$ term in the t_1 equation (4) and the $\langle ic||ak\rangle t_j^c t_k^b$ term in the t_2 equation (8) must be neglected. Finally, all linear terms in t_1 in the set of intermediates for the t_2 equation should also be excluded [see Eqs. (11)–(13)].

Therefore, the QCISD equations are

$$E_{\rm corr} = \frac{1}{4} \sum_{\substack{ij \\ ab}} \langle ij||ab\rangle t_{ij}^{ab}, \quad (14)$$

$$\sum_b h_b^a t_i^b - \sum_j h_i^j t_j^a + \sum_{jb} (h_b^j t_{ij}^{ab} + \langle ib||aj\rangle t_j^b) - \frac{1}{2} \sum_{jbc} \langle ja||bc\rangle t_{ij}^{bc} - \frac{1}{2} \sum_{jkb} \langle jk||ib\rangle t_{jk}^{ab} = 0, \quad (15)$$

$$h_b^a = \epsilon_a \delta_{ab} - \frac{1}{2} \sum_{jkc} \langle jk||bc\rangle t_{jk}^{ac}, \quad (16)$$

$$h_i^j = \epsilon_i \delta_{ij} + \frac{1}{2} \sum_{kbc} \langle jk||bc\rangle t_{ik}^{bc}, \quad (17)$$

$$h_b^j = \sum_{kc} \langle jk||bc\rangle t_k^c, \quad (18)$$

$$\langle ij||ab\rangle + \frac{1}{2} \sum_{kl} a_{ij}^{kl} t_{kl}^{ab} + \frac{1}{2} \sum_{cd} \langle ab||cd\rangle t_{ij}^{cd} + P_{ab}\left(\sum_c h_c^a t_{ij}^{cb} + \sum_k \langle ka||ij\rangle t_k^b\right) - P_{ij}\left(\sum_k h_i^k t_{kj}^{ab} - \sum_c \langle ab||cj\rangle t_i^c\right) + P_{ij}P_{ab}\left(\sum_{kc} h_{ic}^{ak} t_{jk}^{bc}\right) = 0, \quad (19)$$

$$a_{ij}^{kl} = \langle ij||kl\rangle + \frac{1}{2} \sum_{cd} \langle kl||cd\rangle t_{ij}^{cd}, \quad (20)$$

$$h_{ic}^{ak} = \langle ic||ak\rangle - \frac{1}{2} \sum_{ld} \langle kl||cd\rangle t_{il}^{da}, \quad (21)$$

Note that the g and b intermediates of Eqs. (9), (10), and (12) are no longer necessary. However, for comparison purposes between the QCISD equations (15) and (19), and the CCSD equations (4) and (8), we may write for the QCISD case

$$b_{cd}^{ab} = \langle ab||cd\rangle, \quad (22)$$

$$g_c^a = h_c^a, \quad (23)$$

$$g_i^k = h_i^k, \quad (24)$$

$$\tau_{ij}^{ab} = \tfrac{1}{2} t_{ij}^{ab}. \quad (25)$$

The reader should keep in mind these relations when analyzing the computational cost of the two methods in the next section (see also Table I).

DISCUSSION

The notation employed here for the QCISD equations makes quite simple a term by term comparison with the set presented by Pople *et al.*[1] Although derived from different perspectives, after some elementary manipulations (due to our different definitions of intermediate products) it is easily proven that the two sets are equivalent. As described above only a few terms need to be dropped to obtain QCISD from CCSD. Consequently, analytic energy gradients for QCISD[8] may be directly obtained from our published formulas,[9] by simply neglecting the appropriate terms.

Our QCISD equations were computationally implemented by simply commenting out a few lines of code in our CCSD program.[6,7] Our numerical tests for the water molecule with the DZP basis set at three different geometries gave agreement with Ref. 1 to all six published decimal places.

We next turn to analyze the computational requirements of both QCISD and CCSD according to the present formulation. Let $n(N)$ be the number of occupied (unoccupied) spin–orbitals in the system. Both QCISD and CCSD need to be solved iteratively[10] and because of the common terms in the two methods, we can safely assume that both procedures will roughly require the same number of iterations to achieve convergence. The detailed number of FPO required in each iteration to evaluate all the terms described above is presented in Tables I and II for the two methods together with CISD for comparison purposes. (For a detailed analysis of the CISD method see Ref. 6.)

In obtaining the computational cost of each of the terms depicted in Table I, one should keep in mind the antisymmetry property of the two electron integrals and t_2 amplitudes. For example, term 3 in Table I, say $q_{ij}^{ab} = \Sigma_{kl} a_{ij}^{kl} \tau_{kl}^{ab}$, needs to be evaluated only for $i>j$ and $a>b$ due to its symmetry properties.

$$q_{ij}^{ab} = -q_{ji}^{ab} = -q_{ij}^{ba} = +q_{ji}^{ba}. \quad (26)$$

Simultaneously, the internal contraction over indices k,l may be reduced to $k>l$ by simply using

TABLE I. A term by term analysis of the computational cost of CISD, QCISD, and CCSD; $n(N)$ is the number of occupied (unoccupied) spin–orbitals.

Entry	Term	Cost	CISD	QCISD	CCSD
1	$\sum_{jbc}\langle ja\|\|bc\rangle\tau_{ij}^{bc}$	$\frac{1}{2}n^2N^3$	×	×	×
2	$\sum_{jkb}\langle jk\|\|ib\rangle\tau_{jk}^{ab}$	$\frac{1}{2}n^3N^2$	×	×	×
3	$\sum_{kl}a_{ij}^{kl}\tau_{kl}^{ab}$	$\frac{1}{8}n^4N^2$	×	×	×
4	$\sum_{cd}b_{cd}^{ab}\tau_{ij}^{cd}$	$\frac{1}{8}n^2N^4$	×	×	×
5	$\sum_{c}g_c^a t_{ij}^{cb}$	$\frac{1}{2}n^2N^3$	×	×	×
6	$\sum_{k}g_i^k t_{kj}^{ab}$	$\frac{1}{2}n^3N^2$	×	×	×
7	$\sum_{c}\langle ab\|\|cj\rangle t_i^c$	$\frac{1}{2}n^2N^3$	×	×	×
8	$\sum_{k}\langle ka\|\|ij\rangle t_k^b$	$\frac{1}{2}n^3N^2$	×	×	×
9	$\sum_{kc}h_{ic}^{ak}t_{jk}^{bc}$	n^3N^3	×	×	×
10	$\sum_{cd}\langle kl\|\|cd\rangle\tau_{ij}^{cd}$	$\frac{1}{8}n^4N^2$		×	×
11	$\sum_{ld}\langle kl\|\|cd\rangle\tau_{il}^{da}$	n^3N^3		×	×
12	$\sum_{jkc}\langle kj\|\|bc\rangle\tau_{jk}^{ac}$	$\frac{1}{2}n^2N^3$		×	×
13	$\sum_{kbc}\langle jk\|\|bc\rangle\tau_{ik}^{bc}$	$\frac{1}{2}n^3N^2$		×	×
14	$\sum_{c}\langle ic\|\|kl\rangle t_j^c$	$\frac{1}{2}n^4N$			×
15	$\sum_{k}\langle ak\|\|cd\rangle t_k^b$	$\frac{1}{2}nN^4$			×
16	$\sum_{l}\langle ic\|\|lk\rangle t_l^a$	n^3N^2			×
17	$\sum_{d}\langle dc\|\|ak\rangle t_i^d$	n^2N^3			×
18	$\sum_{kc}\langle ic\|\|ak\rangle t_j^c t_k^b$	$2n^3N^2$			×

[a] × indicates that the term is included in this method.

TABLE II. Total number of floating point operations (FPO) per iteration; $n(N)$ is the number of occupied (unoccupied) spin–orbitals; $o(v)$ is the number of occupied (unoccupied) closed-shell molecular orbitals.

	m^6 loops			m^5 loops			
Spin–orbital basis	n^2N^4	n^3N^3	n^4N^2	nN^4	n^2N^3	n^3N^2	n^4N
CISD	1/8	1	1/8	0	3/2	3/2	0
QCISD (this work)	1/8	2	1/4	0	2	2	0
CCSD	1/8	2	1/4	1/2	3	5	1/2
QCISD (Refs. 1 & 13)	1/8	3	3/8	0	2	2	0
Closed-shell basis	o^2v^4	o^3v^3	o^4v^2	ov^4	o^2v^3	o^3v^2	o^4v
CISD	1/4	2	1/4	0	2	2	0
QCISD (this work)	1/4	4	1/2	0	4	4	0
CCSD	1/4	4	1/2	1	7	7	1

$$\sum_{kl}a_{ij}^{kl}\tau_{kl}^{ab}=2\sum_{k>l}a_{ij}^{kl}\tau_{kl}^{ab}. \tag{27}$$

These reductions in the three pairs of indices makes the computational requirement for this term proportional to $1/8\ n^4N^2$. Similar analyses hold for the rest of the terms in Table I.

At both the m^5 and m^6 level,[5] Table I shows that CISD, QCISD, and CCSD involve the evaluation of 9, 13, and 18 terms, respectively. The total number of FPO per iteration for the three methods is presented in Table II. The most important conclusion drawn from these tables is that QCISD and CCSD have the same computational requirements at the m^6 level. CCSD is more demanding at the m^5 level, but this is only a small fraction of the total time in actual calculations. On the other hand, CISD is definitely less expensive than QCISD and CCSD. As a numerical example, the DZP water test case mentioned above took 14.2 (CISD), 24.6 (QCISD), and 26.8 (CCSD) s of CPU to achieve convergence in the correlation energy to six decimal figures, on a one processor IBM 9370 model 90 computer running in scalar mode. These timings closely follow the theoretical factors depicted in Table II.

CONCLUDING REMARKS

It is worth mentioning that the present formulation of QCISD appears to be more efficient than the one proposed by Pople *et al.* The reduction from $3n^3N^3$ to $2n^3N^3$ FPO for the so-called particle–hole couplings, may be achieved by using the same concepts described in Ref. 6 (for the closed-shell case) and first proposed by Saebo, Meyer, and Pulay[11,12] in the context of the self-consistent electron pairs theory. The reduction from $3/8\ n^4N^2$ to $2/8\ n^4N^2$ comes from properly employing the a_{ij}^{kl} intermediate to eliminate one m^6 product. Pople *et al.*[1,13] defined three $1/8\ n^4N^2$terms [see fourth term of Eq. (2-36) of Ref. 1, Eq. (17) of Ref. 13, and first term of Eq. (21) of Ref. 13] but only two are necessary as shown in this work.

Contrary to typical statements in the literature,[14] the leading term in QCISD and CCSD is generally $2n^3N^3$. Only for $N>16n$ (a very large basis set!) is $1/8\ n^2N^4$ greater than $2n^3N^3$. (For Pople *et al.*'s implementation[1] the transition value is $N>24n$.) Similar conclusions hold for the closed-shell case.[6] For the sake of completeness we also include in Table II the corresponding number of FPO per iteration for the closed-shell case. The interested reader may look into Ref. 6 for a detailed analysis of these closed-shell figures.

In summary, we have shown that

(1) If properly formulated in terms of effective ($\tau=\frac{1}{2}t_2+t_1^2$) amplitudes the algebraic CCSD equations are at most quadratic in the cluster amplitudes. Cubic and quartic terms do not appear explicitly in CCSD.

(2) Therefore, the CCSD equations are not considerably more complex than the QCISD equations.[15]

(3) Most important, the computational cost of QCISD is identical at the m^6 level to that of CCSD. The difference between the two methods expressed by terms 14–18 of Table I, has computational expenses proportional to m^5.

In conclusion, QCISD is an approximate CCSD method with essentially the same computational requirements as the more complete and better theoretically based full CCSD method. Although much younger than its CISD counterpart, the CCSD method is in the process of becoming a standard, or "black box" method. Recent applications by the Florida group[16] and the Georgia group[17] have shown CCSD to be a valuable technique, especially when compared to CISD.[17]

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