

Computational Complexity of CCSD(T) algorithms in electron correlation studies for atoms and molecules¹

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Abstract

The CCSD(T) method, a coupled cluster approach including all single and double excitations together with an *a posteriori* perturbative correction for connected triple excitations, is believed to provide an optimum balance between accuracy and efficiency in electron correlation studies. In this report, we analyze the computational complexity of CCSD(T) algorithms. After considering a prototypical fourth order triple excitation energy diagram in the many-body perturbation theory (MBPT) expansion for a closed-shell system, we consider the tensor contraction which arises in the evaluation of the corresponding energy component and also the use of spin-adaption and the efficiencies which follow in the computational algorithm from its effective exploitation. The CCSD(T) approximation is presented in a compact form and the algebraic complexity of algorithms for this approximation considered in detail. Reduced-complexity algorithms for CCSD(T) calculations are considered. In particular, we consider low-order scaling techniques for extended molecular systems, Laplace transform techniques, and Cholesky decomposition techniques.

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1 Introduction

The description of electron correlation effects is an essential ingredient of accurate descriptions of molecular energetics, structure and properties [1], [2]. The CCSD(T) method[3], [4], an augmented coupled cluster approach including all single and double excitations together with a perturbative correction for connected triple excitations, is believed to provide an optimum balance between accuracy and efficiency in electron correlation studies. In a previous report[5], we have made a critical analysis of the CCSD(T) model. The CCSD(T) theory employs an *a posteriori* correction formula to the CCSD method to account for some higher order effects which is only loosely based on perturbation theory.¹ There is some cancellation of error in the CCSD(T) model since it has been established, for example, in calculations of molecular binding energies that the CCSDT theory, which fully incorporates the triple excitation energy component, achieves slightly worst agreement with experiment than does the CCSD(T) model. The CCSD(T) model breaks down when significant quasidegeneracy is present as, for example, in describing bond breaking processes. (The renormalized and (completely renormalized) augmented CCSD(T) theory extends the range of geometries that can be considered, but destroys the extensivity of the method.) Multireference methods are found to give more accurate results in studies of bond-breaking than the best single reference methods including CCSD(T) and should eventually become the method of choice.

The CCSD(T) model leads to one of the most computationally intensive parts of many quantum chemistry program packages, including GAUSSIAN[8], CADPAC[9], GAMESS[10], MOLPRO[11], ACES[12] and DALTON[13]. For molecular systems which are well described by a Hartree-Fock reference function, the CCSD(T)

¹Stanton[6] and, more recently, Head-Gordon and his co-workers[7] have developed perturbation series with respect to a CCSD reference. Head-Gordon *et al* [7] propose a method designated CCSD(2) which is distinct from CCSD(T).

method predicts bond energies, ionization potentials, and electron affinities to an accuracy of ± 0.5 kcal/mol, bond lengths accurate to ± 0.0005 Å, and vibrational frequencies to ± 5 cm $^{-1}$. Such a level of accuracy is sufficient for many studies of chemical species and processes.

The computational demands of the CCSD method, coupled cluster theory restricted to single and double excitations, scale as $\mathcal{O}(n^6)$, where n is a measure of the size of the system which is usually related to the number of basis functions. Adding triple excitations into the iterative coupled cluster scheme, giving the CCSDT method, leads to an algorithm which scales as $\mathcal{O}(n^8)$. Using the converged amplitudes from a CCSD calculation to calculate a perturbative correction for the triple excitation energy component leads to an algorithm which scales as $\mathcal{O}(n^7)$. This CCSD(T) method is regarded as a compromise between speed of computation and accuracy of results. However, an $\mathcal{O}(n^7)$ scaling implies that simply doubling the size of a problem leads to an increase in the computational demands by a factor of 128. Dunning and Peterson[14] write

“... using a basis set with double the number of functions in the set or doubling the number of atoms in the molecule with the same basis set increases the cost of the calculation by two orders of magnitude.”

They continue

“This steep dependence of the CCSD(T) method on the number of basis functions greatly restricts the range of applicability of this otherwise promising theoretical approach.”

In their conclusions, Dunning and Peterson[14] write

“To achieve high accuracy ... large basis sets must be used. Since the computational cost of the CCSD(T) method increases as N^7 , where N is the number of basis functions used in the calculations, CCSD(T) calculations become prohibitively expensive for large molecules.”

Because of the computational demands of molecular electronic structure calculations based on CCSD(T) theory, the method provides an interesting topic for the study of algorithms for use in quantum chemistry. In this report, we analyze the computational complexity of CCSD(T) algorithms. We consider only algorithms for serial computing machines here. Algorithms for parallel computers will be addressed in a subsequent report[15]. In section 2, we consider the fourth order triple excitation energy in the many-body perturbation theory (MBPT) expansion for a closed-shell system. We consider the tensor contraction which arises in the evaluation of a typical fourth-order, triple excitation term. We also consider spin-adaption and the efficiencies which follow in the computational algorithm from its effective exploitation. The CCSD(T) approximation is presented in a compact form in section 3 and the algebraic complexity of algorithms for this approximation is considered in 4. In section 5, we turn our attention to algorithms for CCSD(T) calculations of reduced complexity. In particular, we consider low-order scaling techniques for extended molecular systems, Laplace transform techniques, and Cholesky decomposition algorithms. Our discussion and conclusions are presented in section 6.

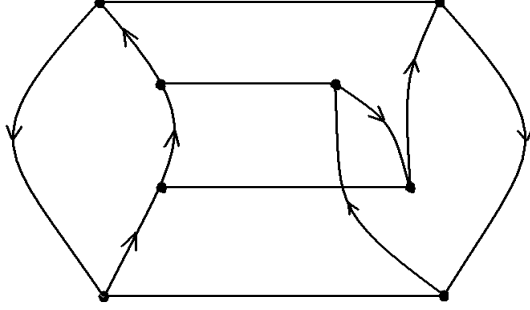


Figure 1: Fourth order triple excitation diagram labelled A_T in the nomenclature of Wilson and Silver[16].

2 Fourth order triple excitation energy

Of the 39 fourth order linked energy diagrams which arise in the many-body perturbation expansion for a closed shell system described with respect to a single Hartree-Fock reference function constructed from canonical orbitals, 16 involve intermediate states which are triply excited with respect to the reference function. The algorithms for evaluating the energy components corresponding to these 16 triple excitation diagrammatic terms are the most demanding of those which arise from fourth order. They scale as N^7 , where N is the number of basis functions employed.

2.1 Energy diagram A_T

For our present purposes it is sufficient to consider a single fourth order triple excitation diagram. We consider the diagram labelled A_T by Wilson and Silver[16], who first published these terms in 1978. This diagram is shown in Figure 1.

Using the convention that the indices i, j, k, \dots label occupied spin orbitals or hole lines and a, b, c, \dots label unoccupied spin orbitals or particle lines, the corresponding energy component can be written using standard rules as follows

$$E_4(A_T) = -\frac{1}{2} \sum_{ijk} \sum_{abcde} \frac{\langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle cb | \hat{O} | ek \rangle \langle ed | \hat{O} | ij \rangle}{D_{ij}^{ab} D_{ijk}^{bcd} D_{ij}^{de}} \quad (1)$$

where

$$\hat{O} = \frac{I - (12)}{r_{12}}, \quad (2)$$

and r_{12} being the interelectronic distance, I the identity and (12) the permutation that exchanges the co-ordinates of electrons 1 and 2, so that

$$\begin{aligned} \langle pq | \hat{O} | rs \rangle &= \langle pq | \frac{1}{r_{12}} | rs \rangle - \langle pq | \frac{1}{r_{12}} | sr \rangle \\ &= [pr | qs] - [ps | qr] \end{aligned} \quad (3)$$

where the indices p, q, r, s denote spin orbitals which are either occupied or unoccupied.

$$D_{ij}^{ab} = \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b, \quad (4)$$

is a double excitation denominator, in which ε_p is the orbital energy for the p^{th} orbital, and

$$D_{ijk}^{abc} = \varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c, \quad (5)$$

is the triple excitation denominator. The direct evaluation of the expression (1) involves a summation over 8 indices and thus an algorithm that scales as N^8 or, more precisely, $N_o^3 N_u^5$, where N_o is the number of occupied spin orbitals and N_u is the number of unoccupied spin orbitals.

2.2 Tensor contraction

In general, the evaluation of many-body perturbation theory and coupled cluster expansions can be expressed in terms of tensor contractions of the form

$$X = \sum_i \sum_j \sum_k \sum_a \sum_b \sum_c \sum_d \sum_e A_{ijab} B_{akcd} C_{cbek} D_{edij} \quad (6)$$

where each summation runs over either an occupied or an unoccupied spin orbital. A_{ijab} , B_{akcd} , C_{cbek} and D_{edij} are “two-electron integral-like”. We have used in (6) the form of the numerator in the expression for the energy corresponding to diagram A_T . The final result X can be computed in many different ways because of commutativity, associativity and distributivity. We shall consider some of the possibilities here.

Writing (6) in the form

$$X = \sum_i \sum_j \sum_k \sum_a \sum_b \sum_c \sum_d \sum_e A_{ijab} \times B_{akcd} \times C_{cbek} \times D_{edij} \quad (7)$$

in which the floating-point multiplications are explicitly shown, we see that the total number of floating point operations required is

$$4N_o^3 N_u^5 \sim N^8 \quad (8)$$

Evaluation of X using the expression (7) leads to the following code:-

```
X:=0;
for i, j, k, a, b, c, d, e
  X:=X+A(i,j,a,b)*B(a,k,c,d)*C(c,b,e,k)*D(e,d,i,j);
```

This straightforward and most direct of algorithms requires no memory for intermediates.

Noting that A_{ijab} and B_{akcd} in (6) have one index (a) in common and that likewise C_{cbek} and D_{edij} have the index e in common, we can evaluate X as follows:-

$$X = \sum_i \sum_j \sum_k \sum_b \sum_c \sum_d \left[\sum_a (A_{ijab} B_{akcd}) \sum_e (C_{cbek} D_{edij}) \right] \quad (9)$$

The summation over a requires $2N_u$ floating point operators and a similar number are required for the summation over e . Let us write

$$F_{ijkbcd} = \sum_a (A_{ijab} B_{akcd}) \quad (10)$$

and

$$G_{ijkbcd} = \sum_e (C_{cbek} D_{edij}) \quad (11)$$

so that

$$X = \sum_i \sum_j \sum_k \sum_b \sum_c \sum_d F_{ijkbcd} G_{ijkbcd} \quad (12)$$

We can then see that the evaluation of X requires

$$2N_o^3 N_u^3 \cdot (2N_u + 2N_u) = 8N_o^3 N_u^4 \sim N^7 \quad (13)$$

floating point operations. The scaling of the summation scheme (9) is an order of magnitude less than that of scheme (6). However, scheme (9) may require that the temporary arrays F_{ijkbcd} and G_{ijkbcd} be stored. A direct implementation of scheme (9) can be achieved by the following code:-

```
X:=0;
for i, j, k, b, c, d
  F(i,j,k,b,c,d):=0
for i, j, k, b, c, d
  for a
    F(i,j,k,b,c,d):=F(i,j,k,b,c,d)+A(i,j,a,b)*B(a,k,c,d);
for i, j, k, b, c, d
  G(i,j,k,b,c,d):=0;
for i, j, k, b, c, d
  for e
    G(i,j,k,b,c,d):=G(i,j,k,b,c,d)+C(c,b,e,k)*D(e,d,i,j);
for i, j, k, b, c, d
  X:=X+F(i,j,k,b,c,d)*G(i,j,k,b,c,d);
```

The above code requires storage of the intermediates F_{ijkabc} and G_{ijkabc} . A reduced memory implementation of the same scheme is provided by the following code:-

```
X:=0;
for i, j, k, b, c, d
  F:=0
  for a
    F:=F+A(i,j,a,b)*B(a,k,c,d);
  G:=0;
  for e
    G:=G+C(c,b,e,k)*D(e,d,i,j);
  X:=X+F*G;
```

Inspecting expression (6) again, we see that A_{ijab} and D_{edij} have two indices in common, namely i and j . Likewise, B_{akcd} and C_{cbek} also have two indices

in common, namely k and c . The following expression for X can therefore be written

$$X = \sum_a \sum_b \sum_d \sum_e \left[\sum_i \sum_j (A_{ijab} D_{edij}) \sum_k \sum_c (B_{akcd} C_{cbek}) \right] \quad (14)$$

The summation over i and j involves $2N_o^2$ floating point operations, whilst the summation over k and c involves $2N_o N_u$ floating point operations. Putting

$$F_{abed} = \sum_i \sum_j (A_{ijab} D_{edij}) \quad (15)$$

and

$$G_{abed} = \sum_k \sum_c (B_{akcd} C_{cbek}) \quad (16)$$

we can write

$$X = \sum_a \sum_b \sum_d \sum_e F_{abed} G_{abed} \quad (17)$$

We can then see that the evaluation of X requires

$$2N_u^4 (2N_o^2 + 2N_o N_u) = 4N_o N_u^4 (N_o + N_u) \sim N^6 \quad (18)$$

floating point operations, an order of magnitude less than scheme (9) and two orders of magnitude less than the first scheme considered, scheme (6). Scheme (14) may require that the temporary arrays F_{abed} and G_{abed} be stored. A direct implementation of (14) can be achieved by the following code:-

```
X:=0;
for a, b, e, d
  F(a,b,e,d):=0
for a, b, e, d
  for i, j
    F(a,b,e,d):=F(a,b,e,d)+A(i,j,a,b)*D(e,d,i,j);
for a, b, e, d
  G(a,b,e,d):=0;
for a, b, e, d
  for k, c
    G(a,b,e,d):=G(a,b,e,d)+B(a,k,c,d)*C(c,b,e,k);
for i, j, k, b, c, d
  X:=X+F(a,b,e,d)*G(a,b,e,d);
```

The above code requires storage of the intermediates F_{abed} and G_{abed} . A reduced memory implementation of the same scheme is provided by the following code:-

```
X:=0;
for a, b, e, d
  F:=0
  for i, j
    F:=F+A(i,j,a,b)*B(a,k,c,d);
  G:=0;
  for k, c
    G:=G+C(c,b,e,k)*D(e,d,i,j);
  X:=X+F*G;
```


In the above analysis, we have not exhausted the number of possible multiplication scheme for the determination of X . There are a total of 6 possibilities corresponding to different contraction schemes which are summarized in Table 1. In this Table, the rows and columns are labelled by the tensor quantities A_{ijab} , B_{akcd} , C_{cbek} and D_{edij} . In the upper triangle, the number of common indices in a given pair of tensors is recorded whilst in the lower triangle the common indices themselves are recorded.

Even the outline of schemes summarized in Table 1 does not exhaust all possibilities since, for example, a summation over, say, an unoccupied spin orbital index can be further subdivided and the following substitution may be made

$$\sum_a \equiv \sum_{a=1}^{N_u} \rightarrow \sum_{a=1}^m + \sum_{a=m+1}^{N_u} \quad (19)$$

for some suitably chosen m . To our knowledge such schemes have not been explored.

Table 1: Summary of the possible tensor contractions available for the evaluation of X in equation(6). The rows and columns of this table are labelled by A_{ijab} , B_{akcd} , C_{cbek} and D_{edij} . In the upper triangle of the table the number of shared indices is given. In the lower half of the table the shared indices are given.

	A_{ijab}	B_{akcd}	C_{cbek}	D_{edij}
A_{ijab}	—	1	1	2
B_{akcd}	a	—	2	1
C_{cbek}	b	k, c	—	1
D_{edij}	i, j	d	e	—

In the above discussion, we have discussed the evaluation of the quantity X defined in (6). The evaluation of the fourth order energy component $E_4(A_T)$ can be complicated by the presence of the denominators. In particular, whilst schemes (6) and (9) can be applied to the case where denominators are present; thus we have for the $\mathcal{O}(N^8)$ algorithm

$$X = \sum_i \sum_j \sum_k \sum_a \sum_b \sum_c \sum_d \sum_e \frac{A_{ijab} B_{akcd} C_{cbek} D_{edij}}{D_{ij}^{ab} D_{ijk}^{bcd} D_{ij}^{de}} \quad (20)$$

and for the $\mathcal{O}(N^7)$ algorithm

$$X = \sum_i \sum_j \sum_k \sum_b \sum_c \sum_d \frac{1}{D_{ijk}^{bcd}} \left[\sum_a \left(\frac{A_{ijab} B_{akcd}}{D_{ij}^{ab}} \right) \sum_e \left(\frac{C_{cbek} D_{edij}}{D_{ij}^{de}} \right) \right]; \quad (21)$$

for scheme (14), the for the $\mathcal{O}(N^6)$ algorithm, the structure of the denominators destroys the algorithm. However, it will be shown in section 5.2 that an algorithm which scales as $\mathcal{O}(N^6)$ can be recovered when the Laplace transform technique is used to eliminate the denominators.

Now let us turn to the $\mathcal{O}(N^7)$ algorithm for the fourth order triply excitation energy diagrams originally introduced by Wilson and Saunders[17]. By defining the intermediates

$$f_{ijk}^{abc} = \sum_d \frac{\langle ij | \hat{O} | db \rangle \langle dk | \hat{O} | ac \rangle}{D_{ij}^{bd}} \quad (22)$$

and

$$g_{ijk}^{abc} = \sum_l \frac{\langle jl | \hat{O} | ba \rangle \langle ik | \hat{O} | lc \rangle}{D_{jl}^{ab}}, \quad (23)$$

these authors showed that each of the 16 diagrammatic terms which arise in fourth order may be written in the form

$$K \sum_{ijk} \sum_{abc} \frac{\phi_{ijk}^{abc} \left\{ P(ijk) P(abc) \gamma_{ijk}^{abc} \right\}}{D_{ijk}^{abc}}, \quad (24)$$

where ϕ_{ijk}^{abc} and γ_{ijk}^{abc} denote either an f_{ijk}^{abc} or a g_{ijk}^{abc} intermediate, K is a constant and $P(ijk)$ and $P(abc)$ are permutation operators. Specifically, the following expression arises for the diagram labelled A_T

$$E_4(A_T) = -\frac{1}{2} \sum_{ijk} \sum_{abc} \frac{f_{ijk}^{abc} f_{ijk}^{acb}}{D_{ijk}^{abc}}. \quad (25)$$

The computation of this term scales as $N_o^3 N_u^4 \sim N^7$.

2.3 Spin-adaption

The tensor contractions described in the previous section involve summations over spin orbital indices. In this section, we consider the spin free formulation for closed-shell systems.

The nine different possible spin cases which arise in the evaluation of the intermediates f_{ijk}^{abc} are summarized in Table 2. There are also nine different possible spin cases which arise in the evaluation of the intermediates g_{ijk}^{abc} and they are summarized in Table 3.

We use upper case indices to label (spatial) orbitals. So the indices I, J, K, \dots label occupied orbitals whilst the indices A, B, C, \dots label unoccupied orbitals. Defining the secondary intermediate quantities

$$T_1 = \sum_D \frac{[ID|JB][DA|KC]}{D_{IJ}^{BD}} \quad (26)$$

$$T_2 = \sum_D \frac{[ID|JB][DC|KA]}{D_{IJ}^{BD}} \quad (27)$$

$$T_3 = \sum_D \frac{[IB|JD][DA|KC]}{D_{IJ}^{BD}} \quad (28)$$

$$T_4 = \sum_D \frac{[IB|JD][DA|KC]}{D_{IJ}^{BD}} \quad (29)$$

the various spin-free intermediates are then given by

$$F_{IJK}^{ABC(1)} = T_1 - T_2 - T_3 + T_4, \quad (30)$$

$$F_{IJK}^{ABC(2)} = T_1 - T_4, \quad (31)$$

$$F_{IJK}^{ABC(3)} = -T_2 - T_4, \quad (32)$$

$$F_{IJK}^{ABC(4)} = T_1 - T_2, \quad (33)$$

Table 2: Spin cases for the intermediate F_{IJK}^{ABC}

μ	$\langle IJ \hat{O} DB\rangle$	$\langle DK \hat{O} AC\rangle$	F_{IJK}^{ABC}
1	$\langle \alpha\alpha \hat{P} \alpha\alpha\rangle$	$\langle \alpha\alpha \hat{P} \alpha\alpha\rangle$	$\begin{pmatrix} \alpha & \alpha & \alpha \\ \alpha & \alpha & \alpha \end{pmatrix}$
2	$\langle \alpha\alpha \hat{P} \alpha\alpha\rangle$	$\langle \alpha\beta \hat{P} \alpha\beta\rangle$	$\begin{pmatrix} \alpha & \alpha & \beta \\ \alpha & \alpha & \beta \end{pmatrix}$
3	$\langle \alpha\alpha \hat{P} \alpha\alpha\rangle$	$\langle \alpha\beta \hat{P} \beta\alpha\rangle$	$\begin{pmatrix} \alpha & \alpha & \beta \\ \beta & \alpha & \alpha \end{pmatrix}$
4	$\langle \alpha\beta \hat{P} \alpha\beta\rangle$	$\langle \alpha\alpha \hat{P} \alpha\alpha\rangle$	$\begin{pmatrix} \alpha & \beta & \alpha \\ \alpha & \beta & \alpha \end{pmatrix}$
5	$\langle \alpha\beta \hat{P} \alpha\beta\rangle$	$\langle \alpha\beta \hat{P} \alpha\beta\rangle$	$\begin{pmatrix} \alpha & \beta & \beta \\ \alpha & \beta & \beta \end{pmatrix}$
6	$\langle \alpha\beta \hat{P} \alpha\beta\rangle$	$\langle \alpha\beta \hat{P} \beta\alpha\rangle$	$\begin{pmatrix} \alpha & \beta & \beta \\ \beta & \beta & \alpha \end{pmatrix}$
7	$\langle \beta\alpha \hat{P} \alpha\beta\rangle$	$\langle \alpha\alpha \hat{P} \alpha\alpha\rangle$	$\begin{pmatrix} \beta & \alpha & \alpha \\ \alpha & \beta & \alpha \end{pmatrix}$
8	$\langle \beta\alpha \hat{P} \alpha\beta\rangle$	$\langle \alpha\beta \hat{P} \alpha\beta\rangle$	$\begin{pmatrix} \beta & \alpha & \beta \\ \alpha & \beta & \beta \end{pmatrix}$
9	$\langle \beta\alpha \hat{P} \alpha\beta\rangle$	$\langle \alpha\beta \hat{P} \beta\alpha\rangle$	$\begin{pmatrix} \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix}$

 Table 3: Spin cases for the intermediate G_{IJK}^{ABC}

μ	$\langle JL \hat{O} BA\rangle$	$\langle IK \hat{O} LC\rangle$	G_{IJK}^{ABC}
1	$\langle \alpha\alpha \hat{P} \alpha\alpha\rangle$	$\langle \alpha\alpha \hat{P} \alpha\alpha\rangle$	$\begin{pmatrix} \alpha & \alpha & \alpha \\ \alpha & \alpha & \alpha \end{pmatrix}$
2	$\langle \alpha\alpha \hat{P} \alpha\alpha\rangle$	$\langle \alpha\beta \hat{P} \alpha\beta\rangle$	$\begin{pmatrix} \alpha & \alpha & \beta \\ \alpha & \alpha & \beta \end{pmatrix}$
3	$\langle \alpha\alpha \hat{P} \alpha\alpha\rangle$	$\langle \beta\alpha \hat{P} \alpha\beta\rangle$	$\begin{pmatrix} \alpha & \alpha & \beta \\ \beta & \alpha & \alpha \end{pmatrix}$
4	$\langle \alpha\beta \hat{P} \alpha\beta\rangle$	$\langle \beta\beta \hat{P} \beta\beta\rangle$	$\begin{pmatrix} \beta & \alpha & \beta \\ \beta & \alpha & \beta \end{pmatrix}$
5	$\langle \alpha\beta \hat{P} \alpha\beta\rangle$	$\langle \alpha\beta \hat{P} \alpha\beta\rangle$	$\begin{pmatrix} \beta & \alpha & \beta \\ \alpha & \alpha & \beta \end{pmatrix}$
6	$\langle \alpha\beta \hat{P} \alpha\beta\rangle$	$\langle \alpha\beta \hat{P} \beta\alpha\rangle$	$\begin{pmatrix} \beta & \alpha & \alpha \\ \alpha & \alpha & \beta \end{pmatrix}$
7	$\langle \beta\alpha \hat{P} \alpha\beta\rangle$	$\langle \alpha\alpha \hat{P} \alpha\alpha\rangle$	$\begin{pmatrix} \beta & \alpha & \alpha \\ \alpha & \beta & \alpha \end{pmatrix}$
8	$\langle \beta\alpha \hat{P} \alpha\beta\rangle$	$\langle \alpha\beta \hat{P} \alpha\beta\rangle$	$\begin{pmatrix} \beta & \alpha & \beta \\ \alpha & \beta & \beta \end{pmatrix}$
9	$\langle \beta\alpha \hat{P} \alpha\beta\rangle$	$\langle \beta\alpha \hat{P} \alpha\beta\rangle$	$\begin{pmatrix} \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix}$

$$F_{IJK}^{ABC(5)} = T_1, \quad (34)$$

$$F_{IJK}^{ABC(6)} = -T_2, \quad (35)$$

$$F_{IJK}^{ABC(7)} = -T_3 + T_4 \quad (36)$$

$$F_{IJK}^{ABC(8)} = -T_3 \quad (37)$$

$$F_{IJK}^{ABC(9)} = T_4 \quad (38)$$

Similar spin-free intermediates may be obtained for the g_{ijk}^{abc} intermediates. The energy corresponding to diagram A_T may then be written

$$\begin{aligned} E_4(A_T) = & - \sum_{IJK} \sum_{ABC} \left\{ F_{IJK}^{ABC(1)} F_{IJK}^{ACB(1)} + F_{IJK}^{ABC(3)} F_{IJK}^{ACB(3)} \right. \\ & + F_{IJK}^{ABC(4)} F_{IJK}^{ACB(9)} + F_{IJK}^{ABC(5)} F_{IJK}^{ACB(5)} \\ & + F_{IJK}^{ABC(6)} F_{IJK}^{ACB(7)} + F_{IJK}^{ABC(7)} F_{IJK}^{ACB(6)} \\ & \left. + F_{IJK}^{ABC(8)} F_{IJK}^{ACB(8)} + F_{IJK}^{ABC(9)} F_{IJK}^{ACB(4)} \right\} \end{aligned} \quad (39)$$

The intermediates $F_{IJK}^{ABC(\mu)}$ obey the following permutational symmetry properties

$$F_{IJK}^{ABC(\mu)} = F_{JIK}^{CBA(\mu)} = -F_{JIK}^{ABC(\mu)} = -F_{IJK}^{CBA(\mu)}, \quad \forall \mu. \quad (40)$$

Similar relations exist for the $G_{IJK}^{ABC(\mu)}$ intermediates.

3 The CCSD(T) approximation

The CCSD(T) approximation was first defined for the quadratic configuration interaction model[3] and later for the CCSD approach[4]. The energy correction obtained from the CCSD+T(CCSD) approximation² is augmented by a fifth order term coupling single and triply excitations.

The *a posteriori* energy correction for the “triple excitation” component of the correlation energy can be written in the compact form

$$\Delta E_t = \frac{1}{36} \sum_{ijk} \sum_{abc} D_{ijk}^{abc} t_{ijk}^{abc} \bar{t}_{ijk}^{abc} \quad (41)$$

in which we have continued to employ the convention that the indices i, j, k, \dots label occupied orbitals, a, b, c, \dots label unoccupied orbitals, and p, q, r, \dots label orbitals which can be either occupied or unoccupied. The factor D_{ijk}^{abc} is given by

$$D_{ijk}^{abc} = \varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c, \quad (42)$$

whilst t_{ijk}^{abc} takes the form

$$t_{ijk}^{abc} = P(ijk) P(abc) \left\{ \frac{1}{D_{ijk}^{abc}} \left[\sum_e \left(t_{ij}^{ae} \langle bc | \hat{O} | ek \rangle \right) - \sum_m \left(t_{im}^{ab} \langle mc | \hat{O} | jk \rangle \right) \right] \right\}. \quad (43)$$

²The CCSD+T(CCSD) approximation was introduced by Urban *et al*[18] in 1985. In this approximation, the second order MBPT amplitudes in the fourth order triple excitation energy expressions are replaced by the converged CCSD amplitudes. More recently the CCSD+T(CCSD) method has been dubbed[19] CCSD[T].

and \bar{t}_{ijk}^{abc} is the sum

$$\bar{t}_{ijk}^{abc} = t_{ijk}^{abc} + \tilde{t}_{ijk}^{abc} \quad (44)$$

where the “disconnected triple excitation amplitude” is defined by

$$\tilde{t}_{ijk}^{abc} = P(ijk) P(abc) \frac{1}{D_{ijk}^{abc}} t_i^a \langle bc | \hat{O} | jk \rangle. \quad (45)$$

$P(pqr)$ is the cyclic permutation operator defined by

$$P(pqr) f(pqr) = f(pqr) + f(qrp) + f(rpq). \quad (46)$$

4 Algebraic complexity of algorithms for the CCSD(T) approximation

The *a posteriori* energy correction for the “triple excitation” component of the correlation energy CCSD(T) given by expression (41) involves

$$N_o^3 N_u^3 \quad (47)$$

terms. However, the evaluation of the amplitudes t_{ijk}^{abc} and \bar{t}_{ijk}^{abc} involves additional summations and so we examine the algebraic complexity of these components.

The cyclic permutations (46) arising in (43) can be written explicitly as

$$\begin{aligned} P(ijk) f(ijk) &= f(ijk) + f(jki) + f(kij) \\ P(abc) f(abc) &= f(abc) + f(bca) + f(cab) \end{aligned} \quad (48)$$

Taking account of these permutations, the cluster amplitudes defined in equation (43) can be written

$$\begin{aligned} t_{ijk}^{abc} = & \frac{1}{D_{ijk}^{abc}} \left[\sum_e \left(t_{ij}^{ae} \langle bc | \hat{O} | ek \rangle \right) - \sum_m \left(t_{im}^{ab} \langle mc | \hat{O} | jk \rangle \right) \right. \\ & + \sum_e \left(t_{ij}^{be} \langle ca | \hat{O} | ek \rangle \right) - \sum_m \left(t_{im}^{bc} \langle ma | \hat{O} | jk \rangle \right) \\ & + \sum_e \left(t_{ij}^{ce} \langle ab | \hat{O} | ek \rangle \right) - \sum_m \left(t_{im}^{ca} \langle mb | \hat{O} | jk \rangle \right) \\ & + \sum_e \left(t_{jk}^{ae} \langle bc | \hat{O} | ei \rangle \right) - \sum_m \left(t_{jm}^{ab} \langle mc | \hat{O} | ki \rangle \right) \\ & + \sum_e \left(t_{jk}^{be} \langle ca | \hat{O} | ei \rangle \right) - \sum_m \left(t_{jm}^{bc} \langle ma | \hat{O} | ki \rangle \right) \\ & + \sum_e \left(t_{jk}^{ce} \langle ab | \hat{O} | ei \rangle \right) - \sum_m \left(t_{jm}^{ca} \langle mb | \hat{O} | ki \rangle \right) \\ & + \sum_e \left(t_{ki}^{ae} \langle bc | \hat{O} | ej \rangle \right) - \sum_m \left(t_{km}^{ab} \langle mc | \hat{O} | ij \rangle \right) \\ & + \sum_e \left(t_{ki}^{be} \langle ca | \hat{O} | ej \rangle \right) - \sum_m \left(t_{km}^{bc} \langle ma | \hat{O} | ij \rangle \right) \\ & \left. + \sum_e \left(t_{ki}^{ce} \langle ab | \hat{O} | ej \rangle \right) - \sum_m \left(t_{km}^{ca} \langle mb | \hat{O} | ij \rangle \right) \right] \end{aligned} \quad (49)$$

$$(50)$$

We have used the fact that the denominator is invariant under permutation of the occupied and unoccupied spin orbital indices. The first term in each line of the above expression leads to computation which scales as N_u and there are 9 such terms. Similarly, the second term in each line leads to a computation which scales as N_o and again there are 9 such terms. The computation of the amplitude t_{ijk}^{abc} therefore scales as

$$9(N_u + N_o) \quad (51)$$

The amplitude \bar{t}_{ijk}^{abc} involves an additional term, the “disconnected triple excitation amplitudes”, which we now consider.

The “disconnected triple excitation amplitudes” defined in equation (45) can be written in the following form after explicitly permuting the single particle state indices

$$\begin{aligned} \bar{t}_{ijk}^{abc} = & \frac{1}{D_{ijk}^{abc}} \left[t_i^a \langle bc | \hat{O} | jk \rangle \right. \\ & + t_i^b \langle ca | \hat{O} | jk \rangle + t_i^c \langle ab | \hat{O} | jk \rangle \\ & + t_j^a \langle bc | \hat{O} | ki \rangle + t_j^b \langle ca | \hat{O} | ki \rangle \\ & + t_j^c \langle ab | \hat{O} | ki \rangle + t_k^a \langle bc | \hat{O} | ij \rangle \\ & \left. + t_k^b \langle ca | \hat{O} | ij \rangle + t_k^c \langle ab | \hat{O} | ij \rangle \right] \end{aligned} \quad (52)$$

There are 9 terms (but no summations).

By combining the operation counts given above, it can be seen that the evaluation of the amplitudes t_{ijk}^{abc} and \bar{t}_{ijk}^{abc} scales as

$$[9(N_u + N_o) + 9] \quad (53)$$

The total operation count for the *a posteriori* energy correction given by expression (41) is therefore

$$N_o^3 N_u^3 [9(N_u + N_o) + 9] \sim N^7 \quad (54)$$

terms.

5 Reduced-complexity algorithms for CCSD(T) calculations

The $\mathcal{O}(n^7)$ scaling of the CCSD(T) method implies that simply doubling the size of a problem leads to an increase in the computational demands by a factor of 128. It is not surprising, therefore, that attempts have been made to alleviate the computational demands of CCSD(T) calculations.

In this section, we consider three methods for reducing the complexity of algorithms for performing CCSD(T) calculations. We first consider low-order scaling techniques for extended, *i.e.* large, molecular systems, then we turn our attention to methods based on the Laplace transform approach, before finally considering the use of Cholesky decompositions of the two-electron integral matrix.

5.1 Low-order scaling techniques for extended molecular systems

It is recognized that the steep scaling of algorithms for describing electron correlation in molecular systems is often an artifact of the orthogonal canonical basis, i.e. the solutions of the matrix Hartree-Fock equations, used to construct post-Hartree-Fock correlation theories. The steep scaling is not a consequence of the underlying physics. For example, dynamic correlation is a short-range effect decaying as r^{-6} . Schütz [20] has pointed out that

“The delocalized character of [*Hartree-Fock*] canonical orbitals destroys the locality of correlation effects, leading to a quadratic scaling of the number of electron pairs and a cubic scaling of the number of orbital triples to be correlated, and an overall $\mathcal{O}(n^4)$ and $\mathcal{O}(n^6)$ increase in the number of pair and triple amplitudes, respectively.”

The very steep scaling of the computational demands associated with conventional electron correlation studies arises from the fact that calculations are performed using a basis of canonical molecular orbitals which are, in general, delocalized over the entire molecular system. As Hampel and Werner[21] wrote

“This not only prevents the omission of small correlation effects of distant electrons, but also leads to an unphysically steep increase in the number of virtual orbitals needed for the correlation of each particular electron pair.”

They continue[21]

“It is intuitively clear that a localized description of electron correlation is needed to avoid these problems.”

Local correlation methods were first proposed in the mid-1960s by Sinanoğlu[22] and by Nesbet[23]. Since that time, many workers have suggested variants of the local correlation approach[24]-[118]. However, it is only in recent years that computational resources have emerged which allow applications to systems large enough to demonstrate the potential of local correlation methods. Much of this work is focused on the most widely used[119] correlation method, MP2, since this is the method which is least demanding of computational resources. The local MP2 algorithm described by Hetzer, Schütz, Stoll and Werner[96] is particularly efficient and these authors report that

“... the calculation of the MP2 energy is less expensive than the calculations of the Hartree-Fock energy for large systems.”

Scuseria and Ayala[89] devised a linear scaling coupled cluster algorithm for double excitations, CCD, which, although based on an atomic orbital basis set, is equivalent, within the thresholds used, to the ‘full’ CCD method. Schütz, Werner and their co-workers have described local correlation methods for more complicated algorithms including coupled cluster ‘singles and doubles’ with and without perturbative estimates of the triple excitation component of the correlation energy. These methods, designated LCCSD (Local Coupled Cluster Singles and Doubles) and LCCSD(T) (Local Coupled Cluster Singles and Doubles with

perturbative Triples) and described in References [21] and [110], and in References [91] and [20], respectively.

The Coulomb operator can be written as a sum of a long-range part, $L(r)$, and a short-range part, $S(r)$, as follows

$$\begin{aligned}\frac{1}{r} &= \frac{f(r)}{r} + \frac{1-f(r)}{r} \\ &= L(r) + S(r).\end{aligned}\tag{55}$$

Here $f(r)$ is termed the separation function and is commonly taken to be the error function

$$f(r) = \text{erf}(\omega r)\tag{56}$$

in which ω is a tunable decay parameter. This approach goes back to the work of Ewald in 1921[120] and has recently been re-examined by a number of authors[121]-[131]

The long-range function then takes the form

$$L(r) = \frac{\text{erf}(\omega r)}{r}\tag{57}$$

which is slowly decaying but nonsingular, whilst the short-range function is

$$S(r) = \frac{1 - \text{erf}(\omega r)}{r}\tag{58}$$

and is rapidly decaying but singular.

Consider the exchange integral

$$\begin{aligned}K_{rs}^{ij} &= (ai | bj) \\ &= \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_a(\mathbf{r}_1) \phi_i(\mathbf{r}_1) \frac{1}{r_{12}} \phi_b(\mathbf{r}_2) \phi_j(\mathbf{r}_2).\end{aligned}\tag{59}$$

Splitting the Coulomb operator into a long-range and a short-range part, this integral becomes

$$(ai | bj) = (ai | L(r) | bj) + (ai | S(r) | bj)\tag{60}$$

where

$$(ai | L(r) | bj) = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_a(\mathbf{r}_1) \phi_i(\mathbf{r}_1) \frac{\text{erf}(\omega r)}{r} \phi_b(\mathbf{r}_2) \phi_j(\mathbf{r}_2)\tag{61}$$

and

$$(ai | S(r) | bj) = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_a(\mathbf{r}_1) \phi_i(\mathbf{r}_1) \left[\frac{1 - \text{erf}(\omega r)}{r} \right] \phi_b(\mathbf{r}_2) \phi_j(\mathbf{r}_2)\tag{62}$$

Both of these partial integrals can be evaluated more efficiently than the original integral.

The short-range integral is obtained by a four-index transformation from the short-range integrals over the basis set. Negligible contributions are eliminated by screening the integral list. The Schwartz inequality

$$|(pq | S(r) | rs)| \leq |(pq | S(r) | pq)|^{\frac{1}{2}} |(rs | S(r) | rs)|^{\frac{1}{2}}\tag{63}$$

leads to a computational scaling as $\mathcal{O}(N^2)$. $\mathcal{O}(N)$ scaling is achieved by taking account of the distances between p and r , p and s , etc. Hetzer *et al* [96] use the condition

$$|(pq|S(r)|rs)| \lesssim \max(S_{pq}, S_{pr}, S_{qr}, S_{qs}) \quad (64)$$

where

$$S_{pq} = |(pp|S(r)|rr)| \quad (65)$$

which, unlike the Schwarz inequality is not strict but “works well in practice”

The integral K_{rs}^{ij} may be approximated as follows

$$(ai|bj) \approx \sum_{m,m'} Q_m^{ai} U_{mm'}^{\mathbf{R}_{ij}} Q_{m'}^{bj} \quad (66)$$

where is a multipole of the effective charge distribution

$$\rho_{ai} = \chi_a \chi_i \quad (67)$$

and $U_{mm'}^{\mathbf{R}_{ij}}$ is the interaction coefficient depending only on the vector \mathbf{R}_{ij} connecting the charge centroids of the occupied orbitals i and j . m and m' are compound indices which determine the type of multipole.

The distance between two electrons can be written

$$r_{12} = |\mathbf{R} - \mathbf{r}_1 + \mathbf{r}_2| \quad (68)$$

where the coordinates of electron 1 are

$$\mathbf{r}_1 = (x_1, y_1, z_1) \quad (69)$$

and those of electron 2 are

$$\mathbf{r}_2 = (x_2, y_2, z_2). \quad (70)$$

The vector

$$\mathbf{R} = (R_x, R_y, R_z) \quad (71)$$

connects the two centres. The long-range operator $L(r_{12})$ can be expanded as a polynomial as follows

$$L(r_{12}) = \sum_{l_x, l_y, l_z} D_{l_x l_y l_z}(\mathbf{R}) (x_2 - x_1)^{l_x} (y_2 - y_1)^{l_y} (z_2 - z_1)^{l_z} \quad (72)$$

in which the coefficients $D_{l_x l_y l_z}(\mathbf{R})$ are to be determined.

Rearranging the above expansion gives

$$L(r_{12}) = \sum_{\substack{m_x m_y m_z \\ n_x n_y n_z}} U_{(m_x m_y m_z)(n_x n_y n_z)}^{\mathbf{R}} x_1^{m_x} y_1^{m_y} z_1^{m_z} x_2^{n_x} y_2^{n_y} z_2^{n_z}, \quad (73)$$

with

$$\begin{aligned} U_{(m_x m_y m_z)(n_x n_y n_z)}^{\mathbf{R}} &= (-1)^{m_x + m_y + m_z} \begin{pmatrix} m_x + n_x \\ n_x \end{pmatrix} \begin{pmatrix} m_y + n_y \\ n_y \end{pmatrix} \\ &\times \begin{pmatrix} m_z + n_z \\ n_z \end{pmatrix} D_{m_x + n_x, m_y + n_y, m_z + n_z}(\mathbf{R}) \end{aligned} \quad (74)$$

Substituting this expansion for $L(r_{12})$ into the two-electron integral (61) yields the multipole expansion

$$\begin{aligned}
(ai | L(r_{12}) | bj) &= \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho_{ai}(\mathbf{r}_1) L(r_{12}) \rho_{bj}(\mathbf{r}_2) \\
&= \sum_{m_x, m_y, m_z} \sum_{n_x, n_y, n_z} Q_{m_x m_y m_z}^{ai: \mathbf{R}_{ai}} U_{(m_x m_y m_z)(n_x n_y n_z)}^{\mathbf{R}_{ai} bj} \\
&\quad \times Q_{n_x n_y n_z}^{bj: \mathbf{R}_{bj}}
\end{aligned} \tag{75}$$

in which

$$Q_{m_x m_y m_z}^{ai: \mathbf{R}_{ai}} = \int d\mathbf{r} \rho_{ai}(\mathbf{r}) (x - R_{ai,x})^{l_x} (y - R_{ai,y})^{l_y} (z - R_{ai,z})^{l_z} \tag{76}$$

is a “multipole moment”.

5.2 Laplace transform techniques

A one-dimensional Laplace transform is defined as follows[132]

$$f(s) = \mathcal{L}\{F(t)\} = \int_0^\infty dt \exp(-st) F(t) \tag{77}$$

$F(t)$ is a function of the real variable t and s is a complex variable. $F(t)$ is called the original function and $f(s)$ is called the image function. If $F(t) = 1$ then $f(s) = 1/s$, so that

$$\frac{1}{s} = \int_0^\infty dt \exp(-st). \tag{78}$$

Replacing an energy denominator in a sum-over-states perturbation theory expression by its Laplace transform gives an exponential function

$$\frac{1}{D_{ij\dots}^{ab\dots}} = \int_0^\infty dt \exp(-D_{ij\dots}^{ab\dots} t). \tag{79}$$

The spin orbital energy differences then appear as an exponent which can be split in different ways, *e.g.*

$$D_{ij\dots}^{ab\dots} = D_{i\dots}^{a\dots} + D_{j\dots}^{b\dots} \tag{80}$$

so that, *e.g.*

$$\begin{aligned}
\frac{1}{(D_{i\dots}^{a\dots} + D_{j\dots}^{b\dots})} &= \int_0^\infty dt \exp(-(D_{i\dots}^{a\dots} + D_{j\dots}^{b\dots}) t) \\
&= \int_0^\infty dt \exp(-D_{i\dots}^{a\dots} t) \exp(-D_{j\dots}^{b\dots} t).
\end{aligned} \tag{81}$$

The Laplace transform allows the decoupling of the nested summations in the perturbation theory expressions.

In a paper entitled “*Elimination of energy denominators in Møller-Plesset perturbation theory by a Laplace transform approach*”, Almlöf [133] wrote the

estimate of the correlation energy given by second order perturbation theory, *i.e.*

$$E_2 = -\frac{1}{4} \sum_{ij} \sum_{ab} \frac{\langle ij | \hat{O} | ab \rangle \langle ab | \hat{O} | ij \rangle}{\bar{D}_{ij}^{ab}} \quad (82)$$

where

$$\bar{D}_{ij}^{ab} = \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j \quad (83)$$

in the form

$$E_2 = -\frac{1}{4} \int_0^\infty dt \sum_{ij} \sum_{ab} \langle ij | \hat{O} | ab \rangle \langle ab | \hat{O} | ij \rangle \exp(-\bar{D}_{ij}^{ab} t) \quad (84)$$

which can then be written as

$$E_2 = \int_0^\infty dt \mathbf{e}^{(2)}(t) \quad (85)$$

where

$$\mathbf{e}^{(2)}(t) = -\frac{1}{4} \sum_{ij} \sum_{ab} \langle i(t)j(t) | \hat{O} | a(t)b(t) \rangle \langle a(t)b(t) | \hat{O} | i(t)j(t) \rangle \quad (86)$$

and

$$i(t) = i(0) \exp(\tfrac{1}{2}\varepsilon_i t) \quad (87)$$

$$a(t) = a(0) \exp(-\tfrac{1}{2}\varepsilon_a t) \quad (88)$$

The Laplace transform effectively eliminates the energy denominators provided the integral (85) can be evaluated accurately and efficiently. Häser and Almlöf [134] showed that the function $\mathbf{e}^{(2)}(t)$ is

“quite well behaved and monotonically decreasing”

so that numerical integration

“is not a major computational obstacle.”

These authors[134] show that

“with a suitable choice of quadrature points ... fewer than 10 points are required for 6-7 digits of accuracy, which is usually sufficient to obtain correlation energies within a micro-hartree.”

Häser and Almlöf also note that

“the contributions for different quadrature points can be evaluated in parallel, and the scheme is therefore well suited for many modern, high-performance computer architectures.”

Consider the application of the Laplace transform technique to the energy expression corresponding to diagram A_T

$$E_4(A_T) = \frac{1}{2} \sum_{ijk} \sum_{abcde} \frac{\langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle cb | \hat{O} | ek \rangle \langle ed | \hat{O} | ij \rangle}{\bar{D}_{ij}^{ab} \bar{D}_{ijk}^{bcd} \bar{D}_{ij}^{de}} \quad (89)$$

where the ‘triple excitation’ denominator is given by

$$\bar{D}_{ijk}^{bcd} = \varepsilon_b + \varepsilon_c + \varepsilon_d - \varepsilon_i - \varepsilon_j - \varepsilon_k. \quad (90)$$

Putting

$$T_{ij}^{(1)ab} = \frac{\langle ij | \hat{O} | ab \rangle}{\bar{D}_{ij}^{ab}} \quad (91)$$

this may be written

$$E_4(A_T) = \frac{1}{2} \sum_{ijk} \sum_{abcde} T_{ij}^{(1)ab} \frac{\langle ak | \hat{O} | cd \rangle \langle cb | \hat{O} | ek \rangle}{\bar{D}_{ijk}^{bcd}} T_{ij}^{(1)ed}. \quad (92)$$

$$\bar{D}_{ijk}^{bcd} = (\varepsilon_d - \varepsilon_i - \varepsilon_j) + (\varepsilon_b + \varepsilon_c - \varepsilon_k) \quad (93)$$

$$\begin{aligned} E_4(A_T) &= \frac{1}{2} \int_0^\infty dt \sum_{ijk} \sum_{abcde} T_{ij}^{(1)ab} \langle ak | \hat{O} | cd \rangle \langle cb | \hat{O} | ek \rangle \\ &\quad \times T_{ij}^{(1)ed} \exp(-[(\varepsilon_d - \varepsilon_i - \varepsilon_j) + (\varepsilon_b + \varepsilon_c - \varepsilon_k)]t) \end{aligned} \quad (94)$$

Häser and Almlöf [134] introduced the auxiliary matrices

$$X_{ab,de}(t) = \sum_{ij} T_{ij}^{(1)ab} T_{ij}^{(1)ed} \exp(-(\varepsilon_d - \varepsilon_i - \varepsilon_j)t) \quad (95)$$

and

$$Y_{de,ab}(t) = \sum_{kc} \langle ak | \hat{O} | cd \rangle \langle cb | \hat{O} | ek \rangle \exp(-(\varepsilon_b + \varepsilon_c - \varepsilon_k)t) \quad (96)$$

and then write the energy component under consideration in the form

$$E_4(A_T) \int_0^\infty dt \text{Tr} \{ \mathbf{X}(t) \mathbf{Y}(t) \} \quad (97)$$

The evaluation of this trace is an N^4 process - actually n_u^4 , where n_u is the number of unoccupied orbitals. The number of elements of the matrices \mathbf{X} and \mathbf{Y} is also of order n_u^4 . Each of the matrix elements of \mathbf{X} requires n_o^2 operations. Each of the matrix elements of \mathbf{Y} requires $n_o n_u$ operations. Evaluation of the energy component $E_4(A_T)$ using the Laplace transform technique therefore scales as

$$(n_o^2 + n_o n_u) n_u^4 \sim N^6 \quad (98)$$

The Laplace transform integral

$$\frac{1}{s} = \int_0^\infty dt \exp(-st). \quad (99)$$

which holds for all $s > 0$, is performed numerically using a quadrature of the form

$$\frac{1}{s} = \sum_{p=1}^m w_p \exp(-st_p) \quad (100)$$

with weights w_p and points t_p . This formula may be viewed as the approximation of s^{-1} by a series of exponential functions $\exp(-st_p)$ which is monotonically decreasing and positive everywhere.

The use of the Laplace transform in CCSD(T) calculations has also been considered by Constans *et al* [97] and, very recently, by Constans and Scuseria [135]. Constans *et al* [97] considered the use of logarithmic transformations in performing the numerical integration required to evaluate (94). Logarithmic transformations can prove useful in numerical integration of exponential functions[136]. Equation (94) may be written

$$E_4(A_T) = \frac{1}{2} \int_0^\infty dt \sum_p \omega_p \exp(-D_p t) \quad (101)$$

where

$$\omega_p = T_{ij}^{(1)ab} \langle ak | \hat{O} | cd \rangle \langle cb | \hat{O} | ek \rangle T_{ij}^{(1)ed}, \quad (102)$$

$$D_p = (\varepsilon_d - \varepsilon_i - \varepsilon_j) + (\varepsilon_b + \varepsilon_c - \varepsilon_k), \quad (103)$$

and p denotes the compound index $(ijklabcde)$. Defining the parameter D_{\min} as the “triples gap”, *i.e.* the minimum denominator, we can define the logarithmic transformation

$$t = -\frac{1}{D_{\min}} \ln x \quad (104)$$

so that

$$x = \exp(-D_{\min} t). \quad (105)$$

From the definition (104)

$$dt = -\frac{1}{D_{\min}} \frac{1}{x} dx \quad (106)$$

and the integration limits become

$$\begin{aligned} t = 0 & \rightarrow x = 1 \\ t = \infty & \rightarrow x = 0 \end{aligned} \quad (107)$$

The integrand in (101) becomes a power series in x

$$E_4(A_T) = -\frac{1}{2} \frac{1}{D_{\min}} \int_0^1 dx \sum_p \omega_p x^{\left(\frac{D_p}{D_{\min}} - 1\right)} \quad (108)$$

mapped onto the integration interval 0 to 1. Constans *et al* [97] point out that after making the above logarithmic transformation (104) Gauss-Legendre integration is a particularly useful choice.

5.3 Cholesky decomposition techniques

In 1990, Wilson [140] diagonalized the two-electron integral matrices corresponding to a sequence of small universal basis set. Writing a two-electron integral matrix as

$$V_{\mu\nu} = [pq | rs] \quad (109)$$

with compound indices

$$\mu = (pq), \quad \nu = (rs), \quad (110)$$

Table 4: The difference norm $\Delta(m)$ defined in equation (112) for a sequence of universal even-tempered basis sets. Powers of ten are given. The columns are labelled by the number of functions in the basis set, n . m is the upper limit of the summation in equation (111). $M = (n(n+1))/2$ is given in the final row.

m	9	10	11	12	13	14	15	16	17	18	19	20
1	+02	+02	+02	+02	+02	+02	+02	+02	+03	+03	+03	+03
2	+00	+01	+01	+01	+01	+01	+01	+02	+02	+02	+02	+02
3	-01	-01	+00	+00	+00	+00	+00	+01	+01	+01	+01	+01
4	-02	-02	-02	-01	-01	-01	-01	+00	+00	+00	+00	+00
5	-04	-03	-03	-03	-02	-02	-02	-02	-01	-01	-01	-01
6	-05	-05	-04	-04	-03	-03	-03	-03	-02	-02	-02	-02
7	-07	-06	-05	-05	-05	-04	-04	-04	-03	-03	-03	-03
8	-08	-07	-07	-06	-06	-06	-05	-05	-05	-04	-04	-04
9	-10	-09	-08	-08	-07	-07	-06	-06	-06	-05	-05	-05
10	-11	-11	-10	-09	-09	-08	-08	-07	-07	-06	-06	-06
11	-13	-12	-11	-11	-10	-09	-09	-08	-08	-08	-07	-07
12	-15	-14	-13	-12	-11	-11	-10	-10	-09	-09	-08	-08
13	-17	-15	-14	-13	-13	-12	-11	-11	-10	-10	-10	-09
14	-19	-17	-16	-15	-14	-13	-13	-12	-12	-11	-11	-10
15	-20	-19	-18	-16	-16	-15	-14	-13	-13	-12	-12	-11
M	45	55	66	78	91	105	120	136	153	171	190	210

Taken from the work of Wilson[140]

let \mathbf{v} denote the diagonal matrix of eigenvalues and \mathbf{U} the matrix whose columns are the corresponding eigenvectors. Let the eigenvalues be arranged so that their magnitudes are in non-increasing order. Let the eigenvectors be arranged in the corresponding order. An approximation to the two-electron integral matrix, $V_{\mu\nu}$, may be constructed as follows

$$V_{\mu\nu}^m = \sum_{\lambda=1}^m U_{\mu\lambda} v_{\lambda\lambda} U_{\lambda\nu}^+ \quad (111)$$

where in general the upper limit of the summation over λ , *i.e.* m , will be considerably less than its maximum value of $\frac{1}{2}(n(n+1)) (= M)$, where n is the number of basis functions. The difference norm

$$\Delta(m) = \sum_{\mu,\nu} |V_{\mu\nu}^m - V_{\mu\nu}| \quad (112)$$

provides a measure of the accuracy with which the original two-electron integral matrix is approximated by $V_{\mu\nu}^m$ defined in equation (111). So, for a basis set of 9 functions $\Delta(m)$ is less than 10^{-10} for values of m greater than 9, that is, 20% of M . For a basis set of 20 functions $\Delta(m)$ is less than 10^{-10} for values of m greater than 14, which is just $6\frac{2}{3}\%$ of M .

In 1977, Beebe and Linderberg[137] had suggested a method to simplify the generation and transformation of the two-electron integral matrix using a Cholesky decomposition. They recognized that the two-electron integral matrix may be written

$$V_{\mu\nu} = \sum \lambda^M L_{\mu\lambda} L_{\nu\lambda} \quad (113)$$

where \mathbf{L} is a lower triangular matrix. The importance of this decomposition is that, to a very good approximation the summation over λ may be truncated

$$V_{\mu\nu} = \sum \lambda^m L_{\mu\lambda} L_{\nu\lambda} \quad (114)$$

where $m \ll M$. The Cholesky decomposition of the two-electron integral matrix has been investigated by Røeggen and his coworkers[138], by Wilson[139][140], and, most recently, by Koch *et al*[141]. These authors begin their paper[141] by noting that the use of Cholesky decompositions of the two-electron integral matrix

“does not seem to have received much attention in the quantum chemistry literature.”

but conclude with the following prognosis

“Integral-direct techniques for highly correlated *ab initio* models have expanded the application range for coupled cluster methods. These methods are still very demanding and are considered a serious bottleneck. We anticipate the Cholesky approach will remove this limitation and the future developments of these methods will focus on reducing the scaling, as well as an embarrassingly parallel implementation of the Cholesky decomposition will make applications virtually open ended.”

Beebe and Linderberg[137] presented a very stable algorithm for the construction of \mathbf{L} . For $(pq) = 1, 2, \dots, \frac{1}{2}[n(n+1)]$ where (pq) is the compound index

$$(pq) = \frac{1}{2}[p(p-1)] + q, \quad (p \geq q) \quad (115)$$

we have

$$L_{(pq),(pq)} = \left[V_{(pq),(pq)} - \sum_{(rs)=1}^{(pq)-1} L_{(pq),(rs)} \right]^{\frac{1}{2}} \quad (116)$$

and

$$L_{(tu),(rs)} = \left[V_{(tu),(pq)} - \sum_{(rs)=1}^{(pq)-1} L_{(tu),(rs)} L_{(pq),(rs)} \right] / L_{(pq),(pq)}. \quad (117)$$

The summations are omitted when the upper index is zero.

Beebe and Linderberg[137] proposed the following algorithm for the construction of the lower triangular matrix:-

1. Calculate the diagonal elements of the two-electron integral matrix \mathbf{V} , that is $V_{(pq),(pq)}$ and arrange them in non-increasing order keeping a record of the original order.
2. Take the largest diagonal element, $V_{1,1}$, and set

$$L_{1,1} := \sqrt{V_{1,1}} \quad (118)$$

3. Obtain the entire column of two-electron integrals

$$V_{(pq),1}, \quad (pq) = 1, 2, \dots, \frac{1}{2} [n(n+1)] \quad (119)$$

4. Put

$$L_{(pq),1} := V_{(pq),1}, \quad (pq) = 2, 3, \dots, \frac{1}{2} [n(n+1)] \quad (120)$$

5. Update the diagonal elements

$$V_{(pq),(pq)} := V_{(pq),(pq)} - L_{(pq),1} L_{(pq),1}, \quad (pq) = 2, 3, \dots, \frac{1}{2} [n(n+1)] \quad (121)$$

(It should be noted that $V_{1,1}$ is now set to zero.)

For each value of $(pq) = 2, 3, \dots, \frac{1}{2} [n(n+1)]$ consider in turn the largest remaining diagonal element $V_{(pq),(pq)}$

6 Put

$$L_{(pq),(pq)} := \sqrt{V_{(pq),(pq)}} \quad (122)$$

7 Obtain the partial column

$$V_{(tu),(pq)}, \quad (tu) = \frac{1}{2} [j(j+1)], \dots, \frac{1}{2} [n(n+1)] \quad (123)$$

8 For $(tu) = \frac{1}{2} [j(j+1)], \dots, \frac{1}{2} [n(n+1)]$ put

$$L_{(tu),(pq)} := \left(V_{(tu),(pq)} - \sum_{(rs)=1}^{(pq)-1} L_{(tu),(rs)} L_{(rs),(pq)} \right) / L_{(pq),(pq)} \quad (124)$$

9 Update the diagonal elements according to

$$V_{(tu),(tu)} := V_{(tu),(tu)} - L_{(tu),(pq)}^2 \quad (125)$$

10 If the magnitude of each of the remaining *updated* diagonal elements falls below some specified threshold τ then stop.

11 Go to step 6 and consider the next value of (pq) .

Let m be the value of (pq) for which the above algorithm terminates at step 10. m is the effective numerical rank of the two-electron integral supermatrix. We can write

$$V_{(pq),(rs)} = \sum_{(tu)=1}^m L_{(pq),(tu)} L_{(rs),(tu)} \quad (126)$$

where

$$m \ll \frac{1}{2} [n(n+1)] \quad (127)$$

The Cholesky decomposition of the two-electron integral matrix is illustrated in Table 5 for a universal even-tempered basis set of 5 functions. The updated diagonal elements of the two-electron integral matrix which arise in cycle σ are given for cycles 1, 2, 3, 4, 6 and 8, together with the mapping to original order. The effective exploitation of the computational linear dependence in the two-electron integral matrix by the Cholesky decomposition algorithm significantly

Table 5: Cholesky decomposition of the two-electron integral matrix for a single centred universal even-tempered basis set with $\alpha = 0.5$, $\beta = 1.55$, and $n = 5$. The diagonal elements which arise in each cycle, σ , of the decomposition algorithm are shown together with the mapping on to the original order j .

j	$\sigma = 1$		$\sigma = 2$		$\sigma = 3$
1	0.6250000000	1	0.6250000000	1	0.6250000000
3	0.6250000000	15	0.4964908907	15	0.4964908907
6	0.6250000000	14	0.3919019274	6	0.0719861258
10	0.6250000000	10	0.3823237621	5	0.0554932347
15	0.6250000000	9	0.2733414367	9	0.0519245421
2	0.5417688155	13	0.2350669930	8	0.0401095669
5	0.5417688155	6	0.2231117019	3	0.0374687543
9	0.5417688155	8	0.1482147821	10	0.0374687543
14	0.5417688155	5	0.1286782277	4	0.0280128681
4	0.3574879250	12	0.1120809346	7	0.0213916752
8	0.3574879250	3	0.0673221520	13	0.0146982933
13	0.3574879250	7	0.0643924030	2	0.0121056596
7	0.1858895142	4	0.0548861303	12	0.0117866575
12	0.1858895142	11	0.0447596618	14	0.0081195570
11	0.0797510240	2	0.0187868508	11	0.0062794315
j	$\sigma = 4$		$\sigma = 6$		$\sigma = 8$
1	0.6250000000	1	0.6250000000	1	0.6250000000
15	0.4964908907	15	0.4964908907	15	0.4964908907
6	0.0719861258	6	0.0719861258	6	0.0719861258
3	0.0030254388	3	0.0030254388	3	0.0030254388
10	0.0030254388	10	0.0007763561	10	0.0007763561
2	0.0019348661	14	0.0000125938	14	0.0000125938
13	0.0017038819	2	0.0000100229	2	0.0000043770
14	0.0014766318	9	0.0000032103	9	0.0000000489
4	0.0014303850	5	0.0000030106	5	0.0000000458
9	0.0013350702	13	0.0000017220	8	0.0000000137
5	0.0009273679	4	0.0000010085	4	0.0000000088
12	0.0008826133	8	0.0000007164	13	0.0000000051
11	0.0003170389	11	0.0000002322	11	0.0000000026
8	0.0001535604	12	0.0000000245	7	0.0000000003

Taken from the work of Wilson[140]

reduces both the number of integral which have to be evaluated and the number of “integral-like” quantities which have to be stored.

The potential of the Cholesky decomposition of the two-electron integral matrix can be seen by considering the four-index transformation associated with the change of orbital basis

$$\varphi_i = \sum_{p=1}^n \chi_p c_{pi}. \quad (128)$$

The four-index transformation may be written

$$[ij | kl] = \sum_{p=1}^n \sum_{q=1}^n \sum_{r=1}^n \sum_{s=1}^n c_{pi} c_{qj} c_{rk} c_{sl} [pq | rs] \quad (129)$$

where

$$[ij | kl] \equiv [\varphi_i \varphi_j | \varphi_k \varphi_l] \quad (130)$$

and

$$[pq | rs] \equiv [\chi_p \chi_q | \chi_r \chi_s]. \quad (131)$$

This is usually written as a series of one-index transformations

$$[iq | rs] = \sum_{p=1}^n c_{pi} [pq | rs] \quad (132)$$

$$[ij | rs] = \sum_{q=1}^n c_{qj} [iq | rs] \quad (133)$$

$$[ij | ks] = \sum_{r=1}^n c_{rk} [ij | rs] \quad (134)$$

$$[ij | kl] = \sum_{s=1}^n c_{sl} [ij | ks] \quad (135)$$

giving an algorithm which scales as n^5 . Equation(126) may be written

$$[pq | rs] = \sum_{(tu)=1}^m L_{(pq),(tu)} L_{(rs),(tu)}. \quad (136)$$

Introducing (136) into (129) gives

$$\begin{aligned} [ij | kl] &= \sum_{(tu)=1}^m \sum_{p=1}^n \sum_{q=1}^n \sum_{r=1}^n \sum_{s=1}^n c_{pi} c_{qj} c_{rk} c_{sl} L_{(pq),(tu)} L_{(rs),(tu)} \\ &= \sum_{(tu)=1}^m \left(\sum_{p=1}^n \sum_{q=1}^n c_{pi} c_{qj} L_{(pq),(tu)} \right) \left(\sum_{r=1}^n \sum_{s=1}^n c_{rk} c_{sl} L_{(rs),(tu)} \right) \end{aligned} \quad (137)$$

Putting

$$L_{(ij),(tu)} = \sum_{p=1}^n \sum_{q=1}^n c_{pi} c_{qj} L_{(pq),(tu)} \quad (138)$$

and

$$L_{(kl),(tu)} = \sum_{r=1}^n \sum_{s=1}^n c_{rk} c_{sl} L_{(rs),(tu)} \quad (139)$$

allows (137) to be written in the form

$$[ij | kl] = \sum_{(tu)=1}^m L_{(ij),(tu)} L_{(kl),(tu)} \quad (140)$$

6 Discussion and Conclusions

We have considered the computational complexity of CCSD(T) algorithms in molecular electron correlation studies. The CCSD(T) model leads to one of the most computationally intensive parts of many quantum chemistry program packages formally scaling as $\mathcal{O}(N^7)$, where N typically denotes the size of the basis set, but leads to some of the most accurate computed molecular properties. This $\mathcal{O}(N^7)$ scaling implies that simply doubling the size of a problem leads to an increase in the computational demands by a factor of 128. This steep scaling of algorithms for CCSD(T) theory has fuelled a search for reduced-complexity algorithms. In this report, we have considered both $\mathcal{O}(N^7)$ algorithms for CCSD(T) calculations and three approaches to reduced-complexity algorithms: low-order scaling techniques for extended (*i.e.* large) molecules, Laplace transform techniques, and techniques based on Cholesky decomposition.

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