

Fifth-Order Møller-Plesset Perturbation Theory: Comparison of Existing Correlation Methods and Implementation of New Methods Correct to Fifth Order

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Full fifth-order Møller-Plesset perturbation theory of electron correlation is presented in algebraic form and used to compare the behavior of other approximate methods that are size-consistent and exact for two electrons. Considering only single and double substitutions, quadratic configuration interaction (QCISD), coupled cluster (CCSD), and Brueckner doubles (BD) theories are shown to deviate from each other in fifth order. The BD method contains the most parts of the fifth-order energy in a correct manner. The corresponding methods with noniterative triples corrections QCISD(T), CCSD(T), and BD(T) are also analyzed. These methods are all correct in those parts of the fifth-order energy that are linear in the higher (triple, quadruple) substitutions. Finally, new noniterative corrections are proposed that lead to theories completely correct in fifth order. These are QCISD(TQ), CCSD(TQ), and BD(TQ). The first and third of these have been implemented and are compared with full configuration interaction results for some simple systems.

1. Introduction

There exist several methods for treating the electron correlation problem starting from a Hartree-Fock (HF) single determinantal wave function.¹ Configuration interaction²⁻⁴ (CI), Møller-Plesset (MP) (or many-body) perturbation theory,⁵⁻¹¹ and the coupled cluster (CC) method¹²⁻²⁰ have been some of the widely used formalisms to calculate the electron correlation energy. The CI method is generally performed in the configuration space of all single and double substitutions (CISD) from the HF determinant. However, the CISD energy is not size consistent³ (i.e., the energy is not additive for infinitely separated systems), and typically a correction term (Davidson correction)⁴ is added to remedy this deficiency approximately. The MP perturbation scheme is practical up to fourth-order^{8,9} (MP4) and includes corrections from single, double, triple, and quadruple substitutions from the HF wave function.⁸ Perturbation theory truncated at any order is size consistent. However, the method may be slowly convergent or oscillatory in some cases, indicating the need for higher order terms.¹¹ The CC method is typically carried out including all single and double substitutions¹⁸ (CCSD), and several treatments to include the triple substitutions^{19,20,32} (CCSDT, CCSDT-n, CCSD+T(CCSD)) have also been proposed. This method is also size consistent, but the equations to be solved are quartic in the configuration expansion coefficients (for CCSD) and considerably more complex than the CI equations.

Recently, we have introduced a correlation method that is intermediate between configuration interaction and coupled cluster theory.²¹ In this technique, termed quadratic configuration interaction (QCI), the CI linear equations are modified by the introduction of additional terms that are quadratic in the configuration expansion coefficients. When formulated in the space of single and double substitutions (QCISD), the method has the desirable features of size consistency and exactitude (within the given basis) for a two-electron system. The quadratic equations of QCISD are intermediate in complexity between the linear equations of CISD and the quartic equations of CCSD. Further, the QCISD equations may themselves be derived from CCSD theory by omission of certain terms.^{21,22} Thus QCISD can be regarded as an approximation to CCSD.

In addition to QCISD, we have also proposed²¹ a noniterative treatment of triple substitutions, leading to an improved procedure termed QCISD(T). A similar correction has also been developed

for CCSD, leading to a corrected method CCSD(T).²³

Another procedure for handling electron correlation at the singles-doubles level is the Brueckner doubles (BD) method, originally implemented (under the name CCD($\hat{T}=0$)) by Chiles and Dykstra²⁴ and recently pursued by Handy et al.²⁵ In this

(1) For a general introduction to Hartree-Fock-based methods, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(2) Shavitt, I. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 3, page 189.

(3) Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quantum Chem. Symp.* 1977, 11, 149.

(4) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* 1974, 8, 61.

(5) Møller, C.; Plesset, M. S. *Phys. Rev.* 1934, 46, 618.

(6) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* 1976, 10, 1.

(7) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* 1978, 14, 91.

(8) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* 1980, 72, 4244.

(9) Bartlett, R. J.; Shavitt, I. *Chem. Phys. Lett.* 1977, 50, 190. Bartlett, R. J.; Purvis, G. D. *J. Chem. Phys.* 1978, 68, 2114. Bartlett, R. J.; Sekino, H.; Purvis, G. D. *Chem. Phys. Lett.* 1983, 98, 66.

(10) Kucharski, S. A.; Bartlett, R. J. *Adv. Quantum Chem.* 1986, 18, 281.

(11) Knowles, P. J.; Somasundram, K.; Handy, N. C.; Hirao, K. *Chem. Phys. Lett.* 1985, 113, 8. Laidig, W. D.; Fitzgerald, G.; Bartlett, R. J. *Chem. Phys. Lett.* 1985, 113, 151. Nobes, R. H.; Pople, J. A.; Radom, L.; Handy, N. C.; Knowles, P. J. *Chem. Phys. Lett.* 1987, 138, 481.

(12) Cizek, J. *J. Chem. Phys.* 1966, 45, 4256.

(13) Cizek, J.; Paldus, J. *Int. J. Quantum Chem.* 1971, 5, 359. Paldus, J.; Cizek, J.; Shavitt, I. *Phys. Rev. A* 1972, 5, 50.

(14) Taylor, P. R.; Bacskay, G. B.; Hush, N. S.; Hurley, A. C. *Chem. Phys. Lett.* 1976, 41, 444.

(15) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* 1978, 14, 545.

(16) Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* 1978, 14, 561. Bartlett, R. J. *Ann. Rev. Phys. Chem.* 1981, 32, 359.

(17) Chiles, R. A.; Dykstra, C. E. *J. Chem. Phys.* 1981, 74, 4544.

(18) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* 1982, 76, 1910.

(19) Lee, Y. S.; Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* 1984, 81, 5906. Urban, M.; Noga, J.; Cole, S. J.; Bartlett, R. J. *J. Chem. Phys.* 1985, 83, 4041. Noga, J.; Bartlett, R. J.; Urban, M. *Chem. Phys. Lett.* 1987, 134, 126.

(20) Noga, J.; Bartlett, R. J. *J. Chem. Phys.* 1987, 86, 7041.

(21) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* 1987, 87, 5968.

(22) Paldus, J.; Cizek, J.; Jeziorski, B. *J. Chem. Phys.* 1989, 90, 4356. Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* 1989, 90, 4635. Scuseria, G. E.; Schaefer, H. F. *J. Chem. Phys.* 1989, 90, 3700.

(23) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* 1989, 157, 479.

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method, the Hartree–Fock orbitals are replaced by a new set of occupied orbitals such that the singles amplitudes vanish if CCSD theory is applied with this new reference determinant. Again, a BD calculation may be followed by a perturbative correction for triple substitutions, leading to a method termed BD(T).²⁵

The first purpose of the present paper is to compare the various correlation methods by means of an expansion in a Møller–Plesset perturbation series up to fifth order. It is recognized that many of the methods (MP4, CCSDT, CCSDT-n, CCSD+T(CCSD), QCISD(T), CCSD(T), and BD(T)) are completely accurate up to fourth order; it is in fifth order that they begin to diverge. We begin in section 2 with an exposition of full MP5 theory. Kucharski and Bartlett^{10,26} have already treated this topic using a diagrammatic approach; we follow an entirely algebraic formulation to identify all fifth-order terms in a somewhat different arrangement. This is followed in section 3 by an analysis of the parts of the fifth-order energy that are included in the other correlation methods. It turns out that all (except the very recent XCC(5) and UCC(5) introduced by Bartlett and coworkers²⁷) are inaccurate in some fifth-order term. A preliminary account of this part of the work has been given elsewhere.²³

The second objective of the present work is the development of a new set of corrections to QCISD, CCSD, and BD theories to make them fully accurate to fifth order. It will be shown, in section 4, that three such corrections are needed, which are quadratic in the higher (triple, quadruple) substitutions. Finally, in section 5, two of the new methods, termed QCISD(TQ) and BD(TQ), are evaluated by some preliminary applications.

2. Møller–Plesset Perturbation Expansion to Fifth Order

The starting point of Møller–Plesset (MP) expansion is the single-determinant Hartree–Fock (HF) wave function Ψ_0 , containing n occupied spin orbitals χ_i ($i = 1, \dots, n$) and $(N - n)$ unoccupied (virtual) spin orbitals χ_a ($a = n + 1, \dots, N$), where N is the dimension of the basis used for spin orbital expansion. Corresponding one-electron energies will be denoted by ϵ_i, ϵ_a . We shall follow the common convention of using suffices i, j, k, \dots for occupied and a, b, c, \dots for virtual spin orbitals.

Other determinantal wave functions are derived from Ψ_0 by substitution of occupied spin orbitals by virtual spin orbitals. These may be classified as single (S), double (D), triple (T), quadruple (Q), ..., substitutions, each associated with an amplitude. The full correlated wave function may then be written in the form

$$\Psi = \Psi_0 + \sum_{s>0} a_s \Psi_s \quad (2.1)$$

There will be an exact value of a_s , obtainable in principle by full configuration interaction (FCI). In addition, each a_s may be expanded in an MP series $a_s^0 + a_s^1 + a_s^2 + \dots$, and terminated at any order. In section 3, we shall examine the values of a_s obtained by other (nonexact) correlation methods.

It is well-known, from Brillouin's theorem²⁸ and the two-body nature of the Hamiltonian, that the MP wave functions Ψ^1, Ψ^2 are

$$\begin{aligned} \Psi^1 &= \sum_s^D a_s^1 \Psi_s & a_s^1 &= (E_0 - E_s)^{-1} V_{s0} \\ \Psi^2 &= \sum_s^{SDTQ} a_s^2 \Psi_s & a_s^2 &= (E_0 - E_s)^{-1} \sum_t \bar{V}_{st} a_t^1 \end{aligned} \quad (2.2)$$

where E_0, E_s are eigenvalues of the unperturbed (Fock) Hamiltonian F and $\bar{V} = V - E^1$, where the full Hamiltonian is written

as $H = F + V$. The corresponding energy expressions are

$$\begin{aligned} E^2 &= \sum_s^D V_{0s} a_s^1 \\ E^3 &= \sum_{st}^D a_s^1 \bar{V}_{st} a_t^1 \\ E^4 &= \sum_s^D \sum_t^{SDTQ} a_s^1 \bar{V}_{st} a_t^2 - E^2 \sum_s^D |a_s^1|^2 \\ E^5 &= \sum_{st}^{SDTQ} a_s^2 \bar{V}_{st} a_t^2 - 2E^2 \sum_s^D a_s^1 a_s^2 - E^3 \sum_s^D |a_s^1|^2 \end{aligned} \quad (2.3)$$

Thus E^2 and E^3 involve only double substitutions D while E^4 and E^5 involve S, D, T , and Q . E^4 from (2.3) can be conveniently partitioned⁷ as

$$E^4 = E_S^4 + E_D^4 + E_T^4 + E_Q^4 \quad (2.4)$$

where the first three parts arise from S, D, T , summation for t in E^4 and the final part includes the Q sum and the renormalization term, which provides a partial cancellation of the Q sum. It is easily shown that the four parts of (2.4) are individually size consistent.

The fifth-order energy E^5 can be partitioned in a similar manner, according to the parts of the double st summation in (2.3). We write

$$E^5 = E_{SS}^5 + E_{DD}^5 + E_{TT}^5 + E_{QQ}^5 + 2E_{SD}^5 + 2E_{ST}^5 + 2E_{DT}^5 + 2E_{DQ}^5 + 2E_{TQ}^5 \quad (2.5)$$

Note that we have included factors of two in off-diagonal terms such as E_{SD}^5 , since there are really two equals parts E_{SD}^5 and E_{DS}^5 . The E^2 renormalization term is incorporated in $2E_{DQ}^5$ and the E^3 renormalization term in E_{QQ}^5 , since there are partial cancellations. Again, the individual terms in (2.5) are size consistent.

To convert the energy expressions in (2.3) to summations involving individual spin orbitals, it is useful to introduce a *general linear array function*:

$$u_s = \sum_t \bar{V}_{st} a_t \quad (2.6)$$

which may be further separated into sums over $t =$ singles, $t =$ doubles, Thus

$$\bar{u}_s = \sum_t^S \bar{V}_{st} a_t, \quad \bar{\bar{u}}_s = \sum_t^D \bar{V}_{st} a_t, \quad \dots \quad (2.7)$$

Explicit forms for \bar{u}_s and $\bar{\bar{u}}_s$ in terms of two-electron integrals have been derived previously^{3,7,8,15,21} and are

$$\bar{u}_i^a = -\sum_{jb} (ja||ib) a_j^b \quad (2.8)$$

$$\bar{\bar{u}}_i^a = -\frac{1}{2} \sum_{jbc} (ja||bc) a_j^b a_c^c - \frac{1}{2} \sum_{jkb} (jk||ib) a_j^k a_b^c \quad (2.9)$$

$$\bar{u}_{ij}^{ab} = \frac{1}{2} \mathcal{A}_{ij}^{ab} [\sum_c (ab||cj) a_c^c + \sum_k (ka||ij) a_k^c] \quad (2.10)$$

$$\bar{\bar{u}}_{ij}^{ab} = \frac{1}{2} \sum_{cd} (ab||cd) a_{ij}^{cd} + \frac{1}{2} \sum_{kl} (kl||ij) a_{kl}^{ab} - \mathcal{A}_{ij}^{ab} \sum_{kc} (kb||ic) a_k^c \quad (2.11)$$

$$\bar{u}_{ijk}^{abc} = \frac{1}{4} \mathcal{A}_{ijk}^{abc} (jk||bc) a_i^c \quad (2.12)$$

$$\bar{\bar{u}}_{ijk}^{abc} = \frac{1}{4} \mathcal{A}_{ijk}^{abc} [\sum_e (bc||ek) a_e^e - \sum_m (mc||jk) a_m^a] \quad (2.13)$$

Here we have used the symbol \mathcal{A}_{ijk}^{abc} for $\mathcal{A}_{ijk} \mathcal{A}^{abc}$ where \mathcal{A}_{ijk} and \mathcal{A}^{abc} are simple antisymmetrizing operators $\sum_P (-1)^P P$ over permutations P of the appropriate indices.

In the Møller–Plesset expansion, the matrix elements \bar{V}_{st} are first order in the expansion parameter, so the u vectors at order n are given by

$$u_s^n = \sum_t \bar{V}_{st} a_t^{n-1} \quad (s = S, D, T, \dots) \quad (2.14)$$

The first-order coefficients a_s^1 ($= -(\Delta_{ij}^{ab})^{-1} (ab||ij)$) are used to

(24) Chiles, R. A.; Dykstra, C. E. *J. Chem. Phys.* **1981**, *74*, 4544.

(25) Handy, N. C.; Pople, J. A.; Head-Gordon, M.; Raghavachari, K.; Trucks, G. W. *Chem. Phys. Lett.* **1989**, *164*, 185.

(26) Kucharski, S. A.; Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1989**, *90*, 7282.

(27) Bartlett, R. J.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1989**, *155*, 133. Bartlett, R. J.; Noga, J. *Chem. Phys. Lett.* **1988**, *150*, 29. Watts, J. D.; Trucks, G. W.; Bartlett, R. J. *Chem. Phys. Lett.* **1989**, *157*, 359.

(28) Brillouin, L. *Actual. Sci. Ind.* **1933**, *71*; **1934**, 159.

(29) Salter, E. A.; Trucks, G. W.; Bartlett, R. J. *J. Chem. Phys.* **1989**, *90*, 1752.

compute \bar{u}_s^2 ($s = S, D, T, Q$) from (2.14). The second-order coefficients a_s^2 are then

$$a_s^2 = (E_0 - E_s)^{-1} \bar{u}_s^2 \quad (s = S, D, T, Q) \quad (2.15)$$

and can be used further to evaluate \bar{u}_s^3 , \bar{u}_s^4 ($s = S, D, T$) from (2.14). The fourth-order energy components are then expressible in computable form as

$$E_S^4 = \sum_s \bar{u}_s^2 a_s^2 \quad (2.16)$$

$$E_D^4 = \sum_s \bar{u}_s^2 a_s^2 \quad (2.17)$$

$$E_T^4 = \sum_s \bar{u}_s^2 a_s^2 \quad (2.18)$$

$$E_Q^4 = \sum_s a_s^2 \left[\sum_t \bar{V}_{st} a_t^2 - E^2 a_s^2 \right] \quad (2.19)$$

Evaluation of E_Q^4 requires the second-order quadruples amplitudes:

$$a_i^2 = (E_0 - E_i)^{-1} \sum_u \bar{V}_{iu} a_u^1 \quad (2.20)$$

These can be shown to have the form

$$\begin{aligned} a_{ijkl}^{abcd}(2) = & a_{ij}^{ab} a_{kl}^{cd} - a_{ij}^{ac} a_{kl}^{bd} + a_{ij}^{ad} a_{kl}^{bc} + a_{ij}^{bd} a_{kl}^{ac} + a_{ij}^{cd} a_{kl}^{ab} - \\ & a_{ik}^{ab} a_{jl}^{cd} + a_{ik}^{ac} a_{jl}^{bd} - a_{ik}^{ad} a_{jl}^{bc} - a_{ik}^{bd} a_{jl}^{ac} + a_{ik}^{cd} a_{jl}^{ab} - \\ & a_{il}^{ab} a_{jk}^{cd} + a_{il}^{ac} a_{jk}^{bd} - a_{il}^{ad} a_{jk}^{bc} + a_{il}^{bd} a_{jk}^{ac} \end{aligned} \quad (2.21)$$

In this expression, all amplitudes on the right are understood to be first order. Equation 2.19 then becomes

$$E_Q^4 = \sum_s v_s^3 a_s^1 \quad (2.22)$$

where v_s^3 is a third-order array $Q_{ij}^{ab}(I, a \times a)$, using the general notation²⁷

$$\begin{aligned} Q_{ij}^{ab}(I, a \times b) = & \frac{1}{8} \sum_{klcd} (kl||cd) [a_{ij}^{cd} b_{kl}^{ab} - 2(a_{ij}^{ac} b_{kl}^{bd} + \\ & a_{ij}^{ad} b_{kl}^{bc}) - 2(a_{ik}^{ab} b_{jl}^{cd} + a_{ik}^{ac} b_{jl}^{bd}) + \\ & 4(a_{ik}^{ad} b_{jl}^{bc} + a_{il}^{ab} b_{jk}^{cd}) + \\ & \text{corresponding terms with } a \text{ and } b \text{ arrays interchanged}] \end{aligned} \quad (2.23)$$

Here I is shorthand for the two-electron integral array $(kl||cd)$, but the notation can be used more generally.

We now turn to the decomposition of the fifth-order energy E^5 . It follows easily that

$$E_{SS}^5 = \sum_s \bar{u}_s^3 a_s^2 \quad (2.24)$$

$$E_{SD}^5 = \sum_s \bar{u}_s^3 a_s^2 \quad (2.25)$$

$$E_{DD}^5 = \sum_s \bar{u}_s^3 a_s^2 \quad (2.26)$$

$$E_{ST}^5 = \sum_s \bar{u}_s^3 a_s^2 \quad (2.27)$$

$$E_{DT}^5 = \sum_s \bar{u}_s^3 a_s^2 \quad (2.28)$$

$$E_{bQ}^5 = \sum_s v_s^3 a_s^2 \quad (2.29)$$

E_{TQ}^5 can be further developed by using the second-order quadruples amplitudes from (2.21). Thus

$$E_{TQ}^5 = \sum_s \sum_t a_s^2 \bar{V}_{st} a_t^2 = \sum_s w_s^3 a_s^2 \quad (2.30)$$

where w_s^3 is a triples array, which could also be written as u_s^3 with four bars:

$$w_s^3 = \sum_t \bar{V}_{st} a_t^2 \quad (s = T) \quad (2.31)$$

For a particular triple substitution $ijk \rightarrow abc$, only those quadruple substitutions with five or more coincidences with $(ijkabc)$ will give nonvanishing matrix elements. Thus

$$w_{ijk}^{abc} = -\frac{1}{4} \mathcal{A}^{abc} \sum_{lde} (lc||de) a_{ijkl}^{abde} - \frac{1}{4} \mathcal{A}_{ijk} \sum_{lmd} (lm||kd) a_{ijlm}^{abcd} \quad (2.32)$$

where orders are omitted. Since the quadruples coefficients a_{ijkl}^{abcd} (at second order) are products of two doubles coefficients (eq 2.21), these coincidences may be distributed (4,1) or (3,2). It is convenient to separate w_{ijk}^{abc} into two parts, $w_{ijk}^{abc}(I)$ and $w_{ijk}^{abc}(II)$, according to this distinction. E_{TQ}^5 will then also split into parts $E_{TQ}^5(I)$ and $E_{TQ}^5(II)$.

Explicitly, part I of w_{ijk}^{abc} is given by

$$w_{ijk}^{abc}(I) = \frac{1}{8} \mathcal{A}_{ijk}^{abc} a_{ij}^{ab} \left[\sum_{lde} (lc||de) a_{kl}^{de} + \sum_{lmd} (lm||kd) a_{lm}^{cd} \right] \quad (2.33)$$

by using eq 2.21. This can be combined with eq 2.12 to some computational advantage. Thus

$$\bar{u}_{ijk}^{abc} + w_{ijk}^{abc}(I) = -\frac{1}{4} \Delta_{ijk}^{abc} \mathcal{A}_{ijk}^{abc} a_i^1 a_j^1 a_k^1 \quad (2.34)$$

lowest nonvanishing orders being implied. (2.34) is a triples array, which can be contracted with a_{ijk}^{abc} (order 2) to give $E_{ST}^5 + E_{TQ}^5(I)$.

The other w part, $w_{ijk}^{abc}(II)$, can be written by using (2.21) as

$$\begin{aligned} w_{ijk}^{abc}(II) = & \frac{1}{8} \mathcal{A}_{ijk}^{abc} \left\{ - \sum_{lde} (lc||de) [2a_{ij}^{ab} a_{kl}^{cd} + 2a_{ij}^{bd} a_{kl}^{ac} + a_{ij}^{cd} a_{kl}^{ab}] \right. \\ & - \sum_{lmd} (lm||kd) [2a_{im}^{ab} a_{jl}^{cd} + 2a_{ij}^{ab} a_{lm}^{cd} + a_{im}^{cd} a_{jl}^{ab}] \left. \right\} = \\ & \frac{1}{8} \mathcal{A}_{ijk}^{abc} \left\{ \sum_l a_{ijl}^{ab} X5(l,c,j,k) + \sum_d a_{ijl}^{cd} X6(a,b,k,d) \right\} \end{aligned} \quad (2.35)$$

where we have introduced two intermediate arrays:

$$X5(l,c,j,k) = - \sum_{de} (lc||de) a_{jk}^{de} + 2 \mathcal{A}_{jk} \sum_{md} (lm||kd) a_{im}^{cd}$$

$$X6(a,b,k,d) = - \sum_{lm} (lm||kd) a_{lm}^{ab} - 2 \mathcal{A}^{ab} \sum_{le} (la||de) a_{le}^{bc} \quad (2.36)$$

which supplement the intermediate arrays introduced in ref 15. The array $w_{ijk}^{abc}(II)$ can be evaluated in $\mathcal{O}(n^3 N^4)$ steps.

Next we consider E_{TT}^5 , which can be written

$$E_{TT}^5 = \sum_{st} a_s^2 \bar{V}_{st} a_t^2 = \sum_s a_s^2 \bar{u}_s^3 \quad (2.37)$$

For the triple-triple matrix element \bar{V}_{st} to be nonzero, there must be four or more suffix coincidences. This leads to the explicit expression

$$\bar{u}_{ijk}^{abc} = \frac{1}{4} \mathcal{A}^{abc} \sum_{de} (bc||de) a_{ijk}^{de} + \frac{1}{4} \mathcal{A}_{ijk} \sum_{lm} (lm||jk) a_{ilm}^{abc} - \frac{1}{4} \mathcal{A}_{ijk}^{abc} \sum_{ld} (lc||kd) a_{ijld}^{abcd} \quad (2.38)$$

The three different summations in (2.38) require $\mathcal{O}(n^3 N^5)$, $\mathcal{O}(n^3 N^3)$, and $\mathcal{O}(n^4 N^4)$ computational steps, respectively; the evaluation of E_{TT}^5 is the most demanding of all the terms in an MP5 calculation.

Finally we deal with E_{bQ}^5 , given by

$$E_{bQ}^5 = \sum_s a_s^2 w_s^3 - E^3 \sum_s |a_s^1|^2 \quad (2.39)$$

where

$$w_s^3 = \sum_t \bar{V}_{st} a_t^2 \quad (s = Q) \quad (2.40)$$

Again, note that w_s^3 could be written as u_s^3 with four bars. With (2.21) and the antisymmetric nature of a_i^1 and w_s^3 , (2.39) can be written

$$E_{bQ}^5 = \frac{1}{32} \sum_{ijkl} \sum_{abcd} a_{ij}^{ab} a_{kl}^{cd} w_{ijkl}^{abcd} - \frac{1}{4} E^3 \sum_{ijab} |a_{ij}^{ab}|^2 \quad (2.41)$$

where the orders are omitted on the right.

The quadruple substitutions s and t in (2.40) can differ by not more than two orbital indices for \bar{V}_{st} to be nonzero. Since a_i^j is itself a sum of products of doubles coefficients, these two suffices (which differ from $ijklabcd$ in (2.41)) may be either in the *same* doubles coefficient (type I or disconnected terms) or *split* across two *different* coefficients (type II or connected terms). This leads to a separation of $w_s^3(w_{ijkl}^{abcd})$ into two parts, $w_s(I)$ and $w_s(II)$, and hence to a corresponding separation of E_{QQ}^5 into $E_{QQ}^5(I)$ and $E_{QQ}^5(II)$. The final (renormalization) term in (2.41) is incorporated in $E_{QQ}^5(I)$. The quadruples array $w_{ijkl}^{abcd}(I)$ can be developed from (2.40) in three parts, depending on whether the two suffices differing from $ijklabcd$ are both virtual, both occupied, or one of each. However, the three parts may be combined using the definition of \bar{u}_{kl}^{cd} (eq 2.11) to give the final expression

$$E_{QQ}^5(I) = \frac{1}{4} \sum_{ijab} a_{ij}^{ab} Q_{ij}^{ab}(\bar{u}, a \times a) \quad (2.42)$$

The Q array required here needs the same general algorithm as used in MP4 theory (see eq 2.23). This involves only $\mathcal{O}(n^3N^3)$ operations.

The other portion $w_{ijkl}^{abcd}(II)$ can be developed in a similar manner, leading to the full result

$$E_{QQ}^5(II) = \frac{1}{8} \sum_{ijkl} \sum_{abcd} a_{ij}^{ab} a_{kl}^{cd} \{ [(cd||ef) \times (-a_{ij}^{ab} a_{kl}^{cd} + 2a_{ij}^{ab} a_{kl}^{cd}) + (bd||ef)(a_{ij}^{ab} a_{kl}^{cd} + a_{ij}^{ab} a_{kl}^{cd} - 4a_{ij}^{ab} a_{kl}^{cd})] + \sum_{mn} [(mn||kl)(-a_{im}^{ab} a_{jn}^{cd} + 2a_{im}^{ab} a_{jn}^{cd}) + (mn||jl)(a_{im}^{ab} a_{kn}^{cd} + a_{im}^{ab} a_{kn}^{cd} - 4a_{im}^{ab} a_{kn}^{cd})] - 2 \sum_{me} [(md||le)(4a_{im}^{ab} a_{je}^{cd} + 2a_{im}^{ab} a_{je}^{cd} + 2a_{km}^{bc} a_{ij}^{de} + a_{km}^{bc} a_{ij}^{de}) + (mb||le)(2a_{im}^{ab} a_{jk}^{cd} + 4a_{im}^{ab} a_{jk}^{cd} + a_{im}^{ab} a_{jk}^{cd} + 2a_{km}^{bc} a_{ij}^{de})] \} \quad (2.43)$$

As written, this expression involves $\mathcal{O}(n^4N^6)$ operations. However, as originally noted by Kucharski and Bartlett,¹⁰ it can be accomplished by using a series of intermediate arrays, requiring no more than $\mathcal{O}(N^6)$ steps. Details are given in the Appendix.

3. Expansion of Other Correlation Methods to Fifth Order

The expressions for the fifth-order energy considered in the previous section apply to the exact solution expanded in orders of the perturbation. We now turn to the other methods, mentioned in the Introduction (which are size consistent and exact for two electrons), and ask which terms are included correctly at each order. All the methods discussed are correct in second and third orders, so we focus mainly on orders four and five.

The first method we consider is quadratic configuration interaction, QCISD, for which the defining equations are²¹

$$\langle \Psi_0 | H | T_2 \Psi_0 \rangle = E_{\text{corr}} \quad (3.1)$$

$$\langle \Psi_0 | \bar{H} | (T_1 + T_2 + T_1 T_2) \Psi_0 \rangle = a_i^j E_{\text{corr}} \quad (3.2)$$

$$\langle \Psi_0 | \bar{H} | (1 + T_1 + T_2 + \frac{1}{2} T_2 T_2) \Psi_0 \rangle = a_{ij}^{ab} E_{\text{corr}} \quad (3.3)$$

The second method is coupled cluster, CCSD, for which the standard equations may be slightly modified and written in the form

$$\langle \Psi_0 | H | T_2 \Psi_0 \rangle = E_{\text{corr}} \quad (3.4)$$

$$\langle \Psi_0 | \bar{H} | (T_1 + T_2 + T_1 T_2 - \frac{1}{3} T_1 T_1 T_1) \Psi_0 \rangle = a_i^j E_{\text{corr}} \quad (3.5)$$

$$\langle \Psi_0 | \bar{H} | (1 + T_1 + T_2 + T_1 T_2 - \frac{1}{3} T_1 T_1 T_1 + \frac{1}{2} T_2 T_2 - \frac{1}{12} T_1 T_1 T_1 T_1) \Psi_0 \rangle = a_{ij}^{ab} E_{\text{corr}} \quad (3.6)$$

In both QCISD and CCSD, the reference determinant is taken to be the Hartree-Fock function Ψ_0 . The third method is Brueckner doubles, BD, for which the defining equations are

$$\langle \Phi_0 | H | (1 + T_2) \Phi_0 \rangle = E \quad (3.7)$$

$$\langle \Phi_0 | \bar{H} | (1 + T_2) \Phi_0 \rangle = 0 \quad (3.8)$$

$$\langle \Phi_{ij}^{ab} | H | (1 + T_2 + \frac{1}{2} T_2 T_2) \Phi_0 \rangle = a_{ij}^{ab} E \quad (3.9)$$

Here the reference determinant Φ_0 is no longer Hartree-Fock but is itself determined by the single-substituted conditions (3.8).

Before expanding these equations in a perturbation series, it is useful to consider the order in which the various terms first contribute to the energy. For example, since T_2 is first order and T_1 second order, the triples product $T_1 T_2$ is third order. This gives a contribution to a_i^j in fourth order through (3.2) or (3.5), which in turn contributes to a_{ij}^{ab} in fifth order through (3.3) or (3.6). This finally leads to only a sixth-order energy contribution from (3.1) or (3.4), so $T_1 T_2$ in (3.2) or (3.5) may be neglected in a discussion of the fifth-order energy. After removing all such terms, which are unnecessary in our fifth-order energy analysis, we may write

$$\langle \Psi_0 | H | T_2 \Psi_0 \rangle = E_{\text{corr}} \quad (3.10)$$

$$\langle \Psi_0 | \bar{H} | (T_1 + T_2) \Psi_0 \rangle = 0 \quad (3.11)$$

$$\langle \Psi_0 | \bar{H} | (1 + T_1 + T_2 + x T_1 T_2 + \frac{1}{2} T_2 T_2) \Psi_0 \rangle = a_{ij}^{ab} E_{\text{corr}} \quad (3.12)$$

where $x = 0$ for QCISD and $x = 1$ for CCSD. In our previous discussion of BD theory,²⁵ we have shown that the fifth-order BD energy can be obtained from (3.10)–(3.12) with $x = 2$. This additional $T_1 T_2$ contribution to the fifth-order energy arises because the doubles projection (3.9) is on a doubly substituted configuration Φ_{ij}^{ab} based on the Brueckner determinant Φ_0 , rather than onto the Ψ_{ij}^{ab} formed from the Hartree-Fock determinant Φ_0 . The use of a properly symmetric treatment gives rise to an extra term, effectively increasing the value of x from 1 to 2.

Writing $\bar{F} + \bar{V}$ for \bar{H} and noting that \bar{V} is first order, the expansions of (3.10)–(3.12) which are needed up to fifth order are

$$\text{order 1} \quad \langle \Psi_0 | \bar{F} T_2 | \Psi_0 \rangle = 0 \quad (3.13)$$

$$\text{order 2} \quad \langle \Psi_0 | \bar{V} T_2 | \Psi_0 \rangle = E^2 \quad (3.14)$$

$$\langle \Psi_0 | \bar{F} T_1 + \bar{V} T_1 | \Psi_0 \rangle = 0 \quad (3.15)$$

$$\langle \Psi_0 | \bar{F} T_2 + \bar{V} T_2 | \Psi_0 \rangle = 0 \quad (3.16)$$

$$\text{order 3} \quad \langle \Psi_0 | \bar{V} T_2^2 | \Psi_0 \rangle = E^3 \quad (3.17)$$

$$\langle \Psi_0 | \bar{F} T_1^2 + \bar{V} T_1^2 + \bar{V} T_2^2 | \Psi_0 \rangle = 0 \quad (3.18)$$

$$\langle \Psi_0 | \bar{F} T_2^2 + \bar{V} T_1^2 + \bar{V} T_2^2 + \frac{1}{2} \bar{V} T_1^2 T_2 | \Psi_0 \rangle = (a^1)_{ij}^{ab} E^2 \quad (3.19)$$

$$\text{order 4} \quad \langle \Psi_0 | \bar{V} T_2^3 | \Psi_0 \rangle = E^4 \quad (3.20)$$

$$\langle \Psi_0 | \bar{F} T_2^3 + \bar{V} T_1^3 + \bar{V} T_2^3 + x \bar{V} T_1^2 T_2 + \bar{V} T_1^2 T_2 | \Psi_0 \rangle = (a^2)_{ij}^{ab} E^2 + (a^1)_{ij}^{ab} E^3 \quad (3.21)$$

$$\text{order 5} \quad \langle \Psi_0 | \bar{V} T_2^4 | \Psi_0 \rangle = E^5 \quad (3.22)$$

In fourth order, the energy is given by (3.20), which requires the third-order doubles amplitudes T_2^3 , determined from (3.19). This includes the correct contributions from singles (T_1^2), doubles (T_2^2), and quadruples ($\frac{1}{2} T_1^2 T_2$). It follows that E^4 gives the S , D , Q parts correctly but not the triples (T) part. This applies to QCISD, CCSD, and BD.

In fifth order, the energy requires T_2^4 , which is given by (3.21). This involves a number of parts. First $\bar{V} T_1^2$ requires T_1^3 , which comes from (3.18) and gives energy components $E_{SS}^3 + E_{SD}^3$. Next, $\bar{V} T_2^3$ requires T_2^3 from (3.19). The $\bar{V} T_1^2$ and $\bar{V} T_2^2$ parts of (3.19) give fifth-order energies $E_{SD}^3 + E_{DD}^3$. Thus all three parts of E^5 , involving singles and doubles only, are given correctly by QCISD, CCSD, and BD. Of course, this is a necessary consequence of the exactitude of the methods for two electrons. Continuing with the partition of the third-order doubles amplitudes T_2^3 , the remaining terms in (3.19) involve the second-order quadruples wave function. The corresponding part of E^5 can be written

$$\Delta E^5 = \sum_i \frac{D}{i} a_i^2 \bar{V}_{ia} a_i^2 - E^2 \sum_i a_i^2 a_i^2 = \sum_i v_i^2 a_i^2 \quad (3.23)$$

TABLE I: Comparison of Correlation Techniques in Fifth Order^a

cost	method	SS	2SD	DD	2ST	2DT	2DQ	TT	2TQ(I)	2TQ(II)	QQ(I)	QQ(II)
iterative N^6	QCISD	x	x	x			x				x	
	CCSD	x	x	x	1/2		x		1/2		x	
	BD	x	x	x	x		x		x		x	
iterative N^6 + one N^7	CCSD+T(CCSD)	x	x	x	1/2	x	x		1/2		x	
	QCISD(T)	x	x	x	x	x	x		x		x	
	CCSD(T)	x	x	x	x	x	x		1/2		x	
iterative N^7	BD(T)	x	x	x	x	x	x		x		x	
	CCSDT-1	x	x	x	x	x	x		1/2		x	
	CCSDT-2,3	x	x	x	x	x	x		1/2	1/2	x	
iterative N^6 + one N^8	QCISD(TQ)	x	x	x	x	x	x	x	x	x	x	x
	CCSD(TQ)	x	x	x	x	x	x	x	x	x	x	x
	BD(TQ)	x	x	x	x	x	x	x	x	x	x	x
iterative N^8	CCSDT	x	x	x	x	x	x	x	1/2	1/2	x	

^ax indicates that the term is included fully. 1/2 indicates that only half this term is included correctly.

This is equal to E_{DQ}^5 (eq 2.29). It may be noted that this is only half of the full DQ contribution in fifth order. The other half is obtained slightly differently, as seen below.

Returning to the parts of the fourth-order doubles amplitudes T_2^3 , given by (3.21), we next consider the contribution from $\bar{V}T_1^1T_2^2$. $T_1^2T_2^1$ comprises a set of third-order quadruples amplitudes, which can be explicitly written as

$$a_{ijkl}^{abcd} = (a^1)_{ij}^{ab}(a^2)_{kl}^{cd} + (a^1)_{kl}^{cd}(a^2)_{ij}^{ab} + 36 \text{ terms} \quad (3.24)$$

where the 36 terms are obtained by permutation of the indices. The second-order amplitudes such as $(a^2)_{kl}^{cd}$ can be replaced by $-(\Delta_{kl}^{cd})^{-1}\bar{u}_{kl}^{cd}$ (eq 2.15). Thus, with some rearrangement

$$a_{ijkl}^{abcd} = (\Delta_{ij}^{ab}\Delta_{kl}^{cd})^{-1}[(ab||ij)\bar{u}_{kl}^{cd} + \bar{u}_{ij}^{ab}(cd||kl)] + 36 \text{ terms} \quad (3.25)$$

With the identity

$$(xy)^{-1} = (x + y)^{-1}(x^{-1} + y^{-1}) \quad (3.26)$$

(3.25) can be grouped into two series of terms:

$$a_{ijkl}^{abcd} = -(\Delta_{ijkl}^{abcd})^{-1}[(ab||ij)(a^2)_{kl}^{cd} + (cd||kl)(a^2)_{ij}^{ab} + 36 \text{ terms}] + [(a^1)_{ij}^{ab}\bar{u}_{kl}^{cd} + (a^1)_{kl}^{cd}\bar{u}_{ij}^{ab} + 36 \text{ terms}] \quad (3.27)$$

The first sum in (3.27) can be easily identified as

$$\Delta a_s^3 = (E_0 - E_s)^{-1} \sum_i V_{si} a_i^2 \quad s = Q \quad (3.28)$$

and, after partial cancellation by the E^2 term on the right of (3.21), the final contribution to E^5 is E_{DQ}^5 , providing the other half of the total DQ contribution $2E_{DQ}^5$. It follows that QCISD and CCSD, like CCD, are correct to fifth order in the DQ interaction, as already noted for CCD by Kucharski and Bartlett.¹⁰

The second part of (3.27) results from a subset of terms in the fifth-order QQ interaction. In fact, the second square-bracketed term is exactly $w_{ijkl}^{abcd}(I)$ as defined in section 2. When the renormalization term is included, the corresponding energy contribution is just $E_{QQ}^5(I)$.

This completes the fifth-order analysis for QCISD. In summary

$$E^5(\text{QCISD}) = E_{SS}^5 + E_{DD}^5 + 2E_{SD}^5 + 2E_{DQ}^5 + E_{QQ}^5(I) \quad (3.29)$$

To obtain the corresponding CCSD fifth-order result, we have to add T_2^3 contributions due to the $\bar{V}T_1^1T_2^2$ term in (3.21). $T_1^2T_2^1$ comprises a set of third-order triples amplitudes, given explicitly by

$$a_{ijk}^{abc} = \mathcal{A}_{ijk}^{abc} a_i^a a_j^b a_k^c = \mathcal{A}_{ijk}^{abc} (\Delta_{ijk}^{abc})^{-1} \bar{u}_i^a (bc||jk) \quad (3.30)$$

Again using the identity (3.26) and rearranging, this can be grouped into two series of terms:

$$a_{ijk}^{abc} = -(\Delta_{ijk}^{abc})^{-1} \mathcal{A}_{ijk}^{abc} [a_i^a (bc||jk) + \bar{u}_i^a a_j^b a_k^c] \quad (3.31)$$

In both (3.30) and (3.31) a_i^a is second order and $a_j^b a_k^c$ is first order. The first sum in (3.31) is easily identified as a partial triples amplitude:

$$\Delta a_s = (E_0 - E_s)^{-1} \sum_i V_{si} a_i^2 \quad s = T \quad (3.32)$$

and the corresponding fifth-order energy is E_{ST}^5 , which is only half of the ST interaction terms.

The second set of terms in (3.29) has already been considered in eq 2.33 in writing $w_{ijk}^{abc}(I)$. Clearly this leads to the fifth-order energy $E_{TQ}^5(I)$. Again only half of the TQ(I) interaction is included. The other half is omitted in CCSD theory.

In summary

$$E^5(\text{CCSD}) = E_{SS}^5 + E_{DD}^5 + 2E_{SD}^5 + E_{ST}^5 + 2E_{DQ}^5 + E_{TQ}^5(I) + E_{QQ}^5(I) \quad (3.33)$$

The corresponding result for BD corresponds to $x = 2$ in (3.12) and is

$$E^5(\text{BD}) = E_{SS}^5 + E_{DD}^5 + 2E_{SD}^5 + 2E_{ST}^5 + 2E_{DQ}^5 + 2E_{TQ}^5(I) + E_{QQ}^5(I) \quad (3.34)$$

This expression has no missing factors of 2, although certain parts of the total fifth-order energy are omitted altogether.

We now consider the triples contributions introduced in a noniterative manner in the techniques QCISD(T), CCSD(T), and BD(T). The additional energy terms may be written

$$\Delta E_T = 1/36 \sum_{ijk} \sum_{abc} (\Delta_{ijk}^{abc})^{-1} [(2-x)\bar{u}_{ijk}^{abc} + \bar{u}_{ijk}^{abc} \bar{u}_{ijk}^{abc}] \quad (3.35)$$

where again $x = 0, 1, 2$ for QCISD(T), CCSD(T), and BD(T), respectively.

The \bar{u}_{ijk}^{abc} elements in (3.35) are second order, so the contributions to ΔE_T begin in fourth order. In fact, \bar{u}_{ijk}^{abc} is correct at second order, so it follows that all three methods QCISD(T), CCSD(T), and BD(T) include the full fourth-order energy E^4 . The correction (3.35), without \bar{u}_{ijk}^{abc} and with \bar{u}_{ijk}^{abc} from CCD theory, was proposed by one of us some time ago³⁰ and shown to give the doubles–triples term $2E_{DT}^5$ correctly. The same applies to all three of these methods. It may be noted that the denominator Δ_{ijk}^{abc} in (3.35) is slightly different in BD(T) theory but only affects ΔE_T in sixth order. Finally, the term $(2-x)\bar{u}_{ijk}^{abc}\bar{u}_{ijk}^{abc}$ in (3.35) corrects for the missing part of the ST energy in fifth order.

The fifth-order results obtained in this section are summarized in Table I, which also contains the corresponding results for some other techniques proposed by Bartlett and co-workers.^{31–33} To complete this section, we discuss the relative merits of the methods at this fifth-order level. In this context, it is important to distinguish between the iterative and non-iterative computational requirements in methods where there is a one-time evaluation at the end of an iterative scheme.

As is well-known, complete E^4 calculation requires $\mathcal{O}(n^3N^4)$ steps, whereas E_{SDQ}^4 which neglects triples contributions, requires

(30) Raghavachari, K. *J. Chem. Phys.* **1985**, *82*, 4607.

(31) Lee, Y. S.; Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1984**, *81*, 5906.

(32) Urban, M.; Noga, J.; Cole, S. J.; Bartlett, R. J. *J. Chem. Phys.* **1985**, *83*, 4041.

(33) Cole, S. J.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 7041.

only $\mathcal{O}(n^2N^4)$ computational steps. However, full treatment of E^5 requires $\mathcal{O}(n^3N^5)$ steps, this being the number of operations needed for the computation of E_{TT}^5 .

Now consider the other techniques. The leading term in the different iterative schemes QCISD, CCSD, and BD is $\mathcal{O}(n^2N^4)$ and is in fact identical for all three methods. These steps have to be applied at each iteration, which requires a further multiplicative factor n_{iter} , the number of iterations required for a converged solution.

The triples contributions introduce another order of complexity but are necessary for a quantitative solution. The schemes CCSD + T(CCSD), QCISD(T), CCSD(T), and BD(T) introduce the triples in a noniterative manner, so that the $\mathcal{O}(n^3N^4)$ step has to be evaluated only once. This, however, is still practical and can be applied to reasonably large problems. In fact, the cost of these triples corrections is very close to that for the triples term in an MP4 calculation.

The approximate CCSDT- n models all include triples contributions in an iterative manner including at least the linear terms. Thus, all these methods require an $\mathcal{O}(n^3N^4)$ computation to be performed in each of n_{iter} iterations. This may limit the applicability of such methods in the case of larger molecules.

The complete CCSDT calculation, which requires the evaluation of the TT interactions, requires $\mathcal{O}(n^3N^5)$ computational steps in each iteration. Thus such a scheme is applicable to only the smallest problems of practical interest. It should be noted that the CISDT method, though not discussed in this paper, also requires $\mathcal{O}(n^3N^5)$ computational steps in each iteration resulting from the calculation of the TT interactions.

Of the methods treating triples in a noniterative manner, QCISD(T), CCSD(T), and BD(T) appear to be close in fifth-order behavior. They differ only in the inclusion of $2E_{TQ}^5(I)$, which is probably smaller than the terms that are linear in T , Q substitutions. This is apparently confirmed by numerical comparison for some simple molecules.²⁵ The method CCSD + T(CCSD), on the other hand, omits part of the singles-triples term $2E_{ST}^5$ at fifth order, sometimes leading to serious errors.³⁴

4. Full Fifth-Order Corrections to QCISD, CCSD, and BD Theories

In the previous section, we have noted the theories QCISD(T), CCSD(T), and BD(T), which are partially corrected for the effects of triple substitutions, have the following properties: (1) The methods are fully correct in fourth order (S , D , T , Q). (2) The methods are correct in fifth order for those terms that are linear in the higher substitutions (T , Q).

In this section, we consider the next theoretical step to further improve the description of electron correlation, while keeping computational cost as low as reasonably possible. A good objective could be to continue to treat the higher substitutions as small perturbations but add further corrections to ensure that the theory is also correct in fifth order for terms that are quadratic in (T , Q). In fact, such a treatment would be fully accurate in fifth order. In terms of Table I, we seek a method that would handle all columns correctly and so would be superior to all the other methods considered in Table I, at least up to fifth order. Clearly, three additional corrections are needed (TT , TQ , and QQ). We shall consider these in turn.

TT Correction. As noted in section 2, the MP5 triples-triples energy contribution takes the form

$$E_{TT} = \sum_{st}^T a_s \bar{V}_{st} a_t \quad (4.1)$$

where a_s is the second-order triples coefficient. For MP5, this is derived from doubles only as

$$a_s = (E_0 - E_s)^{-1} \bar{u}_s \quad (s = T) \quad (4.2)$$

where \bar{u}_s is given in terms of first-order amplitudes by (2.13).

However, in the QCI approach, we have treated single and double substitutions on an equal footing, so that (4.2) might be replaced by

$$a_s = (E_0 - E_s)^{-1} (\bar{u}_s + \bar{u}_s) \quad (s = T) \quad (4.3)$$

using (2.12). However, if this is substituted in the E_{TT} correction (4.1), the size consistency property is lost, so we use the formula

$$E_{TT} = \sum_s^T (E_0 - E_s)^{-1} \bar{u}_s w_s(TT) \quad (4.4)$$

where

$$w_s(TT) = \sum_t^T \bar{V}_{st} (\bar{u}_t + x \bar{u}_t) (E_0 - E_t)^{-1} \quad (s = T) \quad (4.5)$$

x taking values 2, 1, and 0 for QCISD, CCSD, and BD iterative schemes, respectively. In orbital terms, $w_s(TT)$ is evaluated by the formula (2.38), with a_t amplitudes being replaced by $(\bar{u}_t + x \bar{u}_t)(E_0 - E_t)^{-1}$. Size consistency for this correction can be proved, using the methods outlined in ref 21.

As in MP5 theory, this TT correction requires $\mathcal{O}(n^3N^5)$ steps and therefore scales as the eighth power of the size of the system. There appears to be no way to avoid this if the objective of full fifth-order accuracy is to be achieved. However, in this proposed method, this computationally most demanding step has to be carried out only once at the end of the iterative process.

TQ Corrections. In section 2, the TQ fifth-order contribution was divided into two parts, I and II . It is useful to continue to treat these parts separately as QCISD, CCSD, and BD differ in their effective treatment of this interaction (Table I). We will use the direct formula

$$2E_{TQ} = 2 \sum_s^T (E_0 - E_s)^{-1} \bar{u}_s w_s \quad (4.6)$$

where the two parts, $w_s(I)$ and $w_s(II)$, are given by eq 2.33 and 2.35, respectively, with the doubles amplitudes taken from the preceding iterative procedure (QCISD, CCSD, or BD). From Table I, it is clear that the underlying QCISD method has no contribution from TQ in fifth order, so the appropriate correction is $2E_{TQ}(I) + 2E_{TQ}(II)$. For the BD method, on the other hand, only $2E_{TQ}(II)$ is needed, since $2E_{TQ}(I)$ is already included. For the intermediate CCSD theory, the appropriate correction is $E_{TQ}(I) + 2E_{TQ}(II)$.

QQ Corrections. Finally, it is clear from the preceding sections that the fifth-order quadruples-quadruples fifth-order term $E_{QQ}^5(I)$ is correctly incorporated in all three methods, QCISD, CCSD, and BD. It is therefore only necessary to add the other term $E_{QQ}^5(II)$ for each method, by using eq 2.43 with the appropriate doubles amplitudes.

5. Preliminary Applications

We now apply the MP5, QCISD(TQ), and BD(TQ) methods to a number of small systems for which the full configuration interaction energies are either available or easily computed. As with many previous studies, the objective is to test the comparative success of these and other methods in coming close to the FCI energy. MP5 has been previously tested in this manner. The new methods QCISD(TQ) and BD(TQ) are both completely accurate in fifth order and have approximately the same computing cost as MP5. The simpler methods QCISD(T) and BD(T) are exact in fourth order and accurate in fifth order only in the parts linear in the higher substitutions T , Q . It is therefore of interest to compare these levels of theory. In addition, we will make comparisons with some methods developed by Bartlett and co-workers,^{31,33} CCSD+T(CCSD), CCSDT-1, and CCSDT.

In Table II, we present a compilation of the errors, $E(\text{method}) - E(\text{FCI})$, for 12 simple examples. The first seven are small molecules with the STO-3G basis at their HF/STO-3G geometries, except for CN radical, which is at the HF/6-31G* geometry. The other five are water calculations with a double- ζ (DZ) basis at a geometry close to equilibrium and two other geometries with bond lengths stretched by factors 1.5 and 2.0. These DZ water

(34) Stanton, J. F.; Lipscomb, W. N.; Magers, D. H.; Bartlett, R. J. *J. Chem. Phys.* 1989, 90, 1077.

TABLE II: Energy Differences $E(\text{method}) - E(\text{FCI})$ (millihartrees)^a

	STO-3G							DZ				
	<i>R</i>	<i>R</i>	<i>R</i>	<i>R</i>	<i>R</i>	<i>R</i>	<i>U</i>	<i>R</i>	<i>R</i>	<i>R</i>	<i>U</i>	<i>U</i>
	(BH)	(CH ₂)	(H ₂ O)	(CH ₄)	(N ₂)	(HCN)	(CN)	(H ₂ O) (R _c)	(H ₂ O) (1.5R _c)	(H ₂ O) (2R _c)	(H ₂ O) (1.5R _c)	(H ₂ O) (2R _c)
QCISD	0.153	0.462	0.107	0.219	4.447	3.194	-1.020	1.482	4.739	9.554	6.664	11.261
BD	0.128	0.439	0.141	0.219	4.568	3.447	7.677	2.004	6.159	8.306	6.159	11.587
MP4	7.411	6.579	1.707	2.736	4.067	5.077	34.683	0.990	6.126	16.380	53.392	28.593
QCISD(T)	0.112	0.251	0.052	0.090	2.628	2.038	1.635	0.475	1.388	-2.210	4.787	8.030
BD(T)	0.099	0.247	0.068	0.090	2.679	2.140	3.887	0.661	1.808	-6.920	1.808	3.776
MP5	3.760	4.000	0.623	1.015	0.694	2.040	27.850	0.810	4.750	16.048	47.115	27.349
QCISD(TQ)	0.002	0.065	0.007	0.013	0.369	0.278	-1.167	0.162	0.227	1.728	0.912	6.341
BD(TQ)	0.006	0.070	0.009	0.013	0.369	0.265	1.204	0.134	0.053	0.468	0.053	3.204
CCSD+T(CCSD)								0.361	0.750	-11.222		
CCSDT-1								0.451	1.455	-5.575		8.458
CCSDT								0.434	1.473	-2.211		

^a *R* and *U* refer to RHF and UHF starting points.TABLE III: Components of Energy Corrections (millihartrees)^a

basis set	STO-3G							DZ				
	<i>R</i>	<i>R</i>	<i>R</i>	<i>R</i>	<i>R</i>	<i>R</i>	<i>U</i>	<i>R</i>	<i>R</i>	<i>R</i>	<i>U</i>	<i>U</i>
	(BH)	(CH ₂)	(H ₂ O)	(CH ₄)	(N ₂)	(HCN)	(CN)	(H ₂ O) (R _c)	(H ₂ O) (1.5R _c)	(H ₂ O) (2R _c)	(H ₂ O) (1.5R _c)	(H ₂ O) (2R _c)
QCISD corrections												
$\Delta E(T)$	-0.041	-0.211	-0.055	-0.129	-1.819	-1.156	+2.655	-1.007	-3.351	-11.764	-1.877	-3.231
$\Delta E(TT)$	-0.019	-0.088	-0.017	-0.037	-0.331	-0.218	-0.042	-0.127	-0.657	-3.008	-1.264	-1.248
$2\Delta E(TQ)$	-0.003	-0.002	+0.016	+0.002	+0.528	+0.417	+3.667	+0.440	+1.860	+11.056	+2.902	+1.583
$\Delta E(QQ)$	-0.088	-0.096	-0.045	-0.041	-2.456	-1.959	-6.427	-0.626	-2.364	-4.110	-5.513	-2.024
BD corrections												
$\Delta E(T)$	-0.029	-0.192	-0.073	-0.129	-1.889	-1.307	-3.790	-1.343	-4.351	-15.226	-4.351	-7.811
$\Delta E(TT)$	-0.013	-0.079	-0.021	-0.037	-0.333	-0.224	-0.463	-0.135	-0.647	-2.522	-0.647	-1.936
$2\Delta E(TQ)$	+0.008	-0.004	+0.007	+0.001	+0.474	+0.299	+0.795	+0.232	+1.128	+7.705	+1.128	+2.519
$\Delta E(QQ)$	-0.087	-0.094	-0.045	-0.041	-2.451	-1.951	-3.015	-0.624	-2.236	+2.204	-2.236	-1.155

^a *R* and *U* refer to RHF and UHF starting points.

calculations have been used by other authors for similar purposes. The calculations with stretched bonds can be either with a spin-restricted (RHF) or spin-unrestricted (UHF) starting point, since the UHF energy is then lower than RHF. Both sets of results are included in Table II. Table III gives the breakdown of the energy corrections QCISD \rightarrow QCISD(T) \rightarrow QCISD(TQ) and BD \rightarrow BD(T) \rightarrow BD(TQ) into the parts discussed in section 4.

We begin with a discussion of the individual molecules. BH and CH₂ (¹A₁) are both systems with low-lying vacant atomic orbitals at the Hartree–Fock level, leading to low double-substitution configurations ($\sigma^2 - \pi^2$ for BH and $a_1^2 \rightarrow b_1^2$ for CH₂). This leads to slow convergence in the Møller–Plesset series, as recognized for BH some years ago by Laidig et al.³⁵ We also find poor results for MP5 but much improvement at the QCISD(T) and BD(T) levels. The full correction to QCISD(TQ) or BD(TQ) leads to accurate results in both cases.

For H₂O and CH₄ at the STO-3G level, better MP convergence is obtained, but the QCI- and BD-based results are again superior. There is very little residual error at the highest levels. However, these results may not have too much significance because of the small number of virtual orbitals with a minimal basis, giving a very limited description of the whole correlation energy.

The unsaturated triply bonded molecules N₂ and HCN show similar and interesting features. The fifth-order corrections are quite large and give MP5 energies that are substantial improvements over MP4. The QCISD(T) and BD(T) results here are only moderately good, but the remaining error is greatly reduced by the further correction to QCISD(TQ) or BD(TQ). This final correction is dominated by $\Delta E(QQ)$, representing effects of quadruples. The great importance of these quadruple terms is probably associated with the presence of several low-lying double substitutions ($\pi^2 - \pi^{*2}$) in triple bonds.

The CN unsaturated radical is known to be an example of extremely poor convergence in the Møller–Plesset series.³⁵ MP5

is only a slight improvement over MP4. However, QCISD(T) clears up most of the error. The additional correction to QCISD(TQ) causes the energy to move lower than FCI and slightly closer, although the residual absolute error is only slightly improved. Again, the quadruple contribution $\Delta E(QQ)$ dominates the correction.

The calculations of DZ water are interesting as they permit comparison with some other approximate coupled cluster methods, which have errors at fifth order. For the RHF calculations, MP5 is not much better than MP4, although detailed inspection of the components shows that the small value of E^5 arises from cancellation of larger components with opposite signs. The QCISD(T) and BD(T) results are improved and are close to both CCSDT-1 and full CCSDT. For the R_c and 1.5R_c cases, the further correction removes most of the remaining error, the $\Delta E(QQ)$ part again being the most important. At 2R_c, the RHF starting point is becoming poor, and the moderately satisfactory result arises from the cancellation of some large components.

The UHF-based water calculations at 1.5R_c and 2R_c behave rather differently. As previously noted by Laidig et al.,³⁵ the UMP4 and UMP5 results are quite poor, the improvement in going from fourth to fifth order being very modest. The breakdown of the fifth-order energy into components shows all parts becoming small and is not particularly illuminating. We have shown previously²¹ that the unrestricted version of quadratic configuration interaction, UQCISD(T), gives better agreement with FCI, but the errors are still significant. The further correction to UQCISD(TQ) removes most of the remaining error at 1.5R_c, but at 2R_c, the results remain unsatisfactory. It is clearly very difficult to achieve satisfactory convergence for this case of two partially broken bonds.

The BD-based methods behave rather differently when spin-unrestricted methods are used. As has been noted previously,²⁵ UBD wave function in a singlet system collapses back to the restricted RBD form over a wider range of geometries than for Hartree–Fock theory. At $R = 1.5R_c$, this is found to happen, so that the restricted and unrestricted results are identical. At 2R_c,

(35) Laidig, W. D.; Fitzgerald, G.; Bartlett, R. J. *Chem. Phys. Lett.* 1985, 113, 151.

however, RBD and UBD differ, the former giving superior results at the highest correction level.

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6. Appendix

As mentioned in the text, the evaluation of $E_{00}^5(II)$ can be simplified by using a series of intermediate arrays. Initially, it is convenient to define the intermediate products $y1$ - $y8$:

$$y1(b,e) = \sum_{ija} a_{ij}^{ab} a_{ij}^{ae} \quad (A.1)$$

$$y2(j,m) = \sum_{iab} a_{ij}^{ab} a_{im}^{ab} \quad (A.2)$$

$$y3(j,b,m,c) = \sum_{ia} a_{ij}^{ab} a_{im}^{ac} \quad (A.3)$$

$$y4(i,j,k,n) = \sum_{ab} a_{ij}^{ab} a_{kn}^{ab} \quad (A.4)$$

$$y5(a,b,c,f) = \sum_{ij} a_{ij}^{ab} a_{ij}^{cf} \quad (A.5)$$

$$y6(k,l,e,f) = \sum_{cd} a_{kl}^{cd} (cd||ef) \quad (A.6)$$

$$y7(c,d,m,n) = \sum_{kl} a_{kl}^{cd} (mn||kl) \quad (A.7)$$

$$y8(k,e,m,e) = \sum_{id} a_{kl}^{de} (md||le) \quad (A.8)$$

Note that many of these arrays are already available during the course of the evaluation of the lower order energies.

These arrays can then be used to define further intermediate arrays $y9$ - $y14$:

$$y9(k,l,e,f) = -\frac{1}{8} \sum_b y1(b,e) a_{kl}^{bf} + \frac{1}{4} \sum_{jb} y3(j,b,k,e) a_{ij}^{bf} \quad (A.9)$$

$$y10(b,d,e,f) = \frac{1}{8} y1(b,e) y1(d,f) + \frac{1}{8} \sum_{ac} y5(a,b,c,f) y5(c,d,a,e) - \frac{1}{2} \sum_{jk} y3(j,b,k,e) y3(k,d,j,f) \quad (A.10)$$

$$y11(c,d,m,n) = -\frac{1}{8} \sum_j y2(j,m) a_{jn}^{cd} + \frac{1}{4} \sum_{jb} y3(j,b,m,c) a_{jn}^{bd} \quad (A.11)$$

$$y12(m,n,j,l) = \frac{1}{8} y2(j,m) y2(l,n) + \frac{1}{8} \sum_{ik} y4(i,j,k,n) y4(k,l,i,m) - \frac{1}{2} \sum_{bc} y3(j,b,m,c) y3(l,c,n,b) \quad (A.12)$$

$$y13(k,c,m,e) = \sum_{ja} y3(j,a,m,c) a_{jk}^{ce} - \frac{1}{2} \sum_j y2(j,m) a_{jk}^{ce} - \frac{1}{2} \sum_b y1(b,e) a_{km}^{bc} - \frac{1}{4} \sum_{ij} y4(i,j,k,m) a_{ij}^{ce} \quad (A.13)$$

$$y14(m,b,l,e) = \frac{1}{2} \sum_{ik} y3(i,b,k,e) y4(k,l,i,m) - \sum_{jc} y3(j,b,m,c) y3(l,c,j,e) - \frac{1}{4} y1(b,e) y2(l,m) + \frac{1}{2} \sum_{ad} y5(a,b,d,e) y3(l,d,m,a) \quad (A.14)$$

Finally, $E_{00}^5(II)$ can be evaluated by using these intermediate arrays:

$$E_{00}^5(II) = \sum_{kl} y9(k,l,e,f) y6(k,l,e,f) + \sum_{bdef} y10(b,d,e,f) (bd||ef) + \sum_{mncd} y11(c,d,m,n) y7(c,d,m,n) + \sum_{mnlj} y12(m,n,j,l) (mn||jl) + \sum_{kmce} y13(k,c,m,e) y8(k,c,m,e) + \sum_{imbe} y14(m,b,l,e) (mb||le) \quad (A.15)$$

Note that computationally the most demanding step is the evaluation of the array $y10$, which requires $\mathcal{O}(N^6)$ steps. All other intermediates require $\mathcal{O}(n^2 N^4)$ steps or less.

Ab Initio Prediction of the Geometry, Vibration Properties, Polarizabilities, and First Hyperpolarizabilities of Phosphaethyne[†]

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Results of ab initio calculations are presented, using the GAUSSIAN86 code, on the geometry, harmonic vibration frequencies, vibration intensities, the dipole moment, the dipole polarizability tensors, and the first hyperpolarizability tensors for phosphaethyne. It is shown that if a large enough basis set is used, satisfactory results are obtained for the geometry and frequencies by including electron correlation at the MP2 level. However, with a double- ζ quality (DZ2P) basis better results for the geometry and frequencies are obtained by using the CCD or CISD methods. Multiple sets of polarization functions are shown to be necessary to get accurate values of the dipole moment and the polarizabilities. In particular, it is shown that whereas two carefully chosen sets of D polarization functions can give reasonable results for the dipole polarizability tensors, this is not the case for the first hyperpolarizability tensors. The latter require a set of more than four sets of diffuse D functions before stable results are obtained.

Introduction

During the past three decades a number of very sophisticated but "user friendly" computer programs have been developed which enable the nonspecialist to perform ab initio calculations on chemically interesting systems. Among the most successful and most easily available programs in this respect have been the

GAUSSIAN set of programs developed by J. A. Pople and collaborators.¹ In applying such programs to large systems, it is necessary to strike a balance between the need to get reliable and meaningful results on the one hand and computational resources

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(1) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. *Gaussian86* (IBM 3090 version); Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.