

## CHAPTER 16

### COUPLED-CLUSTER THEORY: AN OVERVIEW OF RECENT DEVELOPMENTS

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## 1. Introduction

The intent of this chapter is to present an overview of coupled-cluster (CC) theory,<sup>1-5</sup> which is a highly reliable, correlated method that offers a unified, numerically accurate approach to most of the problems that are addressed by modern day quantum chemical methods. These include molecular structures, vibrational, electronic and photoelectron spectra, and other kinds of molecular properties. In each case, methods have recently been developed to make such studies possible, or easier, and the essential equations will be developed as compactly as possible. Most of the methods presented have been implemented into the ACES II program system,<sup>6</sup> and results obtained with that program will be used to illustrate the accuracy that can be expected.<sup>5</sup>

## 2. Basic Considerations in Coupled-Cluster Theory

The fundamental idea of CC theory is the exponential wave function ansatz,

$$\Psi_{CC} = \exp(T)\Phi_0, \quad (1)$$

where, initially,  $\Phi_0$  is considered to be an independent particle reference, such as the Hartree-Fock, and  $T$  creates excitations from it. Nothing in CC theory is limited to a Hartree-Fock choice, and we will discuss the use of several non-Hartree-Fock references in this article. When a multi-reference method is of interest,  $\Phi_0$  will be replaced by a linear combination of determinants.

In the single-reference case, the operator,

$$T = \sum_p T_p, \quad (2)$$

$$T_1 = \sum_{i,a} t_i^a a^\dagger i,$$

$$T_2 = \frac{1}{(2!)^2} \sum_{\substack{i,j \\ a,b}} t_{ij}^{ab} a^\dagger i b^\dagger j,$$

$$\vdots$$

$$T_p = \frac{1}{(p!)^2} \sum_{\substack{i,j,k,\dots \\ a,b,c,\dots}} t_{ijk\dots}^{abc\dots} a^\dagger i b^\dagger j c^\dagger k \dots, \quad (3)$$

where the creation–annihilation operators for orbitals occupied in  $\Phi_0$  (holes) are  $i^\dagger, j^\dagger, k^\dagger, l^\dagger, \dots$  and  $i, j, k, l, \dots$  and for unoccupied orbitals (particles)  $a^\dagger, b^\dagger, c^\dagger, d^\dagger, \dots$  and  $a, b, c, d, \dots$ . The labels  $p, q, r, s$  will represent either holes or particles. Hence,

$$\begin{aligned} T_1 \Phi_0 &= \sum_{i,a} t_i^a \Phi_i^a, \\ T_2 \Phi_0 &= \frac{1}{4} \sum_{\substack{i,j \\ a,b}} t_{ij}^{ab} \Phi_{ij}^{ab} = \sum_{\substack{i>j \\ a>b}} t_{ij}^{ab} \Phi_{ij}^{ab}, \\ &\vdots \end{aligned}$$

where  $\Phi_i^a, \dots$  are single,  $\Phi_{ij}^{ab}, \dots$  double excitations from  $\Phi_0$ . Consequently, restricting  $T$  to just  $T_2$ , we have the coupled-cluster doubles (CCD) wave function<sup>1,7,8</sup> (originally termed coupled-pair many-electron theory<sup>1</sup> (CPMET))

$$\begin{aligned} \exp(T_2) \Phi_0 &= (1 + T_2 + T_2^2/2 + \dots) \Phi_0 \\ &= \Phi_0 + \frac{1}{4} \sum_{\substack{i,j \\ a,b}} t_{ij}^{ab} \Phi_{ij}^{ab} + \frac{1}{32} \sum_{\substack{i,j,k,l \\ a,b,c,d}} t_{ij}^{ab} t_{kl}^{cd} \Phi_{ijkl}^{abcd} + \dots \quad (4) \end{aligned}$$

CCD already introduces quadruple, hextuple, and higher excitations into the wave function, but has the same number of distinct coefficients  $\{t_{ij}^{ab}\}$  (i.e., amplitudes of the  $T_2$  operator) to determine as there are double excitations. This, of course, is the power of CC theory, as such disconnected terms are often the numerically dominant contributors, as is the case with quadruple excitations (discussed further below).  $T_2$  itself is said to be “connected,” which means it is not further decomposable into a product of single excitations. The wave function in Eq. (4) only truncates when the number of excitations exceeds  $n$ , the number of electrons. As we will see later, the equations for the amplitudes,  $t_{ij}^{ab}$ , are in closed form without imposing any truncation, however.

Clearly, if we include  $T_1$  and  $T_2$  which defines CCSD,<sup>9</sup>

$$\begin{aligned} \Psi_{\text{CCSD}} &= \exp(T_1 + T_2) \Phi_0 \\ &= (1 + T_1 + T_2 + T_2^2/2 + T_1^2/2 + T_1 T_2 + T_1^2 T_2/2 + \dots) \Phi_0 \\ &= \Psi_{\text{CCD}} + (T_1 + T_1^2/2 + T_1 T_2 + T_1^2 T_2/2 + \dots) \Phi_0, \quad (5) \end{aligned}$$

the wave function now includes disconnected triple excitations,  $T_1T_2\Phi_0$ , and additional disconnected quadruple excitations,  $T_1^2T_2/2$ , and many other higher excitations. To include "connected" triple excitations,  $T_3$ , we consider the CCSDT<sup>10-12</sup> wave function

$$\Psi_{\text{CCSDT}} = \exp(T_1 + T_2 + T_3)\Phi_0 = \Psi_{\text{CCSD}} + (T_3 + T_1T_3 + T_2T_3 + T_3^2/2 + \dots)\Phi_0. \quad (6)$$

If we continue up to  $T_n$ , where  $n$  is the number of electrons, we have the exact or full CI solution,

$$\Psi_{\text{FCI}} = (1 + C)\Phi_0 = (1 + C_1 + C_2 + C_3 + C_4 + \dots C_n)\Phi_0, \quad (7)$$

where the CI operators,  $C_p$ , are

$$\begin{aligned} C_1 &= T_1, \\ C_2 &= T_2 + T_1^2/2, \\ C_3 &= T_3 + T_1T_2 + T_1^3/3!, \\ C_4 &= T_4 + T_2^2/2 + T_1^2T_2/2 + T_1T_3 + T_1^4/4! \\ &\vdots \end{aligned} \quad (8)$$

As the ultimate objective of any *ab initio* calculation in a basis set is the full CI, at a given truncation of the respective operators,  $C$  and  $T$ , we might expect CC theory to more rapidly converge to the full CI, due to its much greater inclusion of higher excitations.

The same feature manifests itself in another way, as (size)-extensivity.<sup>7</sup> That means that the wave function (and energy) *scale properly with the number of electrons*.<sup>7</sup> This is characteristic of *many-body* (i.e., many-electron) methods. It is usually illustrated by the asymptotic example of  $N$  non-interacting  $\text{H}_2$  molecules. For such a situation, and assuming localized orbitals, the correct wave function for the supermolecule is  $\Psi(N\text{H}_2) = [\psi(\text{H}_2)]^N$ , with energy  $E(N\text{H}_2) = NE(\text{H}_2)$ . Describing each  $\text{H}_2$  with natural (or Brueckner) orbitals to avoid single excitations, for one  $\text{H}_2$ ,  $\psi(\text{H}_2) = (1 + C_2)\phi_0(\text{H}_2) = \exp(T_2)\phi_0(\text{H}_2)$ , and it then follows immediately that for  $N$  with  $\Psi_0(N\text{H}_2) = \phi_0(1)\phi_0(2) \cdots \phi_0(N)$

$$\begin{aligned} \Psi_{\text{CC}}(N\text{H}_2) &= \exp[T_2(1) + T_2(2) + \cdots + T_2(N)]\Psi_0(N\text{H}_2) \\ &= [\exp(T_2)\phi_0(\text{H}_2)]^N \end{aligned}$$

by properties of the exponential. To the contrary, even though each  $H_2$  molecule is correctly described by CID, the CID *supermolecule wave function* is limited to only double excitations, missing the products of doubles that are in the exact wave function,  $[(1 + C_2)\phi(H_2)]^N$ . The latter would arise as quadruples, hextuples, etc., up to  $2N$ -tuple excitations in the CI description. Thus any CI truncation introduces an extensivity error that can have critical numerical consequences. (Size)-inextensivity in CI arises from the retention of what are called *unlinked diagrams*. These terms, which are not in the correct wave function, are quadratic or higher in  $N$ . This erroneous behavior with  $N$  prohibits any truncated CI method from being able to treat the correlation problem in extended systems. Even for small molecules, higher excitations are frequently numerically significant, and the dominant quadruple excitations arising from  $T_2^2$  are introduced, explicitly, even in the simplest CCD method. Furthermore, *implicitly* all “unlinked diagrams” have been eliminated via simply choosing to use the exponential wave function ansatz, Eq. (1). In other words, Eq. (1), with  $T_p$  defined as “connected,” is a succinct statement of the linked diagram theorem that we can use independently of any diagram considerations.

One last point. Because of the pedagogical non-interacting  $H_2$  example above, it is often thought that correct behavior in the non-interacting case is the definition of extensivity. This is not the case. The non-interacting limit is a necessary but not sufficient condition that a method be extensive. Our definition of extensivity *means the absence of unlinked diagrams*. This still guarantees extensivity even in the interacting case, and using an exponential wave function ansatz guarantees that property, provided that  $T$  itself is separable. Furthermore, the use of an exponential wave function ansatz guarantees correct scaling with the number of electrons for an electron gas, which, like the non-interacting  $N(H_2)$  example, is another limiting case that is often used as a reference for a metal or other extended system. The extensivity property is clearly essential if we are to attempt to describe correlation in extended systems, since *any* truncated CI description will, in the limit of an infinite system, recover *no* correlation energy per unit.

The objective of a CC calculation is to determine the amplitudes,  $t_i^a$ ,  $t_{ij}^{ab}$ , etc. We can accomplish this by inserting the CC wave function into the Schrödinger equation with the usual one- and two-particle electronic Hamiltonian and projecting. With the definitions,

$$H_N = H - \langle \Phi_0 | H | \Phi_0 \rangle,$$

$$E = \langle \Phi_0 | H | \Phi_0 \rangle + \Delta E, \quad (9)$$

we have

$$(H_N - \Delta E)\Psi = (H_N - \Delta E)\exp(T)\Phi_0 = 0. \quad (10)$$

Introducing the two projectors,  $P$  and  $Q$ , where  $P + Q = 1$ ,  $PQ = QP = 0$ , we have the realization,

$$P = |\Phi_0\rangle \langle \Phi_0|,$$

$$Q = |\mathbf{h}\rangle \langle \mathbf{h}| \mathbf{h}^{-1} \langle \mathbf{h}| = |\mathbf{h}\rangle \langle \mathbf{h}| = |\mathbf{h}_1\rangle \langle \mathbf{h}_1| + |\mathbf{h}_2\rangle \langle \mathbf{h}_2| + \dots, \quad (11)$$

$$Q = Q_1 + Q_2 + Q_3 + \dots,$$

where  $\mathbf{h}$  represents the manifold of all orthonormal excitations to  $\Phi_0$  with  $\mathbf{h}_1$  the singles  $\{\Phi_i^a\}$ ,  $\mathbf{h}_2$  the doubles  $\{\Phi_{ij}^{ab}\}$ , etc. Then we have the CC equations

$$\Delta EP = PH_N \exp(T)P, \quad (12a)$$

$$QH_N \exp(T)P = \Delta EQ \exp(T)P. \quad (12b)$$

We also have alternative forms where we premultiply Eq. (10) by  $\exp(-T)$  before projection,

$$\Delta EP = P\bar{H}_N P, \quad (13a)$$

$$Q\bar{H}_N P = 0. \quad (13b)$$

The quantity

$$\bar{H}_N = \exp(-T)H_N \exp(T) \quad (14)$$

is a similarity-transformed Hamiltonian. As such, it must have the same eigenvalues as the original Hamiltonian, while the wave function must be related by the inverse transformation. That is, for any eigenstate  $k$ ,

$$H_N \Psi_k = \Delta E_k \Psi_k,$$

we can insert the identity and left-multiply by  $e^{-T}$  to give,

$$\exp(-T)H_N \exp(T) \exp(-T)\Psi_k = \Delta E_k \exp(-T)\Psi_k ,$$

$$\bar{H}_N \bar{\Psi}_k = \Delta E_k \bar{\Psi}_k .$$

By virtue of the similarity transformation, we have decoupled  $\bar{H}_N = (P + Q)\bar{H}_N(P + Q) = P\bar{H}_NP + Q\bar{H}_NQ + P\bar{H}_NQ + Q\bar{H}_NP$  to  $\bar{H}_N$  by making  $Q\bar{H}_NP = 0$ . This is an example of a Van Vleck or contact type transformation.

An attractive feature of  $\bar{H}_N$  is that it may be represented in the well-known commutator expansion,

$$\begin{aligned} \bar{H}_N = H_N + [H_N, T] + \frac{1}{2} [[H_N, T]T] + \frac{1}{3!} [[[H_N, T]T]T] \\ + \frac{1}{4!} [[[[H_N, T]T]T]T] . \end{aligned} \quad (15)$$

Note,  $\bar{H}_N$  terminates after four-fold commutators because  $H_N$  contains only one- and two- particle operators. Since at least one operator in each  $T$  has to be contracted with one of the four creation–annihilation operators in the two-particle part of  $H_N$ , there can be only four  $T$ 's. Also, the commutator expansion means all terms in the second quantized form of  $H_N$  (see later) and  $T$  are *connected* by common indices, since otherwise they would vanish. So we often simply speak of  $\bar{H}_N = (H_N \exp(T))_C$  where the  $C$  indicates “connected.” This feature ensures the maximum cancellation in  $\bar{H}_N$  and, particularly, facilitates the derivation of the CC equations. This operator will play a central role in this paper for properties, excited states, multi-reference applications, and for computational factorization of the CC equations.

The first form of the CC equations in Eq. (12) can be used to transparently further emphasize the distinction between CC and CI. In terms of the CI coefficients in Eq. (8), we can write the CCSDT equations as,

$$Q_1 H_N (1 + C_1 + C_2 + C_3) P = \Delta E Q_1 C_1 P , \quad (16a)$$

$$Q_2 H_N (1 + C_1 + C_2 + C_3 + C'_4) P = \Delta E Q_1 C_2 P , \quad (16b)$$

$$Q_3 H_N (1 + C_1 + C_2 + C_3 + C'_4 + C''_5) P = \Delta E Q_3 C_3 P , \quad (16c)$$

where  $C'_4 = C_4 - T_4$  and  $C''_5 = C_5 - T_5 - T_1 T_4$ . We refer to Eq. (16a)–(16c) as the  $T_1$ ,  $T_2$  and  $T_3$  equations, respectively. Since  $H_N$  has no more than two-particle operators, the various contributions can differ by only two excitations from the target. The energy is

$$\Delta EP = PH_N Q_2 C_2 P + PH_N Q_1 C_1 P. \quad (17)$$

The CISDT equations and energy are exactly the same except for the role of  $C'_4$  and  $C''_5$ . The latter terms, which would arise in a CI only if quadruple and pentuple excitations were included, are responsible for important higher excitation effects and extensivity.

Another aspect of extensivity is that, unlike CI, the equations for the coefficients must be energy-independent. Whereas CI methods lead to eigenvalue equations, the CC equations are algebraic. This is immediately apparent from the second form (Eq. (13b)) of the CC equations, since  $\Delta E$  is already eliminated. In this form, we have for CCSDT,

$$0 = Q_1 \bar{H}_N P = Q_1 [H_N(1 + C_1 + C_2 + C_3)]_C P, \quad (18a)$$

$$0 = Q_2 \bar{H}_N P = Q_2 [H_N(1 + C_1 + C_2 + C_3 + C'_4)]_C P, \quad (18b)$$

$$0 = Q_3 \bar{H}_N P = Q_3 [H_N(C_2 + C_3 + C'_4 + C''_5)]_C P. \quad (18c)$$

From another viewpoint, some contributions arising from  $C'_4$  and  $C''_5$  in Eq (16) will exactly cancel the  $\Delta E$  dependent terms.

Although it might not yet be clear without some consideration of diagrammatics, the exclusion to “connected” further eliminates terms that might appear to be present, like  $C_1$  in the  $T_3$  equation. Similarly, terms like  $T_1^5$ , which is formally in  $C''_5$ , cannot be present because  $\bar{H}_N$  is limited to, at most, a product of four  $T$ ’s. Certain other contributions will fail to be connected, further simplifying the equations.

To obtain CCSDTQ,<sup>13</sup>  $\Psi_{\text{CCSDTQ}} = \exp(T_1 + T_2 + T_3 + T_4)\Phi_0$ , we would add the  $T_4$  equation

$$0 = Q_4 \bar{H}_N P = Q_4 [H_N(C_3 + C_4 + C'_5 + C''_6)]_C P, \quad (18d)$$

where  $C'_5 = C''_5 + T_1 T_4$  and  $C''_6 = C_6 - T_6 - T_1 T_5$ . We have to also replace  $C'_4$  by  $C_4$  in Eq. (18b) and (18c).



For CCSD,  $\Psi_{\text{CCSD}} = \exp(T_1 + T_2)\Phi_0$  and the equations are

$$0 = Q_1 \bar{H}_N P = Q_1 [H_N(1 + C_1 + C_2 + C'_3)]_C P, \quad (19a)$$

$$0 = Q_2 \bar{H}_N P = Q_2 [H_N(1 + C_1 + C_2 + C'_3 + C''_4)]_C P, \quad (19b)$$

where  $C'_3 = C_3 - T_3$  and  $C''_4 = C_4 - T_4 - T_1 T_3$ , while finally, CCD is simply

$$0 = Q_2 \bar{H}_N P = Q_2 [H_N(1 + T_2 + T_2^2/2)]_C P. \quad (20)$$

In all cases, the energy expression is the same as in Eq. (17), but for CCD,  $C_2 = T_2$  and the  $C_1 = T_1$  term is not present. Note that although we set  $T_3 = T_4 = \dots = 0$  for CCSD, the higher excitation expressions in CC theory are not zero for some truncation of  $T$ . That is, for the CCSD equations,  $Q_3 [H_N \exp(T_1 + T_2)]_C P \neq 0$ . Similarly, in CCD,  $T_1 \neq 0$ . If  $T_1$  is required to vanish, which can be accomplished by an orbital transformation to Brueckner orbitals, we obtain the Brueckner,  $B$ , or maximum overlap, i.e.,  $|\langle B|\Psi \rangle|^2 = \max$ , reference function which defines B-CCD.<sup>14</sup>

To numerically compare CC theory with CI and many-body perturbation theory (MBPT), consider Table 1. As the full CI (FCI) is the ultimate result in a given basis set, we can partly assess the comparative quality of different correlated methods by comparing with the limited number of full CI results available for molecules.<sup>15-17</sup> These are available for BH, FH and H<sub>2</sub>O at the equilibrium bond length,  $R_e$ , and with bonds stretched to 1.5  $R_e$  and 2.0  $R_e$  in a double zeta plus polarization ( $4s2p1d/2s1p$ ) basis. As is well known, the RHF reference function separates incorrectly when going to open-shell fragments, so as bonds are stretched it offers a particularly poor approximation to the correct answer. Since the FCI is the best possible answer, this behavior has no effect on those results, but for a truncated CI, MBPT, or CC calculation, a poor reference places extreme demands on the method. The ability of a correlated method to overcome such a poor reference is a testament to its accuracy and applicability. The errors in the energy relative to FCI for various truncated CI and CC methods are shown in Table 1. The correlation energy in these examples ranges from 102 to 370 mh, with an average of 213.

We can make a few observations. For CI, the variational condition guarantees that the error is above the exact result. Because of incorrect

**Table 1.** Differences between FCI energies and truncated CI, many-body perturbation theory, and coupled-cluster methods (DZP basis sets; millihartrees).

	BH		FH			H <sub>2</sub> O			Mean abs. err.	
	R <sub>e</sub>	1.5 R <sub>e</sub>	2.0 R <sub>e</sub>	R <sub>e</sub>	1.5 R <sub>e</sub>	2.0 R <sub>e</sub>	R <sub>e</sub>	1.5 R <sub>e</sub>		2.0 R <sub>e</sub>
Configuration Interaction										
CID	6.02	9.63	20.8	10.3	18.6	35.5	13.7	34.5	84.8	25.9
CISD	5.21	7.51	14.5	9.38	14.9	27.6	12.9	30.4	75.6	22.0
CISDT	3.60	5.19	10.1	7.01	11.1	19.2	10.6	23.5	60.3	16.7
CISDTQ	0.03	0.06	0.16	0.28	0.49	0.92	0.40	1.55	6.29	1.13
MBPT										
MBPT(2)	28.6	36.1	52.8	7.80	10.6	24.0	13.0	23.3	53.7	27.8
MBPT(3)	11.1	15.7	27.1	5.44	11.9	27.0	7.22	26.4	74.6	22.9
SDQ-MBPT(4)	5.69	8.20	15.0	2.75	5.39	12.5	4.40	13.3	34.2	11.3
MBPT(4)	5.06	7.23	13.3	-0.26	0.77	4.84	0.92	5.76	14.9	5.89
MBPT(5)	2.53	3.31	6.07	0.81	2.29	8.10	0.70	4.98	17.0	5.09
MBPT(6)	1.31	1.45	2.20	-0.23	-0.41	-1.13	0.08	1.82	4.06	1.41
Coupled-Cluster										
CCD	2.72	5.00	12.8	3.76	8.13	21.9	5.01	15.9	40.2	12.8
CCSD	1.79	2.64	5.05	3.01	5.10	10.2	4.12	10.2	21.4	7.06
CCSD(T)	0.41	0.55	0.41	0.40	0.88	-0.26	0.72	2.09	4.63	1.15
CCSDT-1	0.46	0.61	0.74	0.17	0.49	0.22	0.60	1.99	-2.65	0.88
CCSDT	0.07	0.03	-0.09	0.27	0.65	1.13	0.53	1.78	-2.47	0.78
CC5SD[TQ*]	0.05	0.01	-0.59	0.33	0.56	-0.18	0.19	0.13	-1.96	0.44
CC5SDT[Q]	0.04	0.05	0.10	0.06	0.11	0.30	0.05	-0.02	-0.75	0.17
CCSDTQ-1	0.04	0.04	0.07	0.06	0.11	0.35	0.05	-0.03	-1.58	0.26
CCSDTQ	0.00	0.00	+0.00	0.02	0.04	0.06	0.02	0.14	-0.02	0.03

separation of the RHF reference, the errors are greatest at twice the equilibrium  $R_e$ . Comparing the different CI truncations, we see that on average single excitations account for  $\sim 4$  mhartrees; triples for  $\sim 5$  mhartrees; and quadruples for a large  $\sim 15$  mhartrees. The vast improvement of CISDTQ compared to CISDT emphasizes the numerical importance of quadruple excitations in CI. Very accurate methods should include these effects, and CC methods regain most of the quadruple excitation effects very conveniently, because of the “disconnected”  $T_2^2/2$  term that is even in CCD. Since  $T_2^n/n!$  is implicitly in the CCD wave function, the method also benefits from the principal (disconnected) components of hextuple, octuple, etc. excitations.

Allowing for the fact that, unlike CI, CC methods are not variational, we can compare the various CC results with full CI in Table 1. The importance of the “disconnected” quadruple excitations included via CCD is obvious compared to CID. Instead of a mean error of 25.9 mhartrees, the error is 12.8 mhartrees, accounting for most of the  $\sim 15$  mhartrees numerical effect of the quadruple excitations in CISDTQ discussed above. Whereas the average single excitation effect in CI of  $\sim 4$  mhartrees is reflected by the  $\sim 6$  mhartrees effect of singles in CCSD (plus  $T_1T_2$  and  $T_1^3/3!$  triples and  $T_1^2T_2/2$  and  $T_1^4/4!$  quadruples), the net mean error of 7.06 mhartrees is less than one-third of that in CISD. Since CISDT still does not benefit from quadruple excitations, CCSDT<sup>10</sup> reduces the 16.7-mhartree error to only 0.78. Once the quadruples are added, at least for these small molecules, CISDTQ provides a respectable error of 1.13 mhartrees, but CCSDTQ<sup>13</sup> reduces this by almost two orders of magnitude to 0.03 mhartrees. As should be abundantly clear from the theory, barring pathological examples, CC results have to be closer to the truth. However, as the sometimes negative differences from full CI show, CC results are not variational. A variational condition is generally inconsistent with extensivity until the full CI result is reached. We believe that the “extensivity” condition is more important than a variational bound on the total energy (there are seldom any bounds on energy differences) for molecular applications, and it is absolutely requisite for extended systems.

Without further simplification, CI and CC methods that completely include a given level of excitation have the same computational dependence. For CISD or CCSD, that is  $\sim N_{it}n^2N^4$  where  $N_{it}$  is the number of iterations,  $n$  the number of occupied orbitals, and  $N$  the number of excited orbitals. For CCSDT, the dependence becomes  $\sim N_{it}n^3N^5$  and for CCSDTQ,  $\sim N_{it}n^4N^6$ . Because of the role of disconnected terms like

( $T_2^2/2$ ), the  $n^4N^6$  iterative step required to introduce quadruples in CIS-DTQ (or CIDQ) is largely alleviated, as this term requires only an iterative  $n^2N^4$  step in CCD or CCSD. That is, all CI quadruple excitation effects through fourth-order perturbation theory (see Sec. 4) are introduced via ( $T_2^2/2$ ), at a savings of  $n^2N^2$ . "Connected"  $T_4$  makes its first contribution in fifth-order, and further computational simplifications are possible there, too (see Sec. 5), that still require only an  $N^6$  computational step to introduce fifth-order connected quadruples. Even in sixth-order, all  $T_4$  terms can be incorporated with an  $n^4N^5$  step,<sup>18</sup> but in CIDQ these simplifications are not possible.

The MBPT results are the finite order in  $V$  analogs of CC methods ( $V = H - H_0$  where  $H_0$  is the sum of Fock operators, i.e., the Møller-Plesset choice). Since MBPT( $n$ ) means  $n$ th order approximations to CC and, like CC, are based on the linked diagram theorem (see Sec. 4), they also provide extensive results. Recent papers<sup>19</sup> present MBPT(5) and MBPT(6) results.

CCD is correct through MBPT(3) for Hartree-Fock reference cases, while CCSD is correct through MBPT(3) for non-Hartree-Fock references (see Sec. 4). The fourth-order approximation to CCD is DQ-MBPT(4) and, for CCSD, SDQ-MBPT(4). CCSDT is correct through MBPT(4), while CCSDTQ is correct through MBPT(6). The large improvement of MBPT over CI is also due to the exclusion of the unlinked diagrams. CISDTQ is accurate through MBPT(5) while, just like in CCD, large improvements over CISD or CISDT occur once quadruple excitations are introduced. MBPT, on the other hand, is slowly convergent, as indicated by the comparatively poor MBPT(5) results compared to MBPT(4), although the next even order, MBPT(6), is much better. On the other hand, CC theory rapidly introduces important infinite-order corrections.

The next category of simplification in CC theory is illustrated in Table 1 by results for CCSDT-1,<sup>20</sup> CCSD(T),<sup>21-23</sup> CC5SD[TQ\*],<sup>22</sup> CC5SDT[Q]<sup>24</sup> and CCSDTQ-1.<sup>24</sup> Unlike quadruple excitations, the principal numerical effect of triple excitations comes from connected  $T_3$  terms. This requires an  $n^3N^5$  iterative step in CCSDT and limits the method's wide applicability. One way to simplify this is to restrict evaluation to certain lead terms in the CCSDT equations which occur in lowest-order perturbation theory. Such terms have a computational dependence of  $\sim n^3N^4$ , and can be introduced iteratively (CCSDT-1) or non-iteratively CCSD(T). The

former requires  $\sim n^3 N^4$  per iteration, while the latter requires an  $\sim N_{it} n^2 N^4$  CCSD calculation followed by a single  $n^3 N^4$  step. Both are seen to be numerically very accurate compared to full CI. CCSD(T), in particular, appears to be about the equal of CISDTQ, which is a saving of  $\sim n^2 N^2$  in the iterative step and  $N_{it} n N^2$  in the non-iterative step. CC5SD[TQ\*] [= CCSD + TQ\*(CCSD)]<sup>22</sup> provides a procedure, correct through fifth-order in triples and quadruples, that is iterative in SD. Its computational dependence is  $\sim (N_{it} n^2 N^4 + n^3 N^5 + 2n^3 N^4 + N^6)$ . CC5SDT[Q] means the method is accurate through fifth order and is iterative through S, D and T, and then non-iterative for the fifth-order quadruples. Like CCSDT-1, CCSDTQ-1 introduces the lowest order  $T_4$  contributions iteratively. The above, plus other variants, will be presented after discussing the relationship between CC theory and MBPT (Sec. 4), so that the order dependence is apparent.

### 3. Outline of Procedures for Derivation of Explicit Coupled-Cluster Equations

#### 3.1. Normal-Product Hamiltonian

Coupled-cluster equations of interest all depend upon the second-quantized Hamiltonian,

$$H = \sum_{p,q} h_{pq} p^\dagger q + \frac{1}{4} \sum_{p,q,r,s} \langle pq || rs \rangle p^\dagger q^\dagger sr, \quad (21)$$

where we have the usual relations  $[p^\dagger, q]_+ = \delta_{pq}$ ,  $[p^\dagger, q^\dagger]_+ = [p, q]_+ = 0$ . We prefer the normal-ordered form of Eq. (21).<sup>1</sup> The normal product  $\{ABC \dots\}$  is defined by using the anti-commutation relations to put all  $i^\dagger$  or  $a$  operators to the right in a product, keeping track of the sign due to the interchanges. Its virtue is that  $i^\dagger |o\rangle = a |o\rangle = 0$  and that the Fermi vacuum expectation value of any normal-product  $\langle o | \{ABC \dots\} | o \rangle = 0$ . The  $T$  operators in Eq. (3) are automatically in normal product form, since  $a^\dagger i = \{a^\dagger i\}$ , etc.

The difference between an ordinary operator product and its normal-order form is defined to be a contraction,

$$p^\dagger q = \{p^\dagger q\} + \overline{p^\dagger q}.$$

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where  $\{\varphi_j\}$  are the molecular spin orbitals. The fully contracted terms are  $\langle o|H|o\rangle$ , so via its subtraction they are eliminated. The Schrödinger equation now gives the “correlation” correction,  $\Delta E$ , via  $H_N\Psi = \Delta E\Psi$ .

The Fock effective potential arises from the single contraction in the two-particle part of  $H_N$ . Despite the use of the Fock operator, Eq. (22) is a completely general expression for the Hamiltonian, and has no special dependence on choosing Hartree–Fock orbitals as the MO set. To allow for other non-canonical and non-Hartree–Fock choices of reference, we will have need for separating the  $f_N$  part into diagonal ( $D$ ) and off-diagonal ( $f_{OO}$ ) parts;

$$f = -D + f_{OO} + f_{VV} + f_{OV}, \quad (24)$$

where

$$\begin{aligned} -D &= \sum_p f_{pp} \{p^\dagger p\}, \\ f_{OO} &= \sum_{i \neq j} f_{ij} (\{i^\dagger j\} + \{j^\dagger i\}), \\ f_{VV} &= \sum_{a \neq b} f_{ab} (\{a^\dagger b\} + \{b^\dagger a\}), \\ f_{OV} &= \sum_{i,a} f_{ia} (\{a^\dagger i\} + \{i^\dagger a\}). \end{aligned}$$

With the help of these definitions,

$$\begin{aligned} H_N &= -D + f_{OO} + f_{VV} + V = -D + f_{OD} + V \\ &= F_O + V, \end{aligned} \quad (25)$$

where

$$V = f_{OV} + W.$$

Now we are in a position to derive explicit integral and amplitude forms of the CC equations, Eqs. (18)–(20). The easiest way to do that is to employ the generalized Wick’s theorem for normal product operators.<sup>1</sup> Since  $\langle o|\{ABC\dots\}|o\rangle$  vanishes for any product that is not fully contracted, we

need only evaluate the fully contracted products,  $\langle o|\overline{\overline{\overline{ABC\dots}}}|o\rangle$ . Furthermore, for normal product operators all internal contractions have

already been incorporated. Hence, contractions are allowed only among *different* normal product operators.

### 3.2. Energy Equations

To take a simple example to illustrate the procedure, consider the energy expression, Eq. (17), written in connected form,

$$\Delta E = \langle o | [H_N(1 + T_1 + T_2 + T_3 + \cdots + T_1^2/2 + T_1 T_2 + \cdots)]_C | o \rangle.$$

$T_1$ ,  $T_2$  and  $T_1^2/2$  may contribute, while all others have to vanish, since  $H_N$  only has one- and two-particle operators. The identity gives the vanishing contribution,  $\langle o | H_N | o \rangle = 0$ . Hence,

$$\begin{aligned} \Delta E = & \left\langle o \left| \sum_{i,a} t_i^a \sum_{p,q} f_{pq} \{p^\dagger q\} \cdot \{a^\dagger i\} + \sum_{p,q} f_{pq} \{p^\dagger q\} \left( \frac{1}{4} \sum_{\substack{i,j \\ a,b}} t_{ij}^{ab} \{a^\dagger i b^\dagger j\} \right) \right| o \right\rangle \\ & + \left\langle o \left| \frac{1}{4} \sum_{p,q,r,s} \langle pq || rs \rangle \{p^\dagger q^\dagger sr\} \left[ \frac{1}{4} \sum_{\substack{i,j \\ a,b}} t_{ij}^{ab} \{a^\dagger i b^\dagger j\} + \frac{1}{2} \sum_{i,a} \sum_{j,b} t_i^a t_j^b \{a^\dagger i b^\dagger j\} \right] \right| o \right\rangle. \end{aligned}$$

The first term corresponds to  $\overbrace{\{p^\dagger q\}\{a^\dagger i\}} = \delta_{pi}\delta_{qa}$ . Since  $\overbrace{\{p^\dagger q\}\{a^\dagger i b^\dagger j\}}$  cannot contract completely, that term makes no contribution. For the third term, since  $\overbrace{\{a b^\dagger\}} = \delta_{ab}$  and  $\overbrace{\{i^\dagger j\}} = \delta_{ij}$  are the only non-vanishing terms, we have

$$\begin{array}{cc} \left[ \overbrace{\{p^\dagger q^\dagger sr\} \{a^\dagger i b^\dagger j\}} + \overbrace{\{p^\dagger q^\dagger sr\} \{a^\dagger i b^\dagger j\}} \right] & \\ (-) & (+) \\ \delta_{pi}\delta_{qj}\delta_{sa}\delta_{rb} & \delta_{pi}\delta_{qj}\delta_{sb}\delta_{ra} \\ \overbrace{\{p^\dagger q^\dagger sr\} \{a^\dagger i b^\dagger j\}} + \overbrace{\{p^\dagger q^\dagger sr\} \{a^\dagger i b^\dagger j\}} & \\ (+) & (-) \\ \delta_{pj}\delta_{qi}\delta_{sa}\delta_{rb} & \delta_{pj}\delta_{qi}\delta_{sb}\delta_{ra}, \end{array}$$



while the final term has the same four possible contractions, giving

$$\Delta E = \sum_{i,a} f_{ia} t_i^a + \frac{1}{4} \sum_{i,j,a,b} \langle ij || ab \rangle (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a). \quad (26)$$

The factor of four in the last term leaves  $\frac{1}{2} t_i^a t_j^b$ , which may be written in the antisymmetrized form as above. Nothing else contributes to the energy.

### 3.3. Amplitude Equations

To illustrate the amplitude equations, consider the simplest case of CCD. We have from  $Q(H_N \exp(T_2))_C P = 0$ ,

$$\langle \phi_{ij}^{ab} | [H_N(1 + T_2 + T_2^2/2)]_C | o \rangle = 0. \quad (27)$$

Note that the exponential operator was not truncated, the higher  $T_2$  products simply cannot contract with the double excitation  $\phi_{ij}^{ab}$  over  $H_N$  because they correspond to more than quadruple excitations.

To reduce to a Fermi vacuum expectation value of operators, we can write  $\langle \phi_{ij}^{ab} | = \langle o | \{i^\dagger a j^\dagger b\}$ . Then the terms to evaluate are

$$\begin{aligned} & \frac{1}{4} \sum_{\substack{p,q \\ r,s}} \langle pq || rs \rangle \langle o | \{i^\dagger a j^\dagger b\} \{p^\dagger q^\dagger sr\} | o \rangle, \\ & \frac{1}{4} \sum_{\substack{k,l \\ c,d}} \frac{1}{4} \sum_{p,q} f_{pq} \langle o | \{i^\dagger a j^\dagger b\} \{p^\dagger q\} \{c^\dagger k d^\dagger l\} | o \rangle, \\ & \frac{1}{4} \sum_{\substack{k,l \\ c,d}} \frac{1}{4} \sum_{\substack{p,q \\ r,s}} \langle pq || rs \rangle t_{kl}^{cd} \langle o | \{i^\dagger a j^\dagger b\} \{p^\dagger q^\dagger sr\} \{c^\dagger k d^\dagger l\} | o \rangle, \\ & \left(\frac{1}{2}\right) \frac{1}{4} \sum_{\substack{k,l \\ c,d}} \frac{1}{4} \sum_{\substack{m,n \\ e,f}} \frac{1}{4} \sum_{\substack{p,q \\ r,s}} \langle pq || rs \rangle t_{kl}^{cd} t_{mn}^{ef} \langle o | \{i^\dagger a j^\dagger b\} \{p^\dagger q^\dagger sr\} \{c^\dagger k d^\dagger l\} \{e^\dagger m f^\dagger n\} | o \rangle. \end{aligned}$$

Working out the possible contractions of the first term, we have four equivalent non-vanishing possibilities which remove the  $1/4$  from the summation, giving just the two-electron integral  $\langle ij || ab \rangle$ . To be fully contracted, the second term requires that one of the  $p^\dagger$  or  $q$  be contracted with the preceding and the other, the succeeding, operator. Working out the possibilities, we obtain

$$\sum_c (f_{bc} t_{ij}^{ac} + f_{ac} t_{ij}^{cb}) - \sum_k (f_{ik} t_{kj}^{ab} + f_{jk} t_{ik}^{ab}).$$

In the canonical SCF case, this term reduces to  $(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)t_{ij}^{ab}$ . Similarly, the other contractions can be laboriously determined to give the explicit CCD amplitude equations,

$$\begin{aligned} (f_{ii} + f_{jj} - f_{aa} - f_{bb})t_{ij}^{ab} = & \langle ij||ab \rangle + \sum_{c(\neq a,b)} (f_{bc}t_{ij}^{ac} + f_{ac}t_{ij}^{cb}) \\ & - \sum_{k(\neq i,j)} (f_{ik}t_{kj}^{ab} + f_{jk}t_{ik}^{ab}) + \frac{1}{2} \sum_{c,d} \langle ab||cd \rangle t_{ij}^{cd} + \frac{1}{2} \sum_{k,l} \langle kl||cd \rangle t_{kl}^{ab} \\ & + \sum_{c,k} (\langle ak||cj \rangle t_{ik}^{bc} - \langle bk||cj \rangle t_{ik}^{ac} - \langle ak||ci \rangle t_{jk}^{bc} + \langle bk||ci \rangle t_{jk}^{ac}) \\ & + \sum_{\substack{k,l \\ c,d}} \langle kl||cd \rangle \left[ t_{ik}^{ac}t_{lj}^{db} - t_{jk}^{ac}t_{li}^{db} - \frac{1}{2} (t_{ki}^{cd}t_{lj}^{ab} + t_{kj}^{cd}t_{li}^{ab}) \right. \\ & \left. - \frac{1}{2} (t_{kl}^{ca}t_{ij}^{db} + t_{kl}^{cb}t_{ij}^{da}) + \frac{1}{4} t_{ij}^{cd}t_{kl}^{ab} \right]. \end{aligned}$$

The antisymmetrizing permutation operators  $P(ij)$ ,  $P(ab)$  and  $P(ij/ab)$  ( $= P(ab)P(ij)$ ), of the general form  $\sum_P (-1)^p P$ , where  $p$  is the parity of the permutation, are now introduced.  $P(ij)$  means sum over permutations of  $i$  and  $j$  (including identity), and  $P(ab)$  is analogously defined. With these definitions, letting  $\sum$  mean sum over common indices, excluding diagonal  $f$  elements on the right-hand side, and letting  $(D_{ij}^{ab} = f_{ii} + f_{jj} - f_{aa} - f_{bb})$ , the CCD equations are,

$$\begin{aligned} D_{ij}^{ab}t_{ij}^{ab} = & \langle ij||ab \rangle + \sum P(ab)f_{bc}t_{ij}^{ac} - \sum P(ij)f_{jk}t_{ik}^{ab} \\ & + \frac{1}{2} \sum \langle ab||cd \rangle t_{ij}^{cd} + \frac{1}{2} \sum \langle ij||kl \rangle t_{kl}^{ab} + \sum P(ij/ab) \langle ak||cj \rangle t_{ik}^{bc} \\ & + \sum \langle kl||cd \rangle \left( P(ab)t_{ik}^{ac}t_{jl}^{bd} - \frac{1}{2} P(ij)t_{ki}^{cd}t_{lj}^{ab} - \frac{1}{2} P(ab)t_{kl}^{ca}t_{ij}^{db} + \frac{1}{4} t_{ij}^{cd}t_{kl}^{ab} \right). \end{aligned} \quad (28)$$

For facile derivation of the above formula, diagram techniques are far superior. Diagrams are simply expedient ways of working out contractions among second-quantized operators, i.e., they turn a complicated algebraic problem into an easier topological problem. In particular, diagram techniques recognize equivalent contractions so that it is not necessary to obtain the same quantity four times to eliminate a preceding factor of  $1/4$ , for example. Also, they recognize that the double excitation  $\langle \phi_{ij}^{ab} | = \langle o | \{ i^\dagger a j^\dagger b \}$  has a particular structure that, being common for all possible double excitations, need not be explicitly considered in deriving the amplitude formulae. A summary of our unambiguous, systematic procedure for generating CC diagrams is presented in Appendix A, while a more complete description with many examples is presented elsewhere.<sup>25</sup> This procedure easily generates every diagram, and each diagram appears only once.

One obvious way to solve the non-linear CC equations is iteratively. Setting  $t_{ij}^{ab(0)} = 0$ , we obtain  $t_{ij}^{ab(1)} = \langle ab || ij \rangle / D_{ij}^{ab}$  as the initial approximation to  $t_{ij}^{ab}$ . Inserting into the energy formula Eq. (26), we have  $\Delta E^{(2)} = \frac{1}{4} \sum_{ij,ab} |t_{ij}^{ab(1)}|^2 / D_{ij}^{ab}$ , which is the second order (MBPT(2)) approximation using the Møller–Plesset splitting of the Hamiltonian, Eq. (25), which for the canonical case becomes simply  $H_N = H_0 + V = -D + W$ . Inserting this value of  $t_{ij}^{ab(1)}$  into the terms in Eq. (28) that are linear in  $t_{ij}^{ab}$  provides the third order correction,  $\Delta E^{(3)}$ , and a new  $t_{ij}^{ab(2)}$  approximation to  $t_{ij}^{ab}$ . Once  $t_{ij}^{ab(1)}$  is inserted into the quadratic terms, the fourth-order quadruple excitation contribution,  $\Delta E_Q^{(4)}$  is obtained, along with a contribution to  $t_{ij}^{ab(3)}$ ; while inserting  $t_{ij}^{ab(2)}$  into the linear terms gives the double excitation  $\Delta E_D^{(4)}$  fourth-order contribution, and the double excitation part of  $t_{ij}^{ab(3)}$ . The resulting fourth-order model has frequently been called DQ-MBPT(4). Clearly, Eq. (28) accommodates non-canonical HF example cases like using localized HF orbitals by virtue of  $f_{bc} \neq 0$  and  $f_{ik} \neq 0$  either perturbatively or in infinite order. However, since CC theory is invariant to transformations among just-occupied or just-excited orbitals, there is no change in the CCD results. In finite-order perturbation theory, the same invariance property will apply provided that the splitting of the Hamiltonian into  $H_0$  and  $V$  is the same, which typically requires that certain terms be included to all orders. Hence, localized HF orbital  $\Delta E^{(2)}$  will give ex-

actly the same value as that obtained in the canonical case, except that all the terms that depend upon  $f_{bc}$  and  $f_{ik}$  have to be iterated to infinite order. Such an infinite-order iteration is comparatively simple, however, and will usually be offset by the sparseness of the Hamiltonian as manifested in the local orbital basis. Obviously, other categories of excitations like singles and triples can be accommodated by more general CC equations. See Sec. 4 for a more detailed discussion of Generalized Many-Body Perturbation Theory.

### 3.4. Factorized Equations

As the CC equations depend upon  $\bar{H}_N$  in Eq. (15), they can be further organized for computation by a quasi-linearization factorization.<sup>13</sup> That simply means, for example, that the quadratic,  $\frac{1}{2}\langle\phi_{ij}^{ab}|H_N T_2^2|o\rangle$ , term in CCD will be evaluated via  $\langle\phi_{ij}^{ab}|(H_N T_2)T_2|o\rangle$ , where the quantity  $H_N T_2 = \chi$ , linear in  $T_2$ , is an intermediate that could already be known from the evaluation of the linear term,  $\langle\phi_{ij}^{ab}|H_N T_2|o\rangle$ . All  $\chi$  intermediates are *linear* in  $T$  and the procedure is *recursive*. Given a set of  $t$  amplitudes, all  $\chi$ 's are known after forming the integral product. Then, updated  $t$  amplitudes are obtained from the equations in Table 2, which defines a new set of  $\chi$ 's. The CCSDTQ spin-orbital equations in fully factorized form are shown in Table 2, with the  $\chi$  intermediates in Table 3.

To obtain the CCD equations in factorized form, simply eliminate contributions from the single  $t_i^a$ , triple  $t_{ijk}^{abc}$  and quadruple  $t_{ijkl}^{abcd}$  amplitudes. To obtain CCSD, eliminate contributions from the triple and quadruple amplitudes, etc. We normally solve the resulting linear equation in  $T$  by using our Reduced Linear Equation (RLE) method,<sup>26</sup> a preconditioned conjugate gradient procedure, that provides a series of iterations  $T^{(1)}, T^{(2)}, T^{(3)}, \dots, T^{(p)}$ , etc. converging toward the final  $T$ . Then  $T = \sum_{\lambda=1}^p \lambda T^{(\lambda)}$  with  $\lambda$  determined by the RLE procedure or related ones to accelerate convergence. Because of the length of the vectors,  $T^{(p)}$ , we normally only employ vectors of the length of single and double excitations in the acceleration procedure, even when converging the CCSDT or CCSDTQ equations.

**Table 2.** Coupled-cluster equations for the CCSDTQ method in algebraic form, in terms of recursively generated intermediates.

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$$\begin{aligned}
D_i^a t_i^a &= f_i^a + \chi_e^a t_i^e - \chi_m^{ia} t_m^a + \chi_{em} t_{mi}^{ea} + \langle ma || ei \rangle t_m^e + \frac{1}{2} \langle ma || ef \rangle t_{mi}^{ef} \\
&\quad - \frac{1}{2} \langle mn || ei \rangle t_{mn}^{ea} + \langle mn || ef \rangle t_{nmi}^{efa} \\
D_{ij}^{ab} t_{ij}^{ab} &= \langle ab || ij \rangle + P(ab) \chi_e^b t_{ij}^{ae} - P(ij) \chi_m^j t_{im}^{ab} + \chi_{em} t_{mij}^{eab} + \frac{1}{2} \chi_{ef}^{ab} t_{ij}^{ef} \\
&\quad + \frac{1}{2} \chi_{mn}^{ij} t_{mn}^{ab} - P(ab) (ij) \chi_{me}^{ib} t_{mj}^{ae} + P(ij) \chi_e^{abj} t_i^e - P(ab) \chi_m^{ijb} t_m^a \\
&\quad + \frac{1}{2} P(ab) \chi_{fem}^a t_{mij}^{efb} - \frac{1}{2} P(ij) \chi_{nme}^i t_{mnj}^{eab} + \frac{1}{4} \langle mn || ef \rangle t_{mni}^{efab} \\
D_{ijk}^{abc} t_{ijk}^{abc} &= P(c/ab) \chi_e^c t_{ijk}^{abe} - P(k/ij) \chi_m^k t_{ijm}^{abc} + \chi_{me} t_{mijk}^{eabc} + \frac{1}{2} P(c/ab) \chi_{ef}^{ab} t_{ijk}^{efc} \\
&\quad + \frac{1}{2} P(k/ij) \chi_{mn}^{ij} t_{mnk}^{abc} - P(i/jk) (b/ac) \chi_{me}^{ib} t_{mj}^{aec} + P(k/ij) (a/bc) \chi_e^{bck} t_{ij}^{ae} \\
&\quad - P(abc/d) (ij/kl) \chi_m^{kld} t_{ijm}^{abc} + P(a/bcd) (ij/kl) \chi_e^{ibckdl} t_{ij}^{ae} - P(ab/cd) (i/jkl) \\
&\quad \times \chi_m^{ijckdl} t_{im}^{ab} - P(ab/cd) (ij/kl) \chi_{me}^{ikcd} t_{ijm}^{abe} + \frac{1}{2} P(abc/d) (i/jkl) \chi_{mn}^{ijkl} t_{imn}^{abc} \\
D_{ijkl}^{abcd} t_{ijkl}^{abcd} &= P(d/abc) \chi_e^d t_{ijkl}^{abce} - P(l/ijk) \chi_m^l t_{ijkm}^{abcd} + \frac{1}{2} P(ab/cd) \chi_{ef}^{ab} t_{ijkl}^{efcd} \\
&\quad + \frac{1}{2} P(ij/kl) \chi_{ij}^{mn} t_{mnkl}^{abcd} - P(i/jkl) (b/acd) \chi_{me}^{ib} t_{mjk}^{aecdl} + P(ab/cd) (ijk/l) \chi_e^{cdl} t_{ijk}^{abe} \\
&\quad - P(abc/d) (ij/kl) \chi_m^{kld} t_{ijm}^{abc} + P(a/bcd) (ij/kl) \chi_e^{ibckdl} t_{ij}^{ae} - P(ab/cd) (i/jkl) \\
&\quad \times \chi_m^{ijckdl} t_{im}^{ab} - P(ab/cd) (ij/kl) \chi_{me}^{ikcd} t_{ijm}^{abe} + \frac{1}{2} P(abc/d) (i/jkl) \chi_{mn}^{ijkl} t_{imn}^{abc}
\end{aligned}$$


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*Note:* Permutation symbols are the same as in Refs. 13 and 20.  $P(ab/cd)(ijk/l)$  means that in addition to the identity permutation, all possible products involving permutations of just  $a$  and  $b$ ;  $c$  and  $d$ , and  $ij$  and  $k$  are allowed. The sign of the permutation is included.  $\chi$  intermediates are defined in Table 3. Summation over repeated indices is understood.

**Table 3.** Algebraic expressions for the intermediates defined in Table 2.

$$\chi_{ia} = f_{ia} + \langle im||ae \rangle t_m^e \quad (1)$$

$$\chi_b^a = f_b^a + \langle am||be \rangle t_m^e - \chi_{mb} t_m^a - \frac{1}{2} \langle mn||eb \rangle t_{mn}^{ea} \quad (2)$$

$$\chi_i^j = \chi_i'^j + \chi_{ie} t_j^e \quad (3)$$

$$\chi_i'^j = f_i^j + \langle im||je \rangle t_m^e + \frac{1}{2} \langle mi||ef \rangle t_{mf}^e \quad (3a)$$

$$\chi_{bci}^a = \chi_{bci}'^a - \frac{1}{2} \langle mi||bc \rangle t_m^a \quad (4)$$

$$\chi_{bci}'^a = \langle ai||bc \rangle - \frac{1}{2} \langle mi||bc \rangle t_m^a \quad (4a)$$

$$\chi_{ija}^k = \chi_{ija}'^k + \frac{1}{2} \langle ij||ea \rangle t_k^e \quad (5)$$

$$\chi_{ija}'^k = \langle ij||ka \rangle + \frac{1}{2} \langle ij||ea \rangle t_k^e \quad (5a)$$

$$\chi_{cd}^{ab} = \chi_{cd}'^{ab} + \frac{1}{2} \langle mn||cd \rangle t_{mn}^{ab} \quad (6)$$

$$\chi_{cd}'^{ab} = \langle ab||cd \rangle - P(ab) \chi_{cdm}'^a t_m^b \quad (6a)$$

$$\chi_{ij}^{kl} = \langle ij||kl \rangle + P(kl) \chi_{ije}'^k t_l^e + \frac{1}{2} \langle ij||ef \rangle t_{kl}^{ef} \quad (7)$$

$$\chi_{ib}^{ja} = \chi_{ib}'^{ja} + \langle im||eb \rangle t_{jm}^a \quad (8)$$

$$\chi_{ib}'^{ja} = \chi_{ib}''^{ja} - \langle im||jb \rangle t_m^a + \chi_{bei}^a t_j^e \quad (8a)$$

$$\chi_{ib}''^{ja} = \langle ia||jb \rangle - \langle im||jb \rangle t_m^a + \chi_{bei}'^a t_j^e \quad (8b)$$

$$\begin{aligned} \chi_c^{abi} = & \chi_c'^{abi} + \langle ab||ce \rangle t_i^e - P(ab) \chi_{mc}^{ia} t_m^b - \chi_{mc} t_m^{ab} \\ & - P(ab) \chi_{fcm}^b t_{mi}^{af} + \frac{1}{2} \chi_{nmc}^i t_{mn}^{ab} - \frac{1}{2} \langle mn||ce \rangle t_{mn}^{aeb} \end{aligned} \quad (9)$$

$$\chi_c'^{abi} = \langle ab||ci \rangle + \frac{1}{2} \langle ab||ce \rangle t_i^e - P(ab) \chi_{mc}^{ia} t_m^b \quad (9a)$$

$$\chi_i^{jka} = \chi_i''^{jka} + \chi_{ie} t_{jk}^{ea} \quad (10)$$

$$\begin{aligned} \chi_i''^{jka} = & \chi_i'^{jka} - \frac{1}{2} \langle im||jk \rangle t_m^a + P(jk) \chi_{ie}^{ja} t_k^e \\ & + \frac{1}{2} \chi_{fei}^a t_{jk}^{ef} - P(jk) \chi_{mie}^k t_{jm}^{ea} + \frac{1}{2} \langle im||ef \rangle t_{jmk}^{efa} \end{aligned} \quad (10a)$$

Table 3. (Continued)

$$\chi_i^{tjka} = \langle ia || jk \rangle t_m^a \quad (10b)$$

$$\begin{aligned} \chi_d^{tabcj} = & \frac{1}{2} P(c/ab) \chi_{de}^{ab} t_{ij}^{ec} - \chi_{edm}^b P(b/ac) t_{mij}^{aec} \\ & + P(ij) \chi_{nmd}^i t_{mnj}^{abc} - \langle mn || de \rangle t_{mni}^{aebc} \end{aligned} \quad (11)$$

$$\begin{aligned} \chi_i^{tjakbl} = & -\frac{1}{2} P(l/jk) \chi_{im}^{jk} t_{ml}^{ab} + P(ab)(j/kl) \chi_{ie}^{ja} t_{kl}^{eb} \\ & + P(ab) \chi_{fei}^a t_{jkl}^{efb} - P(k/jl) \chi_{mie}^k t_{jml}^{eab} + \langle im || ef \rangle t_{jmk}^{efab} \end{aligned} \quad (12)$$

$$\chi_{ib}^{tjakc} = \langle im || be \rangle t_{mj}^{eac} \quad (13)$$

$$\chi_{ij}^{tklam} = \frac{1}{2} \langle ij || ef \rangle t_{klm}^{efa} \quad (14)$$

#### 4. Generalized Many-Body Perturbation Theory

The relationship of the above CC equations to MBPT can be recognized from the iterative form of Eq. (18). Consider the  $fT_n$  term in each  $T_n$  equation. As discussed above, its evaluation results in a diagonal and off-diagonal part,

$$\langle \phi_i^a | fT_1 | 0 \rangle = (f_{aa} - f_{ii}) t_i^a + \sum_{e(\neq a)} f_{ae} t_i^e - \sum_{m(\neq i)} f_{im} t_m^a, \quad (29a)$$

$$\begin{aligned} \langle \phi_{ij}^{ab} | fT_2 | 0 \rangle = & (f_{aa} + f_{bb} - f_{ii} - f_{jj}) t_{ij}^{ab} \\ & + \sum_{e(\neq a,b)} P(ab) f_{be} t_{ij}^{ae} - \sum_{m(\neq i,j)} P(ij) f_{jm} t_{im}^{ab}. \end{aligned} \quad (29b)$$

Similarly, the diagonal part of the  $T_3$  equation is  $(f_{aa} + f_{bb} + f_{cc} - f_{ii} - f_{jj} - f_{kk}) = -D_{ijk}^{abc}$  and the  $Q$  equation would have the corresponding difference,  $D_{ijkl}^{abcd}$ , of eight diagonal Fock matrix elements.

Moving the diagonal terms to the left side, indicating the appropriate denominator operator by category of excitation, and with all terms connected, the CCSDTQ equations may be written as

$$Q_2 D_2 T_2 P = Q_2 [W + f_{OD} T_2 + W(C_2 + C_1) + W(C_3 + C_4) + f_{OV} C_3]_C P, \quad (30a)$$

$$Q_1 D_1 T_1 P = Q_1 [f_{OV} + f_{OD} T_1 + W(C_2 + C_1) + W(C_3) + f_{OV} C_2]_C P, \quad (30b)$$

$$Q_3 D_3 T_3 P = Q_3 [f_{OD} T_3 + W T_2 + W(C_3 + C_4 + C'_5) + f_{OV} C_4]_C P, \quad (30c)$$

$$Q_4 D_4 T_4 P = Q_4 [f_{OD} T_4 + W T_3 + W(C_4 + C_5 + C''_6) + f_{OV} C'_5]_C P, \quad (30d)$$

which together with the energy expression, Eqs. (12a) and (13a), defines all approximations. The quantity  $(f_{OD} T_p)$  means the off-diagonal part of the  $f T_p$  term, which arises just from  $f_{OO}$  and  $f_{VV}$ . In the canonical SCF case,  $(f_{OD} T_p)$  vanishes, along with any other  $f_{OV}$  dependent terms. In non-canonical SCF, as occurs with localized SCF orbitals,  $(f_{OD} T_p)$  remains, but since  $f_{ia} = f_{ai} = 0$ , any terms that would derive from  $f_{OV}$  would disappear. For non-Hartree-Fock orbitals, as occur in what we call a quasi-restricted Hartree-Fock (QRHF) reference function,<sup>27</sup> or for our treatment for restricted open shell Hartree-Fock (ROHF) cases,<sup>23,27,28</sup> all off-diagonal  $f$  matrix elements in principle remain. However, we can exploit the fact that the CC equations are invariant to transformations that mix just-occupied or just-virtual orbitals to diagonalize the occ-occ and virt-virt block to only retain the diagonal  $f_{ii}$ ,  $f_{aa}$  and the off-diagonal  $f_{ia}$  matrix elements. The latter orbitals are termed semi-canonical<sup>29</sup> and are convenient for several purposes.

In the form of Eq. (30), and for any kind of SCF orbitals,  $T_2$  is first order in correlation,  $W$ ;  $T_1$  is second order, since the first non-vanishing contribution will be  $W T_2$ ; as is  $T_3$  from  $W T_2$ , while  $T_4$  is third order from  $W T_3 + W T_2^2/2$ . For cases where  $f_{OV}$  remains,  $T_1$  is first order in  $f$  and necessarily in  $V$ . Consequently, it is easy to ascribe order in  $W$ ,  $V$ , or separately to  $f$  and  $W$  as in double perturbation theory to all the terms in Eq. (30). In this manner all questions of what order MBPT terms are included in a given CC method become routine.

In the canonical SCF case, carrying out the iterations of Eq. (30) and then inserting the updated approximation to  $T_2$  and  $T_1$  into the energy expression, one can summarize the various MBPT approximations. In second order,

$$\begin{aligned} Q_2 D_2 T_2^{(1)} P &= Q_2 W P, \\ \Delta E^{(2)} P &= P W T_2^{(1)} P. \end{aligned} \quad (31a)$$



Third order,

$$\begin{aligned} Q_2 D_2 T_2^{(2)} P &= Q_2 W T_2^{(1)} P, \\ \Delta E^{(3)} P &= P W T_2^{(2)} P. \end{aligned} \quad (31b)$$

Fourth order follows from the sequence

$$\begin{aligned} Q_1 D_1 T_1^{(2)} P &= Q_1 W T_2^{(1)} P, \\ Q_3 D_3 T_3^{(2)} P &= Q_3 W T_2^{(1)} P, \\ Q_2 D_2 T_2^{(3)} P &= Q_2 \left[ W(T_2^{(2)} + T_1^{(2)} + T_3^{(2)}) + W T_2^{(1)} T_2^{(1)} / 2 \right]_C P, \\ \Delta E^{(4)} P &= P W T_2^{(3)} P, \end{aligned} \quad (31c)$$

and

$$\Delta E[MBPT(4)] = \Delta E^{(2)} + \Delta E^{(3)} + \Delta E^{(4)}.$$

Explicit integral and amplitude expressions for the formulae in Eq. (31) can be written down *immediately* with the aid of CC diagrams, but in this chapter we will restrict ourselves to the operator, algebraic form above. This has its advantages and will usually serve, until writing a program. Recognize, however, that the underlying dependence on the diagrams will make many conclusions transparent that might not be as clear without that understanding.

Another way to write  $\Delta E^{(4)}$  is via the  $2n$  rule of perturbation theory. In linked-diagram, many-body form this is simply,

$$\Delta E^{(4)} = \langle \Psi^{(2)} | E_0 - H_0 | \Psi^{(2)} \rangle_L = \langle \Psi^{(2)} | D | \Psi^{(2)} \rangle_L,$$

where L indicates the limitation to linked diagrams, and

$$|\Psi^{(2)}\rangle = \left( T_2^{(2)} + T_1^{(2)} + T_3^{(2)} + T_2^{(1)} T_2^{(1)} / 2 \right) |o\rangle.$$

(Unlike  $T_p^{(n)}$  which has to be connected,  $\Psi^{(n)}$  only has to be linked (note  $T_2^{(1)} T_2^{(1)}$  form)). In this way, it is not necessary to compute any part of the third-order wave function,  $T_2^{(3)}$ , to evaluate  $\Delta E^{(4)}$ . The quadratic formula also gives an immediate separation into  $\Delta E^{(4)} = \Delta E_D^{(4)} + \Delta E_S^{(4)} + \Delta E_T^{(4)} +$

$\Delta E_Q^{(4)}$ . The quadruple term  $1/4\langle o|T_2^{(1)\dagger}T_2^{(1)\dagger}DT_2^{(1)}T_2^{(1)}|o\rangle$  generates both linked and unlinked components. The latter, which is excluded from the linked expression, is equivalent to  $E^{(2)}\langle\Psi^{(1)}|\Psi^{(1)}\rangle$ , the negative of which is the familiar renormalization term from RSPT. Similarly, we can write

$$\Delta E^{(5)} = \langle\Psi^{(2)}|W|\Psi^{(2)}\rangle_L = \langle\Psi^{(2)}|D|\Psi^{(3)}\rangle_L$$

and

$$\Delta E^{(6)} = \langle\Psi^{(3)}|D|\Psi^{(3)}\rangle_L,$$

where

$$|\Psi^{(3)}\rangle = \left(T_4^{(3)} + T_2^{(3)} + T_1^{(3)} + T_2^{(2)}T_2^{(1)} + T_1^{(2)}T_2^{(1)} + T_3^{(2)}T_2^{(1)} + \left(T_2^{(1)}\right)^3/3!|o\right).$$

Notice that whereas  $\Delta E^{(5)}$  requires only CI excitations through quadruples, since the pentuple excitations  $T_3^{(2)}T_2^{(1)}$  and hextuple excitations  $(T_2^{(1)})^3$  give vanishing contributions,  $\Delta E^{(6)}$  has contributions from both terms. Table 1 shows the comparison of various orders of perturbation theory with full CI.

We can similarly derive a generalized perturbation theory for the *non-HF* case by including the appropriate  $f_{OD}$  and  $f_{OV}$  terms. An example of this type which is computationally important is ROHF-MBPT.<sup>30,31</sup> We mean by ROHF the determination of optimum SCF orbitals for an open-shell high-spin molecule such that orbitals have maximum double occupancy. Given this set of orbitals, we then construct the *spin-orbital*  $f_{pq}$  matrix elements according to Eq. (23). Unlike the ROHF Fock operators, the *spin-orbital*  $f_{pq}$  matrix is not diagonal in any block, so in that respect we are employing the full flexibility of a non-Hartree-Fock reference function. We can now develop a perturbation theory for orders in  $V = f_{OV} + W$ , with  $F_0 = -D + f_{OO} + f_{VV} = -D + f_{OD}$  being zeroth order.

In this case the equations become

$$\begin{aligned} Q_1 D_1 T_1^{(1)} P &= Q_1 \left[ f_{OV} + f_{OD} T_1^{(1)} \right] P, \\ Q_2 D_2 T_2^{(1)} P &= Q_2 \left[ W + f_{OD} T_2^{(1)} \right] P, \end{aligned} \tag{32a}$$

and

$$\Delta E^{(3)} P = P \left( W T_2^{(2)} + f_{OV} T_1^{(1)} \right) P.$$

In third order,

$$\begin{aligned} Q_1 D_1 T_1^{(2)} P &= Q_1 \left[ W T_2^{(1)} + W T_1^{(1)} + f_{\text{OV}} T_2^{(1)} + f_{\text{OD}} T_1^{(2)} \right] P, \\ Q_2 D_2 T_2^{(2)} P &= Q_2 \left[ W T_2^{(1)} + W T_1^{(1)} + f_{\text{OD}} T_2^{(2)} \right] P, \\ \Delta E^{(3)} P &= P \left[ W T_2^{(2)} + f_{\text{OV}} T_1^{(2)} + \frac{1}{2} W (T_1^{(1)})^2 \right] P. \end{aligned} \quad (32b)$$

In fourth order, we require effects of  $T_3$  as well. Here we have

$$\begin{aligned} Q_1 D_1 T_1^{(3)} P &= Q_1 \left[ W T_2^{(2)} + W T_1^{(2)} + f_{\text{OV}} T_2^{(2)} + W T_3^{(2)} + W T_1^{(1)} T_2^{(1)} \right. \\ &\quad \left. + \frac{1}{2} W (T_1^{(1)})^2 + \frac{1}{2} f_{\text{OV}} (T_1^{(1)})^2 + f_{\text{OD}} T_1^{(3)} \right] P, \\ Q_2 D_2 T_2^{(3)} P &= Q_2 \left[ W T_2^{(2)} + W T_1^{(2)} + f_{\text{OV}} T_3^{(2)} + W T_3^{(2)} \right. \\ &\quad \left. + \frac{1}{2} W (T_2^{(1)})^2 + W T_1^{(1)} T_2^{(1)} + f_{\text{OV}} T_1^{(1)} T_2^{(1)} \right. \\ &\quad \left. + \frac{1}{2} W (T_1^{(1)})^2 + f_{\text{OD}} T_2^{(3)} \right] P, \\ Q_3 D_3 T_3^{(2)} P &= Q_3 \left( W T_2^{(1)} + f_{\text{OD}} T_3^{(2)} \right) P, \\ \Delta E^{(4)} P &= P \left[ W T_3^{(2)} + f_{\text{OV}} T_1^{(3)} + W T_1^{(2)} T_1^{(1)} \right] P. \end{aligned} \quad (32c)$$

As above, using the  $2n$  rule of perturbation theory  $\Delta E^{(4)} = \langle V R_o V R_o \times V R_o V \rangle_L = \langle \phi^{(2)} | E_0 - H_0 | \phi^{(2)} \rangle_L$ ,  $\Delta E^{(4)}$  can alternatively be expressed in terms of only second-order  $T_n^{(2)}$  operators, bypassing the need to evaluate  $T_2^{(3)}$  and  $T_1^{(3)}$ . This is shown elsewhere.<sup>30</sup>

The fundamental problem with using Eqs. (32) as they stand is the  $f_{\text{OD}} T_n^{(m)}$  contribution. Such a term requires an iterative calculation, since  $T_n^{(m)}$  appears on both sides of the equation. Here is where we can profitably exploit the invariance of any of the individual diagrams in CC theory to a transformation among just the occupied or virtual orbitals. Hence, instead of actually solving the iterative equation, we can diagonalize the  $f_{\text{OO}}$  and  $f_{\text{VV}}$  blocks to define semi-canonical orbitals, which makes  $f_{\text{OD}} T_n^{(m)} = 0$ .

This is particularly critical for the  $f_{\text{OD}}T_3^{(2)}$  term in the triples equation, Eq. (32c). If it had to be included iteratively, its evaluation would require a repeated  $n^3N^4$  step, which would make the procedure time-consuming. Eliminating these terms instead gives at most a single  $n^3N^4$  step for ROHF-MBPT(4). Hence, Eq. (32) with semi-canonical orbitals provides a completely non-iterative evaluation of any order in perturbation theory. We have used this procedure to evaluate ROHF-MBPT through fourth order for several examples.<sup>30,31</sup> Alternatively, the option to use the iterative form is always available. In particular, it is convenient to use the iterative form, Eq. (32a), in ROHF-MBPT(2) analytical Hessian evaluation.<sup>33</sup> This has the advantage that we only require the solution of the usual coupled-perturbed Hartree-Fock equations, instead of the more demanding determination of semi-canonical coupled-perturbed Hartree-Fock solutions.

**Table 4.** Energy, optimized geometry, harmonic vibrational frequencies, and infrared intensities for the CH<sub>2</sub>N radical calculated at the MBPT(2) and CCSD levels using both restricted open-shell and unrestricted Hartree-Fock reference functions. Energies in hartrees, bond distances in angstroms, angles in degrees, harmonic frequencies in cm<sup>-1</sup>, and infrared intensities in km/mol.<sup>a</sup>

Basis Set	MBPT(2)			CCSD		CCSD(T)	Experiment
	UHF DZP	ROHF		UHF DZP	ROHF DZP	ROHF DZP	
<i>E</i>	-93.725468	-93.735537	-93.795179	-93.764412	-93.764444	-93.774325	—
<i>r</i> <sub>e</sub> (C-N)	1.2261	1.2645	1.2471	1.2648	1.2655	1.2701	—
<i>r</i> <sub>e</sub> (C-H)	1.0999	1.0984	1.0883	1.1010	1.1010	1.1028	—
∠(H-C-N)	121.38	120.99	120.77	121.27	121.27	121.31	—
ω <sub>1</sub> (a <sub>1</sub> )	3099.9	3100.0	3079.1	3066.0	3064.9	3041.8	2820 <sup>b</sup>
ω <sub>2</sub> (a <sub>1</sub> )	2041.5	1677.4	1681.9	1693.6	1689.3	1651.8	1725 <sup>c</sup>
ω <sub>3</sub> (a <sub>1</sub> )	1430.1	1407.5	1409.6	1409.1	1408.5	1394.2	1337 <sup>c</sup>
ω <sub>4</sub> (b <sub>1</sub> )	3182.2	3197.1	3176.1	3144.8	3143.9	3119.8	3103 <sup>c</sup>
ω <sub>5</sub> (b <sub>1</sub> )	954.4	931.3	956.2	952.4	953.1	936.9	913 <sup>c</sup>
ω <sub>6</sub> (b <sub>2</sub> )	1153.8	981.4	988.0	982.8	979.1	953.9	954 <sup>c</sup>
<i>I</i> <sub>1</sub>	0.2	0.0	0.9	0.5	0.5	0.4	—
<i>I</i> <sub>2</sub>	12.0	3.8	5.6	1.8	2.0	3.0	—
<i>I</i> <sub>3</sub>	19.2	7.2	12.2	8.1	7.8	7.1	—
<i>I</i> <sub>4</sub>	8.5	6.8	0.7	13.3	13.4	13.8	—
<i>I</i> <sub>5</sub>	7.5	6.5	9.6	7.9	8.0	7.2	—
<i>I</i> <sub>6</sub>	34.7	39.4	37.3	35.4	35.1	36.1	—

<sup>a</sup>Ref. 33.

<sup>b</sup>D. C. Cowles, M. J. Trovers, J. L. Frueh and G. B. Ellison, *J. Chem. Phys.* **94**, 3517 (1991).

<sup>c</sup>M. E. Jacox, *J. Phys. Chem.* **91**, 6595 (1987).

In cases of high spin contamination, as occurs in the CN radical<sup>30,31</sup> or the methyl imidogen molecule  $\text{CH}_2\text{N}$  (Ref. 33), ROHF-MBPT( $n$ ) shows much better convergence. See Fig. 1 and Table 4. The near equivalence of UHF-CCSD and ROHF-CCSD reflects CCSD and higher approximations' insensitivity to spin contamination (see Sec. 6).

A detailed account of how all fifth-order<sup>25</sup> and sixth-order<sup>19b</sup> MBPT terms arise from higher iterations of Eq. (18) is presented elsewhere.

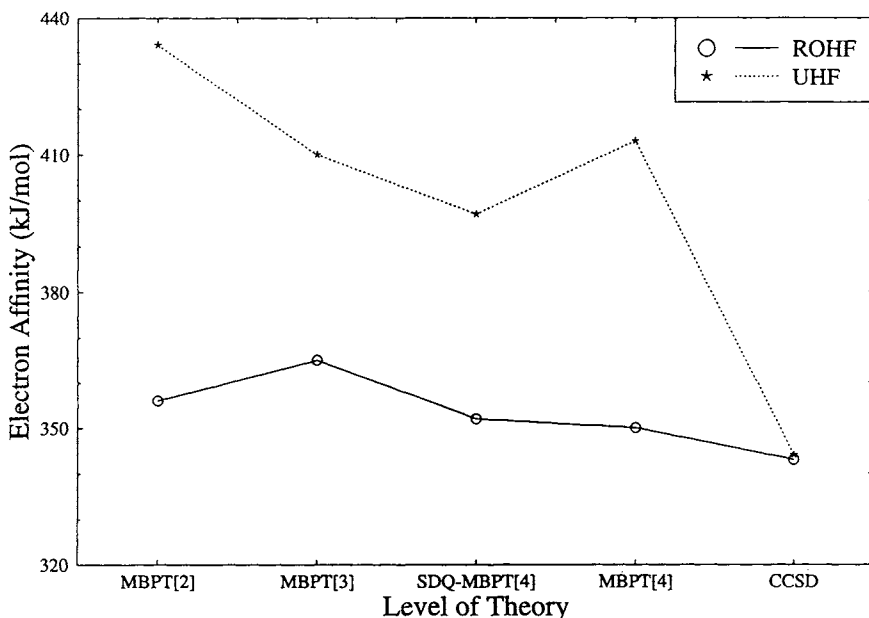


Fig. 1. Electron affinity of CN radical. (○) ROHF; (\*) UHF.

## 5. Simplified CC Methods for Triple and Quadruple Excitations

### 5.1. Iterative Methods

All terms in CCSD are computationally no worse than  $n^2 N^4 N_{it}$  where  $N_{it}$  is the number of iterations. The fourth-order approximation, SDQ-MBPT(4), is also  $n^2 N^4$ , but non-iterative, while the full MBPT(4) is  $n^3 N^4$ . CCSDT is  $n^3 N^5 N_{it}$  and CCSDTQ,  $n^4 N^6 N_{it}$ . So even though very efficient implementations of all have been achieved, it is advantageous to have somewhat

simpler methods for the approximate inclusion of  $T_3$  and  $T_4$ . These fall into two categories: iterative and non-iterative. The first general method to include triple excitations is CCSDT-1.<sup>20</sup> We will choose all terms that arise in the  $T_3$  equation and in the  $T_3$  contribution to  $T_2$  and  $T_1$  that will result in fourth-order in  $V = f_{OV} + W$  contributions to the energy. In this way we are allowing for non-Hartree-Fock cases just as in the ROHF-MBPT approach above. This is important to guarantee that approximate iterative and the full non-iterative CC methods will have the *same invariance properties* as CC theory. Hence, we solve iteratively the following set of equations to define CCSDT-1,

$$\begin{aligned} Q_3 D_3 T_3 P &= Q_3 (W T_2 + f_{OD} T_3) P, \\ Q_2 D_2 T_2 P &= Q_2 (W T_3 + f_{OV} T_3) P + CCSD, \\ Q_1 D_1 T_1 P &= Q_1 W T_3 P + CCSD. \end{aligned} \quad (33)$$

Because the fourth-order triple excitation contribution arises for this sequence, as in MBPT(4) in Eq. (32), CCSDT-1 is correct through the fourth-order energy and second-order wave function. Optional inclusion of the term  $Q W T_1 T_3 D$  into  $Q_2 D_2 T_2 P$  which is the only other  $T_3$  contribution to  $T_2$  or  $T_1$ , and which affects the energy in fifth-order (NHF), distinguishes CCSDT-1a and -1b.<sup>34</sup>

In the Hartree-Fock case,  $f_{OV}$  vanishes, while for canonical Hartree-Fock orbitals, we can also dispense with  $f_{OD}$ . However, since normal CC invariance to occupied-occupied and virtual-virtual orbital transformations should be maintained in any more approximate approach, all formal considerations will be based upon the more general expressions. We immediately know, however, that any *entire* CC diagram has this invariance property. So both parts of a term like  $Q_3 F_O T_3 P = Q_3 (-D + f_{OD}) T_3$  must be retained. By recognizing the invariance of  $Q_3 F_O T_3 P$ , however, we are free to make a transformation to diagonalize  $f_{OD} = f_{OO} + f_{VV}$  (i.e., semi-canonical orbitals) and bypass the  $n^3 N^4 N_{it}$  evaluation of  $f_{OD} T_3$ , just as we did in ROHF-MBPT(4). The reason for the inclusion of  $f_{OV}$  terms is that in the general case order is defined via  $V = f_{OV} + W$ .

Instead of Eq. (33), the CCSDT-2 model<sup>34</sup> uses the approximation for  $T_3$ ,

$$Q_3 D_3 T_3 P = Q_3 (W T_2 + f_{OD} T_3 + V T_2^2 / 2)_{CP}, \quad (34)$$

with the other equations the same as in CCSDT-1b. Except for the  $VT_3$  contribution into the  $T_3$  equation, these are all the fifth-order contributions. The advantage of CCSDT-2 is that in difficult situations such as when large amounts of quasi-degeneracy are present, the sequence of “linear”  $VT_3$  approximations,  $VT_3$  into  $T_2$  and  $VT_2$  into  $T_3$  in CCSDT-1 can overcorrect, while adding the quadratic  $VT_2^2/2$  term to  $T_3$ , a fifth-order contribution, damps such overcorrection. Note the vibrational frequencies for  $O_3$  in

**Table 5.** Vibrational frequencies ( $\text{cm}^{-1}$ ) of  $O_3$  at various levels of theory (DZP basis).

	$\omega_1$	$\omega_2$	$\omega_3$
SCF	1547	859	1428
2R-CISD <sup>a</sup>	1234	745	1352
CASSCF <sup>b</sup>	1098	689	989
MBPT(2)	1167	739	2373
MBPT(4)	1123	695	1547
CCSD <sup>c</sup>	1256	748	1240
CCSD + T(CCSD) <sup>c</sup>	1097	685	128i(327) <sup>h</sup>
CCSDT-1 <sup>c</sup>	1076	674	680
QCISD(T) <sup>d</sup>	1128	697	934
CCSD(T) <sup>e</sup>	1129	703	976
CCSDT-2 <sup>f</sup>	1158	712	1182
CCSDT-3 <sup>g</sup>	1149	707	1118
CCSDT <sup>g</sup>	1141	705	1077
Experiment	1135	716	1089

<sup>a</sup>T. J. Lee, W. D. Allen and H. F. Schaefer III, *J. Chem. Phys.* **87**, 7063 (1987).

<sup>b</sup>S. M. Alder-Golden, S. R. Langhoff, C. W. Bauschlicher and G. D. Carney, *J. Chem. Phys.* **83**, 255 (1985).

<sup>c</sup>J. F. Stanton, W. N. Lipscomb, D. H. Magers and R. J. Bartlett, *J. Chem. Phys.* **90**, 1077 (1989).

<sup>d</sup>K. Raghavachari, G. W. Trucks, J. A. Pople and E. Replogle, *Chem Phys. Lett.* **158**, 207 (1989).

<sup>e</sup>K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).

<sup>f</sup>D. H. Magers, W. N. Lipscomb, R. J. Bartlett and J. F. Stanton, *J. Chem. Phys.* **91**, 1945 (1989).

<sup>g</sup>J. D. Watts, J. F. Stanton and R. J. Bartlett, *Chem Phys. Lett.* **178**, 471 (1991).

<sup>h</sup>This result uses a larger (5s 4p 2d) basis.

Table 5, for example. We still avoid evaluation of  $VT_3$  because that introduces a  $n^3N^5N_{it}$  step. Hence, these methods are  $n^3N^4$  like MBPT(4), but require repeating the step  $N_{it}$  times. An important advantage of CCSDT-1 and CCSDT-2 is that all  $t_{ijk}^{abc}$  amplitudes are evaluated and immediately used in the  $T_2$  and  $T_1$  equation, making it unnecessary to store the  $\sim n^3N^3$  quantities. We also defined a CCSDT-3<sup>34</sup> model on the way to the full CCSDT method. The  $T_3$  equation in CCSDT-3 is

$$Q_3D_3T_3P = Q_3(WT_2 + f_{OD}T_3 + VT_2^2/2 + WT_1T_2 + WT_1^2T_2/2 + WT_2^2T_1/2 + WT_1^3T_2/3!)_CP. \quad (35)$$

While the  $T_1$  and  $T_2$  equations remain the same, CCSDT-3 has the virtue that all contributions from  $T_1$  and  $T_2$  into the CCSDT equations are included regardless of order, while the fifth- and higher-order  $T_3$  contributions into the  $T_3$  equation are still neglected. This permits retaining the same storage advantages and  $n^3N^4N_{it}$  computational dependence of CCSDT-1 and CCSDT-2. The additional inclusion of many  $T_1$  terms makes CCSDT-3 more insensitive to orbital choice than CCSDT-1 or CCSDT-2.

The initial (fifth-order) energy contribution from the  $T_4$  amplitudes is given by

$$Q_4D_4T_4P = Q_4W(T_2^2/2 + T_3)P,$$

which, combined with the following equations

$$\begin{aligned} Q_3D_3T_3P &= Q_3VT_4P + \text{CCSDT}, \\ Q_2D_2T_2P &= Q_2WT_4P + \text{CCSDT}, \\ Q_1D_1T_1P &= \text{CCSDT}. \end{aligned} \quad (36)$$

defines CCSDTQ-1 in analogy to CCSDT-1.<sup>20</sup> This method is correct through MBPT(5). CCSDTQ-1 has an  $n^4N^5N_{it}$  computational dependence. Results are in Table 1.

## 5.2. Non-Iterative Methods

The very high  $N$ -dependence of some of the above methods recommends more practical non-iterative ways to estimate  $T_3$  and  $T_4$  contributions. One obvious way to short-circuit this procedure is simply to use converged  $\bar{T}_2$



and  $\bar{T}_1$  amplitudes, such as obtained from CCSD, to define  $T_3$  or  $T_4$  in the above iterative sequences, then allow that value for  $T_3$  or  $T_4$  to contribute back to  $T_2$  and  $T_1$ , which are then used in  $\Delta E$ . For example, for the canonical orbital case ( $f_{OD} = 0$ ,  $f_{OV} = 0$ ),

$$Q_3 D_3 T_3^{[2]} P = QW \bar{T}_2 P, \quad (37a)$$

$$Q_2 D_2 T_2^{[3,T]} P = Q_2 W T_3^{[2]} P, \quad (37b)$$

$$\Delta E_{Ta}^{[4]} = \langle W T_2^{[3,T]} \rangle = \langle (W/D_2) Q_2 (W Q_3 W \bar{T}_2 / D_3) \rangle, \quad (37c)$$

which is clearly correct through fourth-order,<sup>a</sup> but contains many higher-order terms. The  $Q_3$  and  $Q_2$  indicate that the intermediate states have to be triple and double excitations, respectively.

A superior approach in practice, however, is found to derive from the expectation value (XCC) ansatz,

$$\Delta E_{XCC} = \langle o | e^{T^\dagger} H_N e^T | o \rangle / \langle o | e^{T^\dagger} e^T | o \rangle = \langle o | (e^{T^\dagger} H_N e^T)_C | o \rangle. \quad (38)$$

In the absence of restrictions on  $T$ , it may be shown<sup>32</sup> that  $\Delta E_{XCC}$  is “internally connected,”

$$\begin{aligned} \Delta E_{XCC} &= \langle o | e^{T^\dagger} (H_N e^T)_C | o \rangle \\ &= \langle o | (H_N e^T)_C | o \rangle = \Delta E_{CC}, \end{aligned} \quad (39)$$

since  $Q(H_N e^T)_C | o \rangle = Q e^{T^\dagger} (H_N e^T)_C | o \rangle = 0$ , showing the equivalence to standard CC for that case. Even though the numerator and denominators have to terminate for some  $T > T_n$  for  $n$  electrons, division by the denominator leads to a non-terminating series, and, once  $T$  is truncated, the equivalence does not hold except to some order in perturbation theory. We can see this as follows (internal connection understood here and in the following).

<sup>a</sup>The convention is to use  $T^{[m]}$  to indicate that  $m$ th order is the first order in which the term appears, but that it contains many higher-order contributions while  $T^{(m)}$  is the pure  $m$ th order term.

$$\begin{aligned}
\langle o|e^{\bar{T}_1+\bar{T}_2}(H_N e^{\bar{T}_1+\bar{T}_2})_C|o\rangle &= \langle o|H_N Q_2(\bar{T}_2 + \bar{T}_1^2/2)|o\rangle + \langle o|H_N Q_1 \bar{T}_1|o\rangle \\
&+ \langle o|\bar{T}_2^\dagger Q_2 H_N(e^{\bar{T}_1+\bar{T}_2})|o\rangle \\
&+ \langle o|\bar{T}_1^\dagger Q_1 H_N(e^{\bar{T}_1+\bar{T}_2})|o\rangle \\
&+ \langle o|\bar{T}_1^\dagger \bar{T}_2^\dagger Q_3 H_N(e^{\bar{T}_1+\bar{T}_2})|o\rangle \\
&+ \langle o|(\bar{T}_2^{\dagger 2}/2)Q_4 H_N(e^{\bar{T}_1+\bar{T}_2})|o\rangle \\
&+ \text{higher order terms.}
\end{aligned} \tag{40}$$

The first two terms give the  $\Delta E_{\text{CCSD}}$  energy, while the next two vanish because the CCSD equations are satisfied for  $\bar{T}_1$  and  $\bar{T}_2$ . Those with triple  $Q_3$ , quadruple  $Q_4$ , and higher intermediate states remain in the expectation value, and must be considered in any non-iterative correction. Using the analogous formula for  $\exp(T_1 + T_2 + T_3)$ , we can isolate the initial  $T_3$  corrections to  $\Delta E$  from the other components that arise from the CCSD method, of which no fourth-order internally connected terms arise from  $Q_3$  and  $Q_4$  intermediate states. Then we can extract the terms fourth-order in  $V$ ,

$$\begin{aligned}
\Delta E_T^{[4]} &= \langle o|T_3^{[2]\dagger} Q_3 F_O T_3^{[2]}|o\rangle + \langle o|T_3^{[2]\dagger} Q_3 W \bar{T}_2|o\rangle \\
&+ \langle o|\bar{T}_2^\dagger Q_2 W T_3^{[2]}|o\rangle + \langle o|\bar{T}_2^\dagger Q_2 f_{OV} T_3^{[2]}|o\rangle \\
&+ \langle o|\bar{T}_1^\dagger Q_1 W T_3^{[2]}|o\rangle.
\end{aligned} \tag{41}$$

The intermediate states,  $Q_n$ , are inserted to make clear the number of open lines that are required to give a non-vanishing, necessarily connected, (linked) term. The third term can equally well be written as  $\langle o|\bar{T}_2^\dagger W Q_3 T_3^{[2]}|o\rangle$ , showing that it is the Hermitian conjugate of the second term. The conjugates of the last two terms are eliminated because of the internally connected condition, Eq (39).

Analogous to the  $T_3$  part of Eq. (32c),

$$Q_3 D_3 T_3^{[2]} P = Q_3 (W \bar{T}_2 + f_{OD} T_3^{[2]}) P, \tag{42}$$

or we know that  $Q_3 (F_O T_3^{[2]} + W \bar{T}_2) P = 0$ , causing the first two terms to vanish. To avoid the iterative solution of Eq. (42), we once again appeal to the use of semi-canonical orbitals, which, of course, have no effect on the

reference CCSD energy. Making this choice, we obtain

$$\begin{aligned}\Delta E_T^{[4]} &= \langle o | (T_3^{[2]\dagger} D_3 T_3^{[2]} | o \rangle + \langle o | (\bar{T}_2^\dagger Q_2 f_{OV} T_3^{[2]} | o \rangle \\ &\quad + \langle o | \bar{T}_1^\dagger Q_1 W T_3^{[2]} | o \rangle \\ &= \Delta E_{TT}^{[4]} + \Delta E_{DT}^{[4]} + \Delta E_{ST}^{[4]}.\end{aligned}\quad (43)$$

All these terms arise in CCSDT-1.<sup>20</sup>

The first term gives the *quadratic* triple excitation measure,

$$T(\text{CCSD}) = \Sigma |t_{ijk}^{abc[2]}|^2 / D_{ijk}^{abc} \quad (44)$$

which, unlike Eq. (37c), involves infinite-order effects of  $\bar{T}_2$  twice. In the canonical case, when the second term vanishes and the third is fifth-order, we have the CCSD + T(CCSD) method<sup>34</sup> which is correct through fourth order. In our recent terminology, this becomes CC4SD[T] = CCSD[T], meaning infinite order in SD, and correct through fourth order in  $T$  with [ ] indicating the canonical case. For the non-Hartree-Fock case, we define order in  $V$  instead of  $W$ , so we retain all three terms. We also require the use of semi-canonical orbitals to eliminate the  $f_{OD} T_3^{[2]}$  contribution that would otherwise remain in fourth order. To be consistent with current use, this generalized method is termed CC4SD(T) = CCSD(T),<sup>23,28</sup> where ( ) means it must have exactly the same invariance properties as any infinite-order, CCSD or CCSDT, etc., method.<sup>18</sup> In the canonical case,  $f_{OV} = 0$ , so the second term vanishes, but the third  $\Delta E_{ST}^{[4]}$  remains, establishing the equivalence to the usual *canonical orbital* CCSD(T).<sup>21</sup> In this case, the extra term is *fifth-order* in  $W$ , and though it is much smaller than the  $T(\text{CCSD})$  term, typically by an order of magnitude,<sup>22</sup> it is usually positive and found to offer an important balance to avoid  $T(\text{CCSD})$  overcorrecting in difficult cases. The origin of the correction actually lies in the approximate CC method, QCISD<sup>35</sup> (see Appendix B), which is only defined for canonical orbitals and which alternatively views  $\Delta E_{ST}^{[5]}$  as originating from the equivalent expression  $\langle o | \bar{T}_1^\dagger W Q_3 T_3^{[2]} | o \rangle$ , as a *single excitation* contribution to  $T_3^{[2]}$  so that  $Q_3 D_3 T_3^{[2]'} P = Q_3 (W \bar{T}_2 + W \bar{T}_1) P$ . Then evaluating the  $T$  expression,  $\langle o | T_3^{[2]'} D_3 T_3^{[2]'} | o \rangle - \langle o | \bar{T}_1^\dagger W D_3 W \bar{T}_1^\dagger | o \rangle$ , gives the cross-term twice. In CC theory,  $Q_3 W \bar{T}_1 P$  is not connected, so it does not appear in this way, but instead arises through  $Q_1 D_1 T_1 P = Q_1 W T_3 P$ , and thus has

its origin in triples, instead of the other way around. In CCSD, the  $WT_1T_2$  term (which does not appear in QCISD (see Appendix B)), makes a contribution to the  $T_2$  equation, which in the energy is equivalent to the  $\Delta E_{ST}$  term through fifth-order, necessitating that, as Eq. (41) shows, it should be included only once when added on top of CCSD.

For numerical comparisons with full CCSDT for several molecules (see Table 1) and references,<sup>36,37</sup> CCSD(T) seems to offer an unusually good approximation. This is not always the case, however, as in the  $\text{Be}_2$  potential energy curve<sup>22</sup>; in bond breaking cases as in  $\text{F}_2$  (Ref. 5), where approximate, but iterative methods like CCSDT-1 have advantages; or for the  $\text{O}_3$  vibrational frequencies in Table 5, where though qualitatively right, the CCSD(T) frequencies are in substantial error compared to CCSDT.

Analogous to the cycle that leads to  $\Delta E_{Ta}^{[4]}$ , we can start from a converged CCSDT or CCSDT- $n$  calculation, which gives  $\bar{T}_2$  and  $\bar{T}_3$ , to define an estimate of the fifth-order contribution arising from  $T_4$ ,

$$\begin{aligned} Q_4 D_4 T_4^{[3]} P &= Q_4 V(\bar{T}_2^2/2 + \bar{T}_3) P, \\ Q_2 D_2 T_2^{[Q,4]} P &= Q_2 W T_4^{[3]} P, \\ \Delta E_{Qa}^{[5]} &= \langle W T_2^{[Q,4]} \rangle = \langle (W/D_2) Q_2 W Q_4 T_4^{[3]} \rangle. \end{aligned} \quad (45)$$

Making some manipulations and using the factorization theorem to eliminate the long ( $D_4 \Rightarrow D_{ijkl}^{abcd}$ ) denominator in  $T_4^{[3]}$ , this may be put into the form,<sup>24</sup>

$$\Delta E_{Qa}^{[5]} = \frac{1}{2} \langle (W/D_2) Q_2 (W/D_2) Q_4 [V(\bar{T}_2^2/2 + \bar{T}_3)] \rangle. \quad (46)$$

With the elimination of  $D_4$ , this becomes computationally a non-iterative  $n^3 N^4$  procedure ( $N^6$  for the  $\bar{T}_2^2/2$  term and  $n^3 N^4$  for the  $\bar{T}_3$  part) instead of  $n^4 N^5 N_{it}$  as in CCSDTQ-1, offering a dramatic savings in time.

If we proceed as above, starting from Eq. (39), we obtain another and probably better estimate of  $\Delta E_Q^{[5]}$  as<sup>24</sup>

$$\Delta E_{Qb}^{[5]} = \frac{1}{2} \langle (W/D_2) Q_2 \bar{T}_2^\dagger Q_4 [V(\bar{T}_2^2/2 + \bar{T}_3)] \rangle. \quad (47)$$

This formula defines the Q(CCSDT- $n$ ) correction to be added to a converged CCSDT- $n$  calculation. Notice it differs from Eq. (46) by replacing one  $W/D_2$  by  $\bar{T}_2^\dagger$ . This defines CCSDT + Q(CCSDT) = CC5SDT[Q],<sup>24</sup> which has been found to be quite accurate, as shown in Table 1.

In practice, however, we would like to limit ourselves to only an  $n^2 N^4$  iterative scheme like CCSD, and then non-iteratively include higher contributions from  $T_3$  and  $T_4$ . When this is accomplished based upon the expectation value expression, Eq. (39), we obtain the fourth-order correction in Eq (43), and the four fifth-order correction terms (internal connection understood),

$$\Delta E = \Delta E_{\text{CCSD}} + \Delta E_{\text{T}}^{[4]} + \Delta E_{\text{TT}}^{[5]} + \Delta E_{\text{TQ}}^{[5]} + \Delta E_{\text{QT}}^{[5]} + \Delta E_{\text{QQ}}^{[5]}. \quad (48)$$

The fifth-order corrections<sup>b</sup> are

$$\Delta E_{\text{TQ}}^{[5]} + \Delta E_{\text{TT}}^{[5]} = \langle o | T_3^{[2]\dagger} Q_3 D_3 T_3^{[3]} | o \rangle = \langle o | T_3^{[2]\dagger} Q_3 W (\bar{T}_2^2/2 + T_3^{[2]}) | o \rangle, \quad (49a)$$

$$\Delta E_{\text{QT}}^{[5]} = 1/2 \langle o | \bar{T}_2^\dagger \bar{T}_2^\dagger Q_4 W T_3^{[2]} | o \rangle, \quad (49b)$$

$$\Delta E_{\text{QQ}}^{[5]} = 1/2 \langle o | \bar{T}_2^\dagger \bar{T}_2^\dagger Q_4 (W \bar{T}_2^2/2) | o \rangle. \quad (49c)$$

The  $T_3^{[2]}$  amplitude is defined in Eq. (37), while

$$Q_3 D_3 T_3^{[3]} P = Q_3 W (\bar{T}_2^2/2 + T_3^{[2]}) P. \quad (50)$$

Combining  $\Delta E_{\text{QT}}^{[5]}$  and  $\Delta E_{\text{QQ}}^{[5]}$ , we obtain, analogous to the above quadruple corrections,  $\Delta E_{\text{Qc}}^{[5]} = \Delta E_{\text{QQ}}^{[5]} + \Delta E_{\text{QT}}^{[5]}$ , which we call  $\text{Q}^*(\text{CCSD})$ .<sup>22</sup> Unlike the above  $\Delta E_{\text{Q}}^{[5]}$  estimates, this one is peculiar to a CCSD starting point. The sum of all corrections through fifth order obtained from converged CCSD is designated as  $\text{TQ}^*(\text{CCSD})$ , and  $\text{CCSD} + \text{TQ}^*(\text{CCSD}) = \text{CC5SD}[\text{TQ}^*]$ . Computationally, the rate determining step is the evaluation of  $\Delta E_{\text{TT}}^{[5]}$ , an  $n^3 N^5$  step, while  $\Delta E_{\text{QT}}^{[5]}$ ,  $\Delta E_{\text{TQ}}^{[5]}$ , and  $\Delta E_{\text{T}}^{[4]}$  are  $n^3 N^4$  and  $\Delta E_{\text{QQ}}^{[5]}$  is  $N^6$ . The remaining terms require no more than an  $n^2 N^4$  procedure. Of these terms, for full CI examples,  $\Delta E_{\text{TT}}^{[4]}$  is about an order of magnitude greater than any of the other fifth-order corrections, and is typically two orders of magnitude larger than the sum of the fifth-order terms (including the  $\Delta E_{\text{ST}}^{[4]}$  term which would be

<sup>b</sup>Note that  $\Delta E_{\text{TQ}}^{[5]} \neq \Delta E_{\text{QT}}^{[5]}$  because of the different intermediate states ( $Q_3$  vs.  $Q_4$ ). In Ref. 22,  $\Delta E_{\text{TQ}}^{[5]} = \Delta E_{\text{TD}}^{[5]}$ . This is one of those points where nominal use of diagrams makes this argument clear.

fifth-order in the canonical case) as they have different signs.<sup>22</sup> Typically, the  $\Delta E_{ST}^{[4]}$  and  $\Delta E_{TQ}^{[5]}$  terms are positive, the former always, for the examples we have considered, while the latter is slightly negative in only one instance.<sup>22</sup>  $\Delta E_{TT}^{[5]}$  like  $\Delta E_{TT}^{[4]}$  is always negative, while  $\Delta E_Q^{[5]}$  can have either sign depending upon whether the  $\Delta E_{QQ}^{[5]}$  or the  $\Delta E_{QT}^{[5]}$  term dominates. Eliminating the  $n^3 N^5$  term would be desirable computationally, and this can be done by assuming the approximate cancellation of  $\Delta E_{TT}^{[5]}$  with some of the positive terms. This would leave  $\Delta E_{CCSD} + \Delta E_{TT}^{[4]} + \Delta E_{QQ}^{[5]}$ , for example. Non-iterative methods correct through sixth order are presented elsewhere.<sup>18,38</sup>

All such non-iterative and iterative approximations suffer from the lack of a variational bound in CC theory. Consequently, as there is no monotonic convergence to the correct answer, a single term can significantly affect the result. In the absence of such bounds (approximate bounds would not be helpful since they would differ from the exact, extensive result by terms of at least the same order as those being evaluated), other consistency conditions are imposed to try to restore some order out of the chaos of possible approximations. The simplest is to insist upon the energy being correct through some order in the perturbation  $W$ . Another is to insist that a method be correct through a given order in  $V$  (NHF) instead of  $W$  and, furthermore, to satisfy the same invariance properties as iterative CC theory. This first leads us to CCSD(T), instead of CCSD[T], while the second gives our generalized CCSD(T). Similarly, using the expectation value expression in Eq. (38) instead of short-circuiting the standard iterative procedure offers some basis for improved approximations and this, too, is necessary to obtain CCSD(T). Other consistency relationships can be envisioned, including those based upon the CC energy functional in Eq. (57),<sup>38</sup> or insisting that results be exact for two, three or four electrons. However, no entirely satisfactory recipe has yet been identified to allow a “systematic” extension of such methods toward convergence.

## 6. Open-Shell Applications

The factorized equations in Tables 2 and 3 are written in terms of spin orbitals. This is convenient because they apply equally to single determinant reference open- and closed-shells; to different orbitals for different spin methods like unrestricted Hartree–Fock (UHF)<sup>7,8</sup>; to restricted open-shell Hartree–Fock (ROHF)<sup>27</sup> and even to non-Hartree–Fock choices like quasi-restricted Hartree–Fock (QRHF),<sup>27</sup> where the orbitals to describe an ion

might be taken from the neutral molecule and just occupied appropriately for the ion; or to even a Brueckner determinant reference (B).<sup>14,29,40,41</sup> In practice, of course, as long as pure (instead of general) spin orbitals are used, spin integration is a necessity to provide viable computational equations (e.g., UHF-CC is only  $\sim 3$  times RHF-CC). This integration, though sometimes tedious, is straightforward.

UHF-based CC methods do not preserve spin symmetry, and can break spatial symmetry as well. To assess spin contamination, we evaluate  $\hat{S}^2$  when using a UHF-based CC calculation. It might be argued that the appropriate way to evaluate  $\hat{S}^2$  is via an expectation value,

$$\bar{S}(\bar{S} + 1) = \langle o | \exp(T^\dagger) \hat{S}^2 \exp(T) | o \rangle / \langle o | \exp(T^\dagger) \exp(T) | o \rangle, \quad (51)$$

which can be further simplified to just connected terms,<sup>1</sup>

$$= \langle o | (\exp(T^\dagger) \hat{S}^2 \exp(T))_C | o \rangle.$$

However, such a CC expectation value does not terminate. It could be used to a high order approximation, and has been for some one-electron properties.<sup>42,c)</sup> Instead, we employ the same philosophy as in the CC evaluation of the energy.<sup>43</sup> Namely, we project on the reference function to obtain

$$\bar{S}(\bar{S} + 1) = \langle o | \hat{S}^2 \exp(T) | o \rangle, \quad (52)$$

from which the multiplicity becomes

$$2\bar{S} + 1 = (1 + 4\langle o | \hat{S}^2 | \Psi_{CC} \rangle)^{\frac{1}{2}}. \quad (53)$$

As long as  $|o\rangle$  is UHF,  $2\bar{S} + 1$  is not exactly an integer. For many cases it will be close, because any CCSD (or higher) method has the property that the principal spin contaminant is automatically annihilated from the CCSD wave function.

Consider the spin annihilation operator  $\hat{A}_{S_k} = [\hat{S}^2 - S_k(S_k + 1)]$  for the first contaminating state,  $\Psi_{S_k}$ , an eigenfunction of spin with eigenvalue  $S_k(S_k + 1)$ . The energy associated with the spin-annihilated CC wave function can be obtained from

$$\langle o | (H_N - \Delta E) \hat{A}_{S_k} \exp(T) | o \rangle = 0. \quad (54)$$

<sup>c</sup>An alternative, rigorous terminated expectation-value like procedure is given by the  $\Lambda$ -based CC response density discussed in Secs. 7 and 8.<sup>39</sup>

Since  $[H, \hat{A}_{S_k}] = 0$ ,

$$\langle \hat{A}_{S_k} o | (H_N - \Delta E) \exp(T) | o \rangle = 0.$$

But since  $\hat{S}_k^2$  has only one- and two-particle parts,  $\langle \hat{A}_{S_k} o |$  simply consists of single and double excitations in addition to  $\langle o |$ . By virtue of the CCSD equations being satisfied,

$$Q_1(H_N - \Delta E) \exp(T_1 + T_2) | o \rangle = 0,$$

$$Q_2(H_N - \Delta E) \exp(T_1 + T_2) | o \rangle = 0,$$

these parts make no contribution, and  $\Delta E$  is the same. Hence at the CCSD level, effectively  $\hat{A}_{S_k} \exp(T_1 + T_2) | o \rangle = \exp(T_1 + T_2) | o \rangle$  (Ref. 44). In order to eliminate the two lowest contaminating states, a product annihilator  $\hat{A}_{S_i} \hat{A}_{S_k}$  would be necessary, and this would introduce triple and quadruple excitations. A UHF-CCSDTQ calculation would, thus, automatically benefit from annihilation of the *two* lowest contaminating states.

A superior kind of spin annihilation to that which is implicit in UHF-CCSD is offered by the use of a high spin ROHF reference function, which is an eigenfunction of spin. Such an ROHF-CCSD method was first presented<sup>27</sup> in 1988, and simply consists of using ROHF orbitals instead of UHF orbitals in a CC calculation. Although it would appear that maximum double occupancy of the ROHF orbitals could be used to further simplify the UHF-CC calculation, which typically takes  $\sim 3$  times as long as the closed-shell RHF-CC, in practice this simplification cannot be exploited without other considerations.<sup>45-48</sup> Instead, the advantage of ROHF-CC lies in its spin projection properties.

We can conceive of the correct spin-projected CC eigenfunction to be  $\hat{\theta}_{S_i} \exp(T) | o \rangle$  where  $\theta_{S_i}$  is a spin-projector, i.e.,  $\hat{\theta}_{S_i} = \prod_{k(\neq i)} \hat{A}_{S_k}$ . Even if  $| o \rangle$  represents an ROHF vacuum,  $\exp(T) | o \rangle$  does not preserve spin symmetry for open-shell systems. The linear terms in a truncated  $T$  subject to spin orbitals can break spin symmetry (see below), and in the non-linear part the direct product of  $T * T$  is reducible and can contain several irreducible representations for open-shells. However, the equation for the CC energy for  $\hat{\theta}_{S_i} \exp(T) | o \rangle$  is

$$\begin{aligned} \Delta E &= \langle o | H_N \hat{\theta}_{S_i} \exp(T) | o \rangle / \langle o | \hat{\theta}_{S_i} \exp(T) | o \rangle \\ &= \langle \hat{\theta}_{S_i} o | H_N \exp(T) | o \rangle = \langle o | H_N \exp(T) | o \rangle, \end{aligned}$$



since  $[H_N, \hat{\theta}_{S_i}] = 0$  and  $\hat{\theta}_{S_i}|o\rangle = |o\rangle$  by virtue of  $|o\rangle$  being a high-spin ROHF function, which is an eigenfunction of spin. Unlike the UHF case, this corresponds to a “complete” annihilation.

Furthermore, the amplitude equations are

$$Q(H_N - \Delta E)\hat{\theta}_{S_i} \exp(T)|o\rangle = Q(H_N - \Delta E) \exp(T)|o\rangle,$$

provided that  $\hat{\theta}_{S_i}Q = Q$ . As long as all excitations are generated from ROHF to be similar high spin single determinant eigenfunctions, this, too, holds. Using the projected definition for  $\hat{S}^2$  in Eq. (52), we naturally have for an ROHF-CC that

$$\langle o|\hat{S}^2 \exp(T)|o\rangle = S(S+1).$$

However, the *expectation value* of  $\hat{S}^2$  for the ROHF-CC wave function is not  $S(S+1)$ .<sup>27,39</sup> Because of the approximate spin annihilation property in UHF-CCSD, only in the most extreme, spin contaminated cases should ROHF-CCSD and UHF-CCSD differ much, as shown in the CN and CH<sub>2</sub>N examples of Fig. 1 and Table 4. It is more likely that differences will occur due to other kinds of symmetry breaking that can distinguish UHF and ROHF references. Important differences occur for ROHF-MBPT, though, as in Table 4.

To amplify on the non-spin eigenfunction character of the linear terms in ROHF-CCSD, consider a high spin doublet reference  $\Phi_0 = |\bar{i}\bar{j}\bar{j}k\rangle$ . In ROHF-CCSD, we would introduce the double excitations,  $\Phi_{ii}^{a\bar{b}}$  and  $\Phi_{ii}^{\bar{a}b}$ , which would have the open-shell parts  $ka\bar{b}$  and  $k\bar{a}b$  respectively. As the  $\bar{k}$  orbital is also available to accommodate an electron, we can also form  $\Phi_{ii}^{a\bar{k}b}$ , with open-shell part  $a\bar{k}b$ . But whereas the latter determinant is degenerate with the former, it arises only from  $T_3$  in the spin-orbital CC equations, so it does not appear in ROHF-CCSD. The inability to form the spin-adapted low-spin doublet combination prohibits ROHF-CCSD from being a strict eigenfunction of spin in the expectation value sense. Completely rigorous spin-adapted (SA) ROHF-CC is possible,<sup>45–48</sup> and, in principle, these methods can exploit the double occupancy of most of the orbitals to save the computational factor of  $\sim 3$  compared to UHF, except that they have several additional complications. For example, for rigorous open-shell CC methods, entirely different equations are obtained for doublets, triplets, and other multiplicities,<sup>45–47</sup> while the ROHF-CC equations here assume the same form regardless of multiplicity. Secondly, some approaches<sup>46</sup> require evaluating eight-fold commutators instead of four-fold as in the usual method.

Numerically, however, there is very little difference from the current (sometimes called "projected") ROHF-CC. Using the eight-fold commutator method, Janssen and Schaefer<sup>46</sup> report for the CH<sub>2</sub> singlet-triplet splitting an error from FCI of 0.82 kcal/mol while ROHF-CCSD gives 0.85. For the <sup>2</sup>B<sub>1</sub> and <sup>2</sup>A<sub>1</sub> states of NH<sub>2</sub>, the differences between the methods are typically < 0.2 mhartrees. A better SA-ROHF-CCSD method is offered by Neogrády *et al.*,<sup>47</sup> but it is still more complicated computationally. Their results are given in Table 6. From the above results and those shown in Table 6, it is apparent that, besides being convenient, the original ROHF-CCSD method is quite accurate, and the differences would be reduced by the addition of triples as such excitations introduce additional degenerate configurations as discussed above. The most rigorous ROHF-CC would seem to be the orthogonal spin adapted method of Li and Paldus.<sup>48</sup>

**Table 6.** Comparison of ROHF-CCSD with spin adapted (SA) ROHF-CCSD. Correlation energies [3s 2p] basis (a.u.)<sup>a</sup>.

Molecule	ROHF-CCSD	SA-ROHF-CCSD	Δ (mhartrees)
H <sub>2</sub> O <sup>+</sup> ( <sup>2</sup> B <sub>1</sub> )	0.216894	0.216771	0.12
OH ( <sup>2</sup> Π)	0.217660	0.217536	0.12
NH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> )	0.209644	0.209491	0.15
O <sub>2</sub> H ( <sup>2</sup> A'')	0.464243	0.463493	0.75
CN ( <sup>2</sup> Σ <sup>+</sup> )	0.321720	0.320794	0.93
O <sub>2</sub> ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )	0.403366	0.402880 <sup>b</sup>	0.49
B <sub>2</sub> ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )	0.214268	0.214000 <sup>b</sup>	0.27
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	0.149470	0.149317 <sup>b</sup>	0.63

<sup>a</sup>Results from Ref. 47.

<sup>b</sup>SA1-ROHF-CCSD correlation energies (approximation to full SA-ROHF-CCSD result).

The next variant of reference function for CC theory is the quasi-restricted HF(QRHF) choice.<sup>27</sup> QRHF means to take a single determinant wave function from some convenient related species and construct a reference function for the particular problem by occupying the orbitals accordingly. For high-spin open-shell cases, QRHF is an eigenfunction of spin, like ROHF. Examples of QRHF applications include using NO<sub>3</sub><sup>-</sup> orbitals to describe NO<sub>3</sub> (Ref. 40) and neutral molecule orbitals to describe ionized states.<sup>27</sup> In the first case, QRHF is used to avoid symmetry breaking, which plagues UHF or ROHF treatments of NO<sub>3</sub>. That is, under a displacement

of an N–O bond, neither UHF nor ROHF will smoothly connect the high symmetry  $D_{3h}$  geometry with the lower symmetry  $C_{2v}$  geometry. For  $\text{NO}_3^-$ , though, there is no such problem. Hence, we can take the  $\text{NO}_3^-$  orbitals at appropriate geometries and, by eliminating an electron from the highest orbital, define a QRHF reference for  $\text{NO}_3$  that should be equally appropriate at  $D_{3h}$  and  $C_{2v}$  points. This is critical if we want to use single reference CC to determine whether the  $D_{3h}$  point is lower in energy than a distorted  $C_{2v}$  form.

A related example pertains to inner-shell ionized states. The highest ionized state is usually easily described with either a UHF or ROHF reference. However, a hole state, where an electron is removed from an inner-shell orbital of the same symmetry as higher orbitals, is harder to describe, because of potential variational collapse, as the solution would preferentially choose to reoccupy the lower energy orbital. Even when a hole state SCF can be converged by using careful procedures, the orbitals differ for each state. Alternatively, QRHF can readily describe all states with the *same* orbitals simply by changing the occupation numbers of the neutral molecule orbitals. This also assists in the evaluation of transition moments, dipole strengths, and related properties.

Unlike CI, CC methods that include single excitations like CCSD and beyond are insensitive to orbital choice. This makes it possible to conveniently use non-energy optimum QRHF references. The fundamental reason is the Thouless theorem<sup>49,d</sup> that says that any single determinant  $\Phi$  can be related to another single determinant  $\phi$ , via

$$\Phi = \exp(T_1)\phi. \quad (55)$$

Consequently, the CCSD wave function is

$$e^{T_1+T_2}\phi = e^{T_2}\Phi. \quad (56)$$

Since most of the correlation is introduced by  $T_2$ , the inclusion of  $e^{T_1}$  gives CCSD the flexibility to adjust the orbitals to provide an appropriate description of the system. Hence, the QRHF orbitals are implicitly rotated for  $\phi$  as necessary for the problem at hand. Obviously in CCSDT we also gain the additional coupling between  $T_3$ ,  $T_2$  and  $T_1$  to provide an even

<sup>d</sup>Thouless actually employs the unitary operator  $\tau_1 = T_1 - T_1^\dagger$  in his proof. This preserves orthogonality. However, the theorem applies with just  $T_1$ . See Ref. 50 for a discussion.

better description. At the full CI limit, the energy and density will be completely invariant to orbital choice, but due to  $\exp(T_1)$  even CCSD is insensitive to the orbital choice. Since the theorem requires the exponential operator, CISD has no such insensitivity.

Two examples are chosen to illustrate the insensitivity of CCSD to orbital choice. The first is for the open-shell methyl radical  $\text{CH}_3$ , where UHF, ROHF and QRHF orbitals taken from either  $\text{CH}_3^+$  or  $\text{CH}_3^-$  are chosen.<sup>51a</sup> Results are in Table 7. Note the insensitivity of nearly all properties at even the CCSD level.

**Table 7.** Equilibrium structure, harmonic vibrational frequencies, infrared intensities and one-electron properties calculated for the methyl radical with different open-shell CCSD methods (DZP basis).<sup>a</sup>

	Type of Reference Function			
	QRHF(M $\rightarrow$ M <sup>+</sup> )	QRHF(M $\rightarrow$ M <sup>-</sup> )	UHF	ROHF
E (hartree)	-39.73633	-39.73589	-39.73602	-39.73598
$r_e$ (Å)	1.0882	1.0867	1.0873	1.0873
$\omega_1$ ( $a'_1$ ) ( $\text{cm}^{-1}$ )	3138.8	3156.0	3149.0	3149.0
$\omega_2$ ( $a''_2$ ) ( $\text{cm}^{-1}$ )	414.9	422.8	421.1	418.6
$\omega_3$ ( $e'$ ) ( $\text{cm}^{-1}$ )	1438.2	1441.1	1440.3	1440.3
$\omega_4$ ( $e''$ ) ( $\text{cm}^{-1}$ )	3326.8	3343.8	3337.3	3337.4
$I_1$ (km/mol)	0	0	0	0
$I_2$ (km/mol)	88.0	89.2	88.5	88.5
$I_3$ (km/mol)	4.2	4.8	4.5	4.5
$I_4$ (km/mol)	17.2	14.3	15.2	15.3
$\theta_{\text{ax}}$ (a.u.)	0.707	0.707	0.708	0.708
Spin density ( $e/a_0^3$ ) (C)	0.0708	0.0721	0.0718	0.0685
Spin density ( $e/a_0^3$ ) (H)	-0.0172	-0.0173	-0.0173	-0.0173
Spin multiplicity ( $2S + 1$ )	2.0000	2.0000	2.0005	2.0000

<sup>a</sup>Ref. 51a.

The other example is an extreme case. To describe the molecules shown in Table 8, we used BEBO ("back of envelope bond orbitals"), which means we form appropriate  $sp$ ,  $sp^2$  and  $sp^3$  hybrid orbitals from a minimum basis on C and then make simple bonding and anti-bonding orbitals by taking plus and minus combinations with hydrogen  $1s$  orbitals.<sup>51b</sup> No energy optimization of the orbitals is made. Since we use more than a minimum basis (namely a polarized double zeta basis) in the calculation, the other functions not used in the minimum basis description, after suitable orthogonalizations, are thrown into the  $Q$  space. The poorness of this minimum basis description compared to the full basis SCF is apparent in a

**Table 8.** Summary of CCSD energies (in hartrees) using either canonical SCF or localized BEBO orbitals for water, methane, acetylene, ethylene, and ethane.<sup>a</sup>

Molecule		SCF	BEBO	$\Delta$
H <sub>2</sub> O	$E_{\text{ref}}$	-76.00984	-75.76844	0.24140
	CCSD	-76.15608	-76.15563	0.00045
CH <sub>4</sub>	$E_{\text{ref}}$	-40.20016	-40.01283	0.18733
	CCSD	-40.37221	-40.37326	-0.00105
C <sub>2</sub> H <sub>2</sub>	$E_{\text{ref}}$	-76.82391	-76.61586	0.20805
	CCSD	-77.08558	-77.08447	0.00111
C <sub>2</sub> H <sub>4</sub>	$E_{\text{ref}}$	-78.03950	-77.76405	0.27545
	CCSD	-78.31793	-78.31656	0.00137
C <sub>2</sub> H <sub>6</sub>	$E_{\text{ref}}$	-79.23676	-78.91802	0.31874
	CCSD	-79.53361	-79.53214	0.00147

<sup>a</sup>Ref. 51.

comparison of the reference energies, whose minimum differences of  $> 0.2$  hartrees amounts to  $> 120$  kcal/mol. Despite that, at the CCSD level the largest difference is  $< 1.5$  mhartrees (0.9 kcal/mol), attesting to the power of  $\exp(T_1)$  to correct for poor orbital choices in CCSD.

Some recommend that large values of  $t_i^a$  relative to SCF orbitals, as measured by the Euclidean norm, indicate “multi-reference” character.<sup>52</sup> From the above, it is, instead, preferable to consider such a measure to be indicative of orbital choice. Large ( $> 0.1$  intermediately normalized) amplitudes for other *double excitation* configurations are a more typical indicator for multi-reference problems,<sup>7,94,100</sup> but as that amplitude can change with orbital choice (e.g., for Be with natural orbitals, the amplitude for the  $2p^2$  configuration are larger than for SCF orbitals), there is some synergism between orbital choice and apparent multi-reference character. On the other hand, for Brueckner orbitals  $T_1 = 0$ , so small  $T_1$  amplitudes alone cannot guarantee the absence of multi-reference character (see Refs. 94 and 100 for examples).

Just as in the QRHF examples above, in the treatment of properties other than the energy, the use of unrelaxed orbitals as the molecular orbital basis is often convenient; and by virtue of the implicit orbital rotation

introduced in CCSD, most of the coupled-perturbed Hartree-Fock orbital relaxation is introduced automatically in CCSD.<sup>53</sup> This aspect has been exploited in the treatment of spin-spin coupling constants in ethylene.<sup>54</sup> Orbital relaxation for a perturbation normally requires the solution of the CPHF equations as the first step. However, for the Fermi contact perturbation in spin-spin coupling constants, triplet intermediate states are introduced. Since the CPHF (=RPA,  $\omega = 0$ ) equations are well known to suffer from a triplet instability for many multiply-bonded systems like ethylene, it is impossible to obtain the CPHF solutions for this case due to the singularity in the equations. This failure does not occur for a properly correlated solution, but is, instead, an artifact of CPHF and only affects the calculated results because of the insistence in introducing orbital relaxation via CPHF. Alternatively, we simply use the usual, unrelaxed closed-shell ethylene orbitals (i.e., the QRHF reference) and allow  $\exp(T_1 + T_2)$  in CCSD to simultaneously account for necessary orbital relaxation and correlation effects, which makes it a simple matter to obtain ethylene's spin-spin coupling constants.<sup>54</sup> Further work, using unrelaxed orbitals in spin-spin coupling constants for polycyclic hydrocarbons and for dynamic polarizabilities has been presented elsewhere.<sup>55,56</sup>

In Tables 9–12,<sup>23</sup> we illustrate the behavior of CCSD and various triple excitation augmented CC methods for different reference choices for open-shell molecules.

Table 9 shows results for the singlet-triplet splitting of  $\text{CH}_2$ . The  $^1A_1$  state is closed-shell, so  $\text{ROHF} = \text{UHF} = \text{RHF}$ , but the state manifests some multi-reference character. The open-shell triplet results are closer to the full CI in every case. There is little difference between  $\text{ROHF-CC}$  and  $\text{UHF-CC}$  results, as the  $\text{UHF-CCSD}$  multiplicity of 3.00045, the  $\text{UHF-CCSDT-1}$  value of 3.00014 and the  $\text{UHF-CCSDT}$  multiplicity of 3.000014 would imply. The approximate triple excitation methods reduce the error in the CCSD separation by about a factor of 3, while for CCSDT, the residual error is only 1% of the FCI results. We have also used two-determinant ( $\text{TD-CCSD}$ ) for this problem.<sup>95</sup> This allows for the multi-reference character in the  $^1A_1$  state. It improves the error in the separation to  $<0.14$  kcal/mol without consideration of triples.<sup>95</sup>

In Table 10, we report results for several states of  $\text{CH}_2^+$ . The largest  $\text{UHF-CCSDT}$  multiplicity is 2.000032 for the  $2^2A_1$  state.  $\text{QRHF-CC}$  results are also included. There is little difference due to the reference function at

the CCSD level, and even less for any of the methods that include triple excitations. For CCSDT, the difference with any reference is very small. The ionization potentials relative to  $^1A_1$  CH<sub>2</sub> (Ref. 23, not shown) are within hundredths of an eV, except for the  $2^2A_1$  state, where the CCSD error with

**Table 9.** Difference between  $^3B_1$  CH<sub>2</sub> and  $^1A_1$  CH<sub>2</sub> energies and FCI for various CC methods (mhartree) and energy splitting ( $\Delta E$ ).<sup>a</sup>

Reference <sup>b</sup>	Method	$^3B_1$ CH <sub>2</sub>	$^1A_1$ CH <sub>2</sub>	$\Delta E$ (kcal/mol)
ROHF	CCSD	2.173	3.544	0.86 <sup>b</sup>
ROHF	CCSD(T)	0.404	0.873	0.30
UHF	CCSD	2.090	3.544	0.91
UHF	CCSD(T)	0.360	0.873	0.32
UHF	CCSDT-1	0.352	0.850	0.31
UHF	CCSDT	0.017	0.207	0.12

<sup>a</sup>Ref. 23.

<sup>b</sup>Open-shell reference refers to  $^3B_1$ . For the  $^1A_1$  state, a closed-shell RHF reference is used.

<sup>c</sup>FCI value is 11.971 kcal/mol.

**Table 10.** Differences between FCI and various CC methods for the lowest three states of CH<sub>2</sub><sup>+</sup> (mhartree).<sup>a</sup>

Reference	Method	$1^2A_1$	$2^2A_1$	$2^2B_2$
QRHF	CCSD	1.452	14.026	3.294
QRHF	CCSD(T)	0.559	4.929	0.961
QRHF	CCSDT-1	0.543	5.861	1.061
QRHF	CCSDT	0.023	0.619	0.149
UHF	CCSD	1.673	14.823	3.501
UHF	CCSD(T)	0.367	5.100	0.968
UHF	CCSDT-1	0.365	5.888	0.996
UHF	CCSDT	-0.012	0.739	0.137
ROHF	CCSD	1.699	<sup>b</sup>	3.614
ROHF	CCSD(T)	0.373	<sup>b</sup>	0.955
ROHF	CCSDT-1	0.370	<sup>b</sup>	0.989
ROHF	CCSDT	-0.003	<sup>b</sup>	0.149

<sup>a</sup>Ref. 23.

<sup>b</sup>Variational collapse prohibited the determination of an ROHF reference for this state.

a QRHF or UHF reference is  $\sim 0.3$  eV (22.43 vs. 22.14 eV). At the CCSD(T) level the error is  $\sim 0.1$  eV. CCSDT reduces the error to only 0.01 eV. Of course, treating an *excited*  $2^2A_1$  state with single reference CC is difficult.

Perhaps the most informative examples are those for bond stretching in open-shell molecules. These are shown in Table 11 with mean absolute errors in Table 12. These results are analogous to those presented in Table 1

**Table 11.** Differences between FCI and various CC methods as a function of  $R$  for open-shell molecules (mhartree).<sup>a</sup> ( $2\tilde{S} + 1$  listed in parenthesis).

Reference	Method	1.0 $R_e$	1.5 $R_e$	2.0 $R_e$
$2A''$ CH <sub>3</sub>				
ROHF	CCSD	2.849	8.843	37.322
ROHF	CCSD(T)	0.518	2.113	10.984
ROHF	CCSDT	-0.722	-0.138	4.402
UHF	CCSD	2.790 (2.0005)	8.768 (2.0258)	19.771 (2.1083)
UHF	CCSD + T(CCSD)	0.474	2.230	-32.157
UHF	CCSD(T)	0.499	2.669	-28.908
UHF	CCSDT	-0.744 (2.0000)	-0.108 (2.0023)	1.732 (2.0141)
$2B_1$ NH <sub>2</sub>				
ROHF	CCSD	3.273	8.598	15.341
ROHF	CCSD(T)	0.570	1.732	-2.061
UHF	CCSD	3.211 (2.0004)	9.839 (2.0205)	11.302 (2.8955)
UHF	CCSD + T(CCSD)	0.501	2.809	7.171
UHF	CCSD(T)	0.547	3.772	7.509
UHF	CCSDT-1	0.519	3.735	6.497
UHF	CCSDT	-1.274 (2.0000)	-0.097 (2.0167)	1.142 (2.2301)
$2A_1$ NH <sub>2</sub>				
ROHF	CCSD	3.049	7.918	24.241
ROHF	CCSD(T)	0.550	2.206	11.400
UHF	CCSD	2.992 (2.0002)	7.667 (2.0008)	20.166 (2.2160)
UHF	CCSD + T(CCSD)	0.484	1.930	9.427
UHF	CCSD(T)	0.532	2.192	10.027
UHF	CCSDT-1	0.496	2.116	9.319
UHF	CCSDT	0.223 (2.0000)	0.811 (2.0001)	1.493 (2.0166)
$3B_1$ SiH <sub>2</sub>				
ROHF	CCSD	2.383	8.498	18.815
ROHF	CCSD(T)	0.579	2.680	4.830
UHF	CCSD	2.303 (3.0002)	7.364 (3.0183)	14.340 (3.2819)
UHF	CCSD + T(CCSD)	0.449	2.295	8.052
UHF	CCSD(T)	0.519	2.790	8.146
UHF	CCSDT-1	0.497	2.986	8.241
UHF	CCSDT	-0.029 (3.0000)	0.181 (3.0007)	0.824 (3.0299)

<sup>a</sup> Ref. 23.



**Table 12.** Mean absolute errors for bond stretching examples compared to FCI for various open-shell methods (mhartree).<sup>a</sup>

ROHF-CCSD	11.76
ROHF-CCSD(T)	3.35
ROHF-CCSDT	1.75 <sup>a</sup>
UHF-CCSD	9.21
UHF-CCSD(T)	5.68
UHF-CCSDT-1	3.82 <sup>b</sup>
UHF-CCSDT	0.72

<sup>a</sup>Only ROHF-CCSDT example is  $^2A''$  CH<sub>3</sub>. This example, however, is the most demanding, offering a probable upper bound for the full set of examples, see Table 11.

<sup>b</sup>UHF-CCSDT-1 for  $^2B_1$  NH<sub>2</sub>,  $^2A_1$  NH<sub>2</sub>,  $^3B_1$  SiH<sub>2</sub>.

for closed-shell molecules. The mean errors for CCSD are slightly poorer than in the closed-shell case, 11.76 and 9.21 versus 7.06 mhartrees. This can be largely explained by the more extreme example of CH<sub>3</sub>, where three C–H bonds are stretched simultaneously, which causes a maximum error of 37.3 compared to 21.4 mhartrees for H<sub>2</sub>O. There is some improvement in the mean absolute error for UHF-CCSD, which might be attributed to UHF offering better separation to atoms than ROHF, although this explanation is not supported by the CCSD(T) results. The inclusion of triples using our non-Hartree–Fock generalization of ROHF-CCSD(T)<sup>23</sup> actually behaves relatively well with its mean error of 3.35 compared to 1.15 for the closed-shell examples. The largest error of  $\sim 11$  mhartrees for CH<sub>3</sub> and  $^2A_1$  NH<sub>2</sub> at 2.0  $R_e$  significantly exceeds the 4.63 value for stretched H<sub>2</sub>O. However, the UHF-CCSD(T) results are somewhat poorer, primarily because of the very large (and negative) error for 2.0  $R_e$  stretched CH<sub>3</sub>. The iterative CCSDT-1 method shows some improvement, although closeness to FCI energies is not always a good measure of accuracy. Iterative methods, in particular UHF-CCSDT-1, are known to generally provide better potential energy curves near separation, as occurs for F<sub>2</sub>, than does the non-iterative UHF-CCSD(T).<sup>5</sup>

CCSDT shows the same excellent performance as in the closed-shell examples. The largest error for 2.0  $R_e$  H<sub>2</sub>O of  $-2.47$  mhartrees exceeds in

magnitude any of the UHF-CCSDT errors, even for  $\text{CH}_3$ , although ROHF-CCSDT is poorer for that case despite the large spin contamination in the UHF solution. At  $2.0 R_e$  the UHF  $2\bar{S} + 1$  is 2.69 and at  $1.5 R_e$ , it is 2.30, for example. Per usual, CCSD removes much of the UHF contamination (see multiplicities in Table 11) with CCSDT usually assuming excellent spin eigenfunction character.

Final informative “open-shell” examples are the  $\text{N}_2$  curves in Figs. 2 and 3. When using an RHF reference, breaking the triple bond in  $\text{N}_2$  is difficult, causing even CCSDT to turn over near  $1.9 \text{ \AA}$ . This, of course, is unlike the multi-reference (MR) CI (built from a complete active space (CAS) of 32 spin-adapted configurations, from which all singly and doubly excited configurations lead to 77558 configurations in the MRCI) and properly includes “non-dynamic” correlation.<sup>5</sup> On the other hand, the UHF-based CC methods show good behavior all the way to the separated atom limit, facilitated by the UHF reference correctly separating in this case. The CC results are also better near equilibrium than the MRCI. The spin contamination in the intermediate coupling region is severe, and perturbation

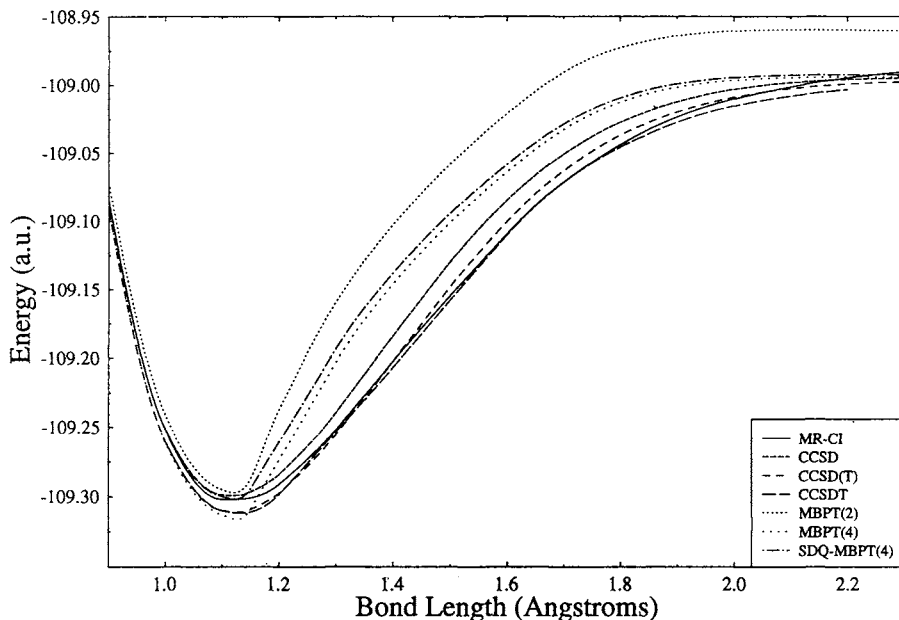


Fig. 2.  $\text{N}_2$  correlated potential curves: UHF reference.

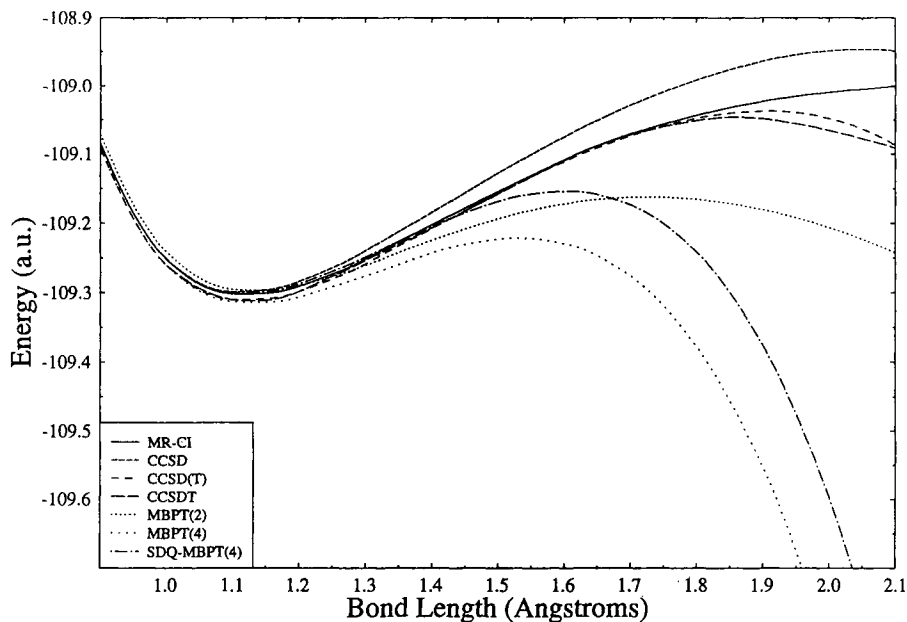


Fig. 3.  $N_2$  correlated potential curves: RHF reference.

theory in particular is usually too slowly convergent to provide reasonable solutions (see the erroneous curvature slightly beyond equilibrium) but CC theory overcomes most of the problem. However, many more iterations are required for convergence, and extreme care must be taken to ensure using the “correct” UHF reference that smoothly connects from point to point. A superior solution for most multiple bond breaking problems would be offered by a multi-reference CC description.<sup>4,57–60</sup> For single bonds, CCSD is usually qualitatively correct and CCSD(T) or CCSDT-1 usually adequate even with an RHF reference.<sup>5</sup>

## 7. Coupled-Cluster Energy Functional

As an alternative derivation of the CC equations, we can consider the “energy functional” of CC theory,<sup>5,32,61</sup> particularly with regard to the treatment of properties including analytical gradients. This is the CC equivalent of the derivation of CI from the Rayleigh–Ritz variational principle, and, as such, offers an informative, useful viewpoint on CC theory.

Allowing for distinct left  $\langle \tilde{\Psi}_{CC} |$  and right  $|\Psi_{CC}\rangle$  eigenvectors, the CC correlation energy functional is

$$\begin{aligned}\Delta\mathcal{E}_{CC} &= \langle \tilde{\Psi}_{CC} | H_N | \Psi_{CC} \rangle / \langle \tilde{\Psi}_{CC} | \Psi_{CC} \rangle, \\ \Delta\mathcal{E}_{CC} &= \langle o | (1 + \Lambda) e^{-T} H_N e^T | o \rangle = \langle o | (1 + \Lambda) \bar{H}_N | o \rangle,\end{aligned}$$

or

$$\Delta\mathcal{E}_{CC}P = P(1 + \Lambda)\bar{H}_NP. \quad (57)$$

The operator  $\Lambda$  is a de-excitation CI-like operator,

$$\begin{aligned}\Lambda &= \Lambda_1 + \Lambda_2 + \Lambda_3 + \dots, \\ \Lambda_1 &= \sum_{i,a} \lambda_a^i \{i^\dagger a\}, \\ \Lambda_2 &= \frac{1}{2!} \sum_{\substack{i,j \\ a,b}} \lambda_{ab}^{ij} \{i^\dagger a j^\dagger b\}, \\ \Lambda_3 &= \frac{1}{3!} \sum_{\substack{i,j,k \\ a,b,c}} \lambda_{abc}^{ijk} \{i^\dagger a j^\dagger b k^\dagger c\}, \\ &\vdots\end{aligned} \quad (58)$$

where all operator products are automatically in normal order. It is CI-like, because, unlike  $T$ , it is not “connected.”<sup>61</sup> That is,  $\Lambda_2$  has disconnected terms in it like  $C_2 = T_2 + T_1^2/2$  does.

Imposing the condition that  $\Delta E$  be stationary with respect to  $\Lambda$ , we have the usual CC equations,

$$0 = Q\bar{H}_NP. \quad (59)$$

This simply follows from recognizing that  $\langle o | \Lambda_a$  creates  $n$ -fold excitations which are the  $n$ -excitation projection equations for CC. Similarly, stationarity with respect to  $T$  yields the  $\Lambda$  equations,

$$0 = P(1 + \Lambda)\bar{H}_NQ - P\Delta E\Lambda Q. \quad (60)$$

Properties follow from a generalized Hellmann–Feynman theorem,

$$\begin{aligned}\frac{\partial \Delta E}{\partial \alpha} &= \Delta E^\alpha = \langle \tilde{\Psi}_{\text{CC}} | H_N^\alpha | \Psi_{\text{CC}} \rangle = \langle o | (1 + \Lambda) e^{-T} H_N^\alpha e^T | o \rangle \\ &= \langle o | (1 + \Lambda) \bar{H}_N^\alpha | o \rangle, \\ \frac{\partial E}{\partial \alpha} &= E_{\text{Ref}}^\alpha + \Delta E^\alpha,\end{aligned}\tag{61}$$

where  $H_N^\alpha$  refers to the total-derivative of the second-quantized Hamiltonian. As such it includes all contributions from MO relaxation and AO changes in it, via terms like  $\langle pq || rs \rangle^\alpha$  and  $f_{pq}^\alpha$  (see later). The stationary conditions in  $\Lambda$  and  $T$  ensure that terms that could potentially arise from  $\langle \tilde{\Psi}_{\text{CC}}^\alpha |$  or  $|\Psi_{\text{CC}}^\alpha \rangle$  do not. Because of the decoupling of  $\Lambda$  and  $T$  in CC theory, we need only determine  $T$  for energies, as seen above, but we will require  $\Lambda$  and  $T$  for properties. We readily have the correlation part of the one- and two-particle *response* densities,

$$\gamma_{pq} = \langle o | (1 + \Lambda) e^{-T} \{p^\dagger q\} e^T | o \rangle, \tag{62a}$$

$$\Gamma_{pqrs} = \langle o | (1 + \Lambda) e^{-T} \{p^\dagger q^\dagger sr\} e^T | o \rangle, \tag{62b}$$

by simply isolating the one- and two-particle parts of the operator,  $H_N^\alpha$ . These densities will play a critical role in the CC treatment of properties and analytical gradients.

The question might arise as to why one should introduce  $\Lambda$  and the functional in Eq. (57). We can offer a more natural introduction of  $\Lambda$  from the usual CC equations.<sup>61</sup> Since

$$\Delta EP = P \bar{H}_N P,$$

$$Q \bar{H}_N P = 0$$

in first order,

$$\begin{aligned}\Delta E^\alpha P &= P [\bar{H}_N^\alpha + (\bar{H}_N T^\alpha)_C] P, \\ Q [\bar{H}_N^\alpha + (\bar{H}_N T^\alpha)_C] P &= 0,\end{aligned}\tag{63}$$

and  $|\Psi^\alpha\rangle = T^\alpha e^T |o\rangle$  defines the first-order perturbation correction in CC theory. Similarly, higher orders like,

$$Q [\bar{H}_N^{\alpha\beta} + (\bar{H}_N^\beta T^\alpha)_C + (\bar{H}_N^\alpha T^\beta)_C + (\bar{H}_N T^{\alpha\beta})_C] P = 0 \tag{64}$$

are readily defined.

We can introduce the usual resolvent operator by exploiting the resolution of the identity,  $1 = P + Q$ , and recognize that  $(\bar{H}_N T^\alpha)_C = [\bar{H}_N, T^\alpha]$  to write

$$\begin{aligned} Q [\bar{H}_N^\alpha + \bar{H}_N(P + Q)T^\alpha - T^\alpha(P + Q)\bar{H}_N] P &= 0 \\ &= Q [\bar{H}_N^\alpha + \bar{H}_N Q T^\alpha P - T^\alpha P \bar{H}_N P] P \\ &= Q [\bar{H}_N^\alpha + \bar{H}_N Q T^\alpha P - \Delta E T^\alpha] P, \end{aligned}$$

and

$$Q T^\alpha P = Q[(\Delta E - \bar{H}_N)^{-1} Q \bar{H}_N^\alpha P = R_o \bar{H}_N^\alpha P], \quad (65)$$

with  $R_o$  the usual resolvent operator of perturbation theory. Substituting into the  $\Delta E^\alpha P$  expression  $Q T^\alpha P$ , we have

$$\Delta E^\alpha P = P \bar{H}_N^\alpha P + P \bar{H}_N R_o \bar{H}_N^\alpha P.$$

Making the identification,  $\Lambda = P \bar{H}_N R_o$ , we obtain Eq. (61). This illustrates the other origin for  $\Lambda$  as introduced in CC gradient theory.<sup>61-64</sup>

By contrast, in CI the analogous steps yield,

$$\begin{aligned} \Delta E_{CI} &= \langle o | C^\dagger H_N C | o \rangle / \langle o | C^\dagger C | o \rangle, \\ \Delta E_{CI} P C^\dagger C P &= P C^\dagger H_N C P, \end{aligned} \quad (66)$$

and the stationary conditions on  $C^\dagger$  and  $C$ ,

$$\begin{aligned} 0 &= Q(H_N C P - \Delta E_{CI} C P), \\ 0 &= (P C^\dagger H_N - \Delta E_{CI} P C^\dagger) Q, \end{aligned} \quad (67)$$

and, with  $C^\dagger$  and  $C$  being related as Hermitian adjoints, we need only know  $C$ . CI also provides an energy upperbound,

$$\Delta E_{CI} P = P H_N C P,$$

and we have the Hellmann-Feynman theorem,

$$\Delta E_{CI}^\alpha \langle \Psi_{CI} | \Psi_{CI} \rangle = \langle \Psi_{CI} | H_N^\alpha | \Psi_{CI} \rangle. \quad (68)$$

Unlike in CI, there is an inherent lack of symmetry in CC theory which is partly responsible for its power. Furthermore,  $\bar{H}_N = e^{-T} H_N e^T$  is not Hermitian, so it has separate left and right eigenvectors.

Hermitian (unitary) forms of CC theory have been considered,<sup>65-67</sup> where  $\tau = T' - T'^{\dagger}$  (the prime indicates that the amplitudes in  $T'$  are different than in  $T$ ), then,

$$\Delta E_{\text{UCC}} = \langle o | e^{\tau^{\dagger}} H e^{\tau} | o \rangle = \langle o | e^{-\tau} H e^{\tau} | o \rangle. \quad (69)$$

However, unlike standard CC, any such expression leads to a non-truncating infinite series of terms, necessitating truncation to obtain viable equations. Such UCC equations, termed UCC( $n$ ) for  $n$ th order truncation, have been derived and illustrated with numerical results including analytical gradients elsewhere.<sup>66,67</sup>

## 8. Coupled-Cluster Treatment of Properties

The starting point for the treatment of all CC properties is the generalized Hellmann-Feynman theorem, Eq. (61).

Consider the derivative of the energy,  $\Delta E^{\alpha} = \frac{\partial \Delta E}{\partial \alpha}$ , with respect to some quantity,  $\alpha$ . In the most general case,  $\alpha = X_{\alpha}$  corresponds to one of the  $3N$  Cartesian nuclear displacements, which leads to expressions for analytical gradients. Our first-quantized Hamiltonian will then contain the perturbation  $h^{\alpha} = \partial h / \partial X_{\alpha} = -\sum_i \partial(Z_{\alpha}/r_{a_i}) / \partial X_{\alpha}$ . In other cases, we might consider the effect of an external electric field ( $\epsilon$ ), so that  $h^{\alpha} = \partial / \partial \epsilon_{\alpha} \left( \sum_i \epsilon \cdot \mathbf{r}_i \right) = \sum_i r_{\alpha i}$ , for  $r_{\alpha}$ , a particular component of the vector. Because we are writing our operators in second-quantization, when we form  $H_N^{\alpha}$  we will also introduce all MO and AO relaxation effects in addition to those for  $h^{\alpha}$ . This will make our expressions exact for finite basis sets.

In terms of the density matrices in Eq. (62),

$$\Delta E^{\alpha} = \sum_{p,q} f_{pq}^{\alpha} \gamma_{pq} + \frac{1}{4} \sum_{p,q,r,s} \langle pq || rs \rangle^{\alpha} \Gamma_{pqrs}. \quad (70)$$

Hence, once  $\Lambda$  and  $\Gamma$  are known, it is easy to evaluate any property. In particular, for a one-particle, first-order property like the dipole moment,  $h^{\alpha} = \theta = \sum_i r_{\alpha i}$ , we would have

$$\bar{\theta} = \langle o | \theta | o \rangle + \sum_{p,q} \theta_{pq} \gamma_{pq}. \quad (71)$$

Now consider the contributions from MO and AO (if any) relaxation via the total derivatives,  $f_{pq}^\alpha$  and  $\langle pq||rs \rangle^\alpha$ . Since any MO  $\varphi_p = \sum_\mu \chi_\mu c_{\mu p}$ , consequently

$$\varphi_p^\alpha = \sum_\mu \chi_\mu^\alpha c_{\mu p} + \sum_\mu \chi_\mu c_{\mu p}^\alpha, \quad (72)$$

where  $\chi_\mu^\alpha = \partial \chi_\mu / \partial \alpha$  would be non-vanishing in the gradient case and other cases where AO's are field dependent, while  $c_{\mu p}^\alpha = \partial c_{\mu p} / \partial \alpha$  corresponds to the change in the MO coefficients with the perturbation. From  $\chi_\mu^\alpha$ , explicit AO derivative terms will arise. For simplicity, since our primary objective here is the introduction of the "relaxed density," a *new* concept that provides a generalization of the density matrix to non-variational methods like CC, with relaxation, we will assume no AO-dependent terms in the following.

Defining Coupled-Perturbed Hartree-Fock (CPHF) coefficients by

$$\frac{\partial c_{\mu q}}{\partial \alpha} = \sum_r U_{rq}^\alpha C_{\mu r}, \quad (73)$$

we have for the MO coefficient part *only*,

$$\frac{\partial f_{pq}}{\partial \alpha} = \sum_r (U_{rp}^\alpha f_{rq} + U_{rq}^\alpha f_{pr}) + \sum_{r,s} U_{rs}^\alpha \delta_{sm} [\langle pr||qs \rangle + \langle ps||qr \rangle], \quad (74)$$

and

$$\frac{\partial \langle pq||rs \rangle}{\partial \alpha} = \sum_t [U_{tp}^\alpha \langle tq||rs \rangle + U_{tq}^\alpha \langle pt||rs \rangle + U_{tr}^\alpha \langle pq||ts \rangle + U_{ts}^\alpha \langle pq||rt \rangle]. \quad (75)$$

With the definition of  $\gamma_{pq}$  and  $\Gamma_{pqrs}$  and making  $U_{pq}^\alpha$  a common factor, we have

$$\begin{aligned} \Delta E^\alpha(\text{orb} - \text{resp}) = & \sum_{p,q} U_{pq}^\alpha \left[ \sum_r f_{pr} \langle o|(1+\Lambda)e^{-T}(\{q^\dagger r\} + \{r^\dagger q\})e^T|o \rangle \right. \\ & + \sum_{r,s} \delta_{qm} (\langle rp||sq \rangle + \langle rq||sp \rangle) \langle o|(1+\Lambda)e^{-T}\{r^\dagger s\}e^T|o \rangle \\ & \left. + \frac{1}{4} \sum_{r,s,t} (\langle pr||st \rangle \langle o|(1+\Lambda)e^{-T}\{q^\dagger r^\dagger ts\}e^T|o \rangle \right] \end{aligned}$$



$$\begin{aligned}
& + \langle rp || st \rangle \langle o | (1 + \Lambda) e^{-T} \{ r^\dagger q^\dagger ts \} e^T | o \rangle \\
& + \langle rs || pt \rangle \langle o | (1 + \Lambda) e^{-T} \{ r^\dagger s^\dagger tq \} e^T | o \rangle \\
& + \langle rs || tp \rangle \langle o | (1 + \Lambda) e^{-T} \{ r^\dagger s^\dagger qt \} e^T | o \rangle \Big] = \sum_{p,q} U_{pq}^\alpha I'_{pq},
\end{aligned} \tag{76}$$

where

$$\begin{aligned}
I'_{pq} = & \sum_r f_{pr} \left( \gamma_{qr}^{(CC-resp)} + \gamma_{rq}^{(CC-resp)} \right) \\
& + \sum_{r,s} \delta_{qm} (\langle rp || sq \rangle + \langle rq || sp \rangle) \gamma_{rs}^{(CC-resp)} \\
& + \frac{1}{4} \sum_{r,s,t} [\langle pr || st \rangle \Gamma_{qrst} + \langle rp || st \rangle \Gamma_{rqst} \\
& + \langle rs || pt \rangle \Gamma_{rsqt} + \langle rs || tp \rangle \Gamma_{rstq}] .
\end{aligned} \tag{77}$$

The next step is to remove the CPHF coefficients. The overlap derivatives which arise in the general case do not arise here, and we have

$$\Delta E^\alpha(orb - resp) = \sum_{p>q} X_{pq} U_{pq}^\alpha, \tag{78}$$

with  $X_{pq} = I'_{pq} - I'_{qp}$ .

Since the  $U_{pq}^\alpha$  satisfy a CPHF-like equation, namely

$$\mathbf{A} \mathbf{U}^\alpha = \mathbf{B}^\alpha, \tag{79}$$

we can use the explicit solution to Eq. (79) to eliminate them. Thus,

$$\Delta E^\alpha(orb - resp) = \sum_{p>q} X_{pq} U_{pq}^\alpha = \mathbf{X}^T \mathbf{U}^\alpha = \mathbf{X}^T \mathbf{A}^{-1} \mathbf{B}^\alpha = \gamma^{(orb-resp)T} \mathbf{B}^\alpha, \tag{80}$$

where the *orbital response* contribution to the density matrix is obtained by solving

$$\gamma^{(orb-resp)T} \mathbf{A} = \mathbf{X}^T. \tag{81}$$

Now, for the molecular property perturbations considered here,  $B_{pq}^\alpha$  is nothing more than  $\theta_{pq}$ . Hence, finally

$$\begin{aligned}\Delta E^\alpha &= \Delta E^\alpha(CC - resp) + \Delta E^\alpha(orb - resp) \\ &= \sum_{p,q} (\gamma_{pq}^{(CC-resp)} + \gamma_{pq}^{(orb-resp)}) \theta_{pq} \\ &= \sum_{p,q} D_{pq} \theta_{pq} .\end{aligned}\tag{82}$$

**D** is the “relaxed-density” matrix for CC/MBPT methods. Once known, all one-electron first-order properties are readily evaluated, including the appropriate orbital relaxation regardless of the particular perturbation. Although it has some formal resemblance to the density matrix of CI methods, it is different in several ways. Most notably it is not defined by  $\langle \Psi | p^\dagger q | \Psi \rangle$  (indeed it may be evaluated for methods with no associated wave function), although it would be equivalent to this in the limit of the exact wave function. Also, it is not necessarily positive definite, meaning that the natural orbital occupation numbers could be negative, but this seldom occurs. Finally, it is not symmetric. The latter is of no particular consequence, since **D** is always combined with a symmetric matrix of one-electron integrals.

CC results compared to those for other methods for a variety of properties are shown in Tables 13–16. All the first order properties; the isotropic hyperfine coupling constants which arise from spin densities (i.e.,  $\theta = \frac{8\pi}{3} g_N g_e \beta_N \beta_e \sum_i 2\hat{S}_{zi} \delta(r_{iN} - R_{iN})$ ); the Darwin  $\left( \theta = \frac{\pi}{2c^2} \sum_{N,j} \delta(r_{Nj}) \right)$

and mass-velocity  $\left( \theta = -\frac{1}{8c^2} \sum_j \nabla_j^4 \right)$  relativistic corrections; and the elec-

tric field gradients  $\left( \theta = q_{z,N} = \sum_i \left( \frac{3z_i^2 - r_{iN}^2}{r_{iN}^5} \right) \right)$  are obtained directly from the “relaxed density” via Eq. (82). Electric polarizabilities, Table 16, a second-order property, are obtained via computing the dipole moment in the presence of a finite field  $\epsilon$  by adding the electric field perturbation to the one-particle Hamiltonian to obtain the induced dipole,  $\mu(\epsilon)$ , from which subsequent numerical differentiation gives the (static) polarizability  $\tilde{\alpha}$  and the hyperpolarizabilities  $\tilde{\beta}$  and  $\tilde{\gamma}$ . Relativistic corrections to dipole moments similarly require a double perturbation method, where the CC energy is computed in the presence of a finite field  $\epsilon$ , and its “relaxed density”

is used to evaluate the Darwin and mass velocity term, from which subsequent differentiation with respect to  $\epsilon$  gives the relativistically corrected dipole. Nuclear quadrupole moments are computed from the electric field gradient,  $q_z$ , and the experimental value for  $eq_zQ$ .

Introducing the AO derivative terms in the above property expression, Eq. (82), and the required overlap derivative, we obtain the more general analytical gradient expression

$$\Delta E^\alpha = \sum_{p,q} D_{pq} f_{pq}^{(\alpha)} + \sum_{p,q,r,s} \Gamma_{pqrs} \langle pq || rs \rangle^{(\alpha)} + \sum_{p,q} I_{pq} S_{qp}^{(\alpha)},$$

where  $f_{pq}^{(\alpha)} = h_{pq}^{(\alpha)} + \sum_m \langle pm || qm \rangle^{(\alpha)}$  depends solely on the AO derivatives, and  $S_{pq}^{(\alpha)} = \sum_{\mu,\nu} c_{\mu p} S_{\mu\nu}^\alpha c_{\nu q}$ .  $I_{pq}$  is closely related to  $I'_{pq}$ . For details, see Ref. 96.

In Table 17, a series of small molecules, whose structure and harmonic frequencies are known, have been studied with most current *ab initio* methods including CC theory. Except for MBPT(2), where analytical Hessians can be used, the harmonic force constants are computed as finite (numerical) differences of analytically computed gradients. All comparisons are

**Table 13.** Isotropic hyperfine coupling constants (in MHz) of first row atoms.<sup>a</sup>

	<sup>11</sup> B( <sup>2</sup> P)	<sup>13</sup> C( <sup>3</sup> P)	<sup>14</sup> N( <sup>4</sup> S)	<sup>17</sup> O( <sup>3</sup> P)	<sup>19</sup> F( <sup>2</sup> P)
Numerical MCSCF <sup>b</sup>	22.2	26.8	10.9	−27.6	261.8
MRSD-CI <sup>c</sup>	6.4	17.8	10.1	−29.1	285.3
UHF	28.37	44.96	20.10	−56.83	526.62
UHF-CCSD(T)	8.19	19.38	10.4	−31.77	300.18
ROHF-CCSD(T)	10.25	21.42	11.00	−33.16	302.87
Experiment	11.6 <sup>d</sup> 18.7 <sup>e</sup>	(21.4) <sup>f</sup> (22.5) <sup>d</sup>	10.4 <sup>g</sup>	34.5 <sup>h</sup>	301.7 <sup>h</sup>

<sup>a</sup>Present calculations use a (23s 12p 10d 4p 2d) even-tempered basis set.<sup>64</sup>

<sup>b</sup>D. M. Chipman, *Phys. Rev. A* **39**, 475 (1989).

<sup>c</sup>D. Feller and E. R. Davidson, *J. Chem. Phys.* **88**, 7580 (1988).

<sup>d</sup>J. S. M. Harvey, L. Evans and H. Lew, *Can. J. Phys.* **50**, 1719 (1972).

<sup>e</sup>W. R. M. Graham and W. Weltner, Jr., *J. Chem. Phys.* **65**, 1516 (1976).

<sup>f</sup>J. R. Macdonald and R. M. Golding, *Theoret. Chim. Acta* **47**, 1 (1978).

<sup>g</sup>W. W. Holloway, Jr., E. Lüscher and R. Novick, *Phys. Rev.* **126**, 2109 (1962).

<sup>h</sup>S. M. Harvey, *Proc. Roy. Soc. London A* **285** 581 (1965). Sign not determined.

Table 14. Relativistic corrections to the dipole moments of diatomic interhalogens ( $^1\Sigma^+$ ) (in a.u.).<sup>a,b</sup>

	ClF	BrF	BrCl	IF	ICl	IBr
RHF + $E^{(1,1)}(\text{SCF})^c$	0.4510	0.6851	0.2287	0.8904	0.5140	0.2961
CCSD	0.3849	0.5928	0.2169	0.8081	0.4676	0.2736
CCSD + $E^{(1,1)}(\text{CCSD})^c$	0.3653	0.5803	0.2064	0.7809	0.4620	0.2635
CCSD(T) + $E^{(1,1)}(\text{CCSD})^c$	0.3540	0.5600	0.1989	0.7556	0.4431	—
Experiment	0.3494 <sup>d</sup>	0.51 <sup>f</sup>	0.204 ± 0.002 <sup>h</sup>	0.766 ± 0.008 <sup>i</sup>	0.49 ± 0.01 <sup>j</sup>	0.290 ± 0.004 <sup>k</sup> 0.286 ± 0.011 <sup>l</sup>

<sup>a</sup>S. A. Perera and R. J. Bartlett, *Chem. Phys. Lett.* **216**, 606 (1993).

<sup>b</sup>Results are based on  $[5s\ 3p\ 2d]$  basis for F from A. J. Sadlej, *Collect. Czech. Chem. Commun.* **53**, 1995 (1988),  $[7s\ 5p\ 2d]$  basis for Cl from A. J. Sadlej, *Theoret. Chim. Acta* **79**, 123 (1991),  $[9s\ 7p\ 4d\ 2f]$  basis for Br from *Theoret. Chim. Acta* **81**, 45 (1992) and  $[11s\ 9p\ 6d\ 2f]$  basis for I from *Theoret. Chim. Acta* **81**, 339 (1992).

<sup>c</sup> $E^{(1,1)}(\text{SCF})$  and  $E^{(1,1)}(\text{CCSD})$  denotes the relativistic corrections to the dipole moment at the Hartree-Fock level and coupled-cluster level respectively.

<sup>d</sup>R. E. Davis and J. S. Muentzer, *J. Chem. Phys.* **57**, 2836 (1972).

<sup>e</sup>J. J. Ewing, H. L. Tigelaar and F. H. Flygare, *J. Chem. Phys.* **56**, 1957 (1972).

<sup>f</sup>D. F. Smith, M. Tidwell and D. V. P. Williams, *Phys. Rev.* **77**, 420 (1950).

<sup>g</sup>K. P. R. Nair, J. Hoefl and E. Tiemann, *J. Mol. Struct.* **78**, 506 (1979).

<sup>h</sup>K. P. R. Nair, J. Hoefl and E. Tiemann, *Chem. Phys. Lett.* **58**, 153 (1978).

<sup>i</sup>K. P. R. Nair, J. Hoefl and E. Tiemann, *Chem. Phys. Lett.* **60**, 253 (1979).

<sup>j</sup>E. Herbst and W. Steinmetz, K. P. R. Nair, J. Hoefl and E. Tiemann, *J. Chem. Phys.* **56**, 5342 (1972).

<sup>k</sup>E. Tiemann and A. Dreyer, *Chem. Phys.* **23**, 231 (1977).

<sup>l</sup>K. P. R. Nair and J. Hoefl, *J. Mol. Struct.* **79**, 227 (1982).

**Table 15.** Nuclear quadrupole moments ( $Q$  in barns) of several atoms from  $eqQ$ , where  $q$  is the electric field gradient at the nucleus.<sup>a</sup>

	<sup>9</sup> Be( <sup>3</sup> P)	<sup>11</sup> B( <sup>2</sup> P)	<sup>11</sup> C( <sup>3</sup> P)	<sup>17</sup> O( <sup>3</sup> P)	<sup>25</sup> Mg( <sup>3</sup> P)
Numerical MCHF	0.05288 <sup>b</sup>	0.04059 <sup>c</sup>	0.03327 <sup>d</sup>	-0.02558 <sup>d</sup>	0.19942 <sup>e</sup>
UHF <sup>f</sup>	0.05384	0.03826	0.03200	-0.02622	0.19510
UHF-CCSD(T) <sup>f</sup>	0.05284	0.04054	0.03338	-0.02581	0.19397
Experiment	—	0.0355 <sup>g</sup>	—	—	0.1964 <sup>h</sup>

<sup>a</sup>Results are obtained from the experimental nuclear quadrupole coupling constant and calculated electric field gradients using the expression  $Q = \frac{e^2 q Q / h}{234.9647 q}$ , where  $q$  is the electric field gradient in a.u.,  $e$  is the electronic charge (in C) and  $Q$  is the nuclear quadrupole moment (in barns) respectively.

<sup>b</sup>D. Sundholm and J. Olsen, *Chem. Phys. Lett.* **177**, 91 (1991).

<sup>c</sup>D. Sundholm and J. Olsen, *J. Chem. Phys.* **94**, 5051 (1991).

<sup>d</sup>D. Sundholm and J. Olsen, *J. Phys. Chem.* **96**, 627 (1992).

<sup>e</sup>D. Sundholm and J. Olsen, *Phys. Rev. Lett.* **68**, 929 (1992).

<sup>f</sup>Be results use a (14s 9p 9d 1f) basis set and B, C, N and O results were obtained using (16s 11p 12d 5f 1g) basis set. Magnesium results use a (18s 13p 13d 3f 1g) basis set. Detailed description of basis sets and theoretical methods are given in S. A. Perera and R. J. Bartlett, to be published, *Phys. Rev.* In each case relativistic corrections at CCSD level were evaluated as in Table 14.

<sup>g</sup>G. Wessel, *Phys. Rev.* **A92**, 1581 (1953).

<sup>h</sup>D. Schwalm, E. K. Warburton and J. M. Olness, *Nucl. Phys.* **A293**, 425 (1977).

**Table 16.** Dipole polarizabilities (a.u.) for molecules.<sup>a,b</sup>

	CO <sub>2</sub>		N <sub>2</sub>		C <sub>2</sub> H <sub>4</sub>		CO	
	$\bar{\alpha}^a$	$\Delta\alpha^b$	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$
SCF	15.8	12.1	11.4	5.4	28.0	12.6	12.2	3.4
MBPT(2)	17.9	15.0	11.5	4.4	27.4	10.2	13.1	3.9
CCSD	17.4	14.4	11.6	4.8	26.9	10.7	12.9	4.0
CCSD(T)	17.6	14.5	11.8	4.9	27.1	10.5	13.0	3.9
Expt.	17.5	13.8	11.8	4.7	28.7	11.0	13.1	3.7
	HF		H <sub>2</sub> O		NH <sub>3</sub>		H <sub>2</sub> S	
	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$
SCF	4.9	1.3	8.5	1.1	12.9	0.5	23.6	0.4
MBPT(2)	5.7	1.1	9.8	0.4	14.4	1.9	24.5	0.9
CCSD <sup>c</sup>	5.6	1.2	9.6	0.6	14.1	1.7	24.3	0.9
Expt.	5.5	1.3	9.8	0.6	14.6	1.9	25.5	—

<sup>a</sup>H. Sekino and R. J. Bartlett, *J. Chem. Phys.* **98**, 3022 (1993).

<sup>b</sup>The POL1 basis is defined by A. J. Sadlej, *Theoret. Chim. Acta* **79**, 123 (1991).

<sup>c</sup>CCSD(T) results in an augmented POL1 basis are in Ref. a, above.

**Table 17.** Differences between theoretical and experimental harmonic frequencies for several small molecules (DZP basis except where indicated).

			DZP Basis							TZ2Pf Basis
		Expt. <sup>c</sup>	SCF <sup>a</sup>	CISD <sup>a</sup>	MBPT(2) <sup>b</sup>	SDQ- MBPT(4) <sup>b</sup>	CCSD <sup>a</sup>	MBPT(4) <sup>b</sup>	CCSD(T) <sup>c</sup>	CCSD(T) <sup>d</sup>
H <sub>2</sub> O	$\omega_1$	3832	332	135	77	89	80	73	64	20
	$\omega_2$	1649	102	44	15	33	34	26	28	13
	$\omega_3$	3943	344	147	112	107	98	92	83	19
NH <sub>3</sub>	$\omega_1$	3506	218	91	67	56	45	40	27	4
	$\omega_2$	1022	97	98	78	97	97	99	100	70
	$\omega_3$	3577	295	165	164	135	123	121	107	56
	$\omega_3$	1691	111	204	12	27	25	20	18	4
CH <sub>4</sub>	$\omega_1$	3026	148	90	86	71	61	62	50	26
	$\omega_2$	1583	88	18	11	5	3	-1	-4	3
	$\omega_3$	3157	137	100	117	85	73	77	63	13
	$\omega_4$	1367	90	30	16	20	18	14	11	-7
C <sub>2</sub> H <sub>2</sub>	$\omega_1$	3497	84	94	54	53	41	30	22	17
	$\omega_2$	2011	194	70	-58	3	8	-60	-29	-1
	$\omega_3$	3415	162	77	49	40	28	23	10	1
	$\omega_4$	624	146	-4	-78	-58	-61	-109	-106	-25
	$\omega_5$	747	116	22	-16	-10	-13	-35	-37	12
H <sub>2</sub> CO	$\omega_1$	2978	171	102	62	47	51	19	26	-25
	$\omega_2$	1778	228	99	-8	28	41	-26	3	0
	$\omega_3$	1529	127	71	39	41	44	19	30	13
	$\omega_4$	1191	144	56	23	21	20	4	1	-11
	$\omega_5$	2997	229	165	132	108	113	78	88	23
	$\omega_6$	1299	68	11	-18	-14	-12	-30	-24	-23
HCN	$\omega_1$	3440	196	109	64	61	53	35	31	10
	$\omega_2$	2128	276	96	-131	-15	17	-119	-25	-2
	$\omega_3$	727	131	35	-11	0	-1	-28	-35	-4
CO <sub>2</sub>	$\omega_1$	1354	159	75	-28	-10	25	-95	-13	-3
	$\omega_2$	2397	193	116	59	27	51	-28	-12	-4
	$\omega_3$	673	94	37	-17	-2	9	-38	21	-10
C <sub>2</sub> H <sub>4</sub>	$\omega_1$	3139	191		108	172		159		34
	$\omega_2$	1655	165		44	57		32		20
	$\omega_3$	1371	101		21	21		6		4
	$\omega_4$	1047	87		18	5		-5		5
	$\omega_5$	3212	183		120	99		7		23
	$\omega_6$	1245	94		15	20		10		11
	$\omega_7$	968	113		-9	-12		-29		0
	$\omega_8$	959	130		-148	-130		-172		-5

Table 17. (Continued)

		DZP Basis							TZ2Pf Basis
	Expt. <sup>c</sup>	SCF <sup>a</sup>	CISD <sup>a</sup>	MBPT(2) <sup>b</sup>	SDQ- MBPT(4) <sup>b</sup>	CCSD <sup>a</sup>	MBPT(4) <sup>b</sup>	CCSD(T) <sup>c</sup>	CCSD(T) <sup>d</sup>
C <sub>2</sub> H <sub>4</sub>	$\omega_9$	3234	187	126	105		92		22
	$\omega_{10}$	843	47	-12	-10		-18		-14
	$\omega_{11}$	3138	165	85	72		57		14
	$\omega_{12}$	1473	113	33	40		30		13
% Error		8.7	3.7	3.2	2.5	2.2	3.1	2.4	0.9

<sup>a</sup>B. H. Besler, G. E. Scuseria, A. C. Scheiner and H. F. Schaefer III, *J. Chem. Phys.* **89**, 360 (1988).

<sup>b</sup>J. F. Stanton, J. D. Watts and R. J. Bartlett, *J. Chem. Phys.* **94**, 404 (1991).

<sup>c</sup>J. R. Thomas, J. B. DeLeeuw, G. Vacek and H. F. Schaefer III, *J. Chem. Phys.* **98**, 1336 (1993).

<sup>d</sup>S. Gwaltney and R. J. Bartlett, *J. Chem. Phys.* **99**, 3151 (1993), for the linear molecules. The others are obtained for this table.

to experimentally extracted harmonic frequencies, so questions of anharmonicity do not confuse the issue.

## 9. Excited States

The next important element in CC theory concerns excited states and UV-vis spectra. Multi-reference approaches based upon Fock space and Hilbert space considerations<sup>57-60</sup> are applicable to this problem, but perhaps the simplest, widely applicable method is the equation-of-motion (EOM-CC) approach.<sup>68-72</sup> Unlike the above, this method is single-reference in concept. EOM-CC is essentially equivalent to what is sometimes called CC linear response theory (CCLR),<sup>74-77</sup> but it suggests different approximations. It is also *conceptually* the same as what has been called symmetry-adapted-cluster CI, i.e., (SAC)-CI,<sup>78</sup> but the latter introduces several approximations that are not made in EOM-CC.

In EOM-CC, the reference state, which is not necessarily the ground state, is described by CC theory. The fundamental idea of EOM-CC is to describe the *k*th excited state wave function as being created from the ground (or reference) state by using an excitation operator  $\mathcal{R}_k$ , defined as a sum of single, double, etc. excitation operators:

$$\mathcal{R}_k = \sum_m r_m(k) q_m^\dagger = r_0(k) + \sum_{i,a} r_i^a(k) \{a^\dagger i\} + \sum_{\substack{i < j \\ a < b}} r_{ij}^{ab}(k) \{a^\dagger i b^\dagger j\} + \dots, \quad (83)$$

i.e., a CI-like description. Amplitudes are to be determined via the EOM-CC equations. In this way, most of the correlation effects that are common to the ground and excited states are conveniently handled, allowing the excited state description to primarily focus on the essential differential correlation effects.

The Schrödinger equation for the excited state

$$H_N|\Psi_k\rangle = \Delta E_k|\Psi_k\rangle,$$

can then be written

$$H_N\mathcal{R}_k|\Psi_0\rangle = H_N\mathcal{R}_ke^T|0\rangle = \Delta E_k\mathcal{R}_ke^T|0\rangle. \quad (84)$$

Multiplying the reference state solution  $H_N|\Psi_0\rangle = \Delta E_0|\Psi_0\rangle$  by  $\mathcal{R}_k$  and subtracting from Eq. (84) yields the EOM,

$$[H_N, \mathcal{R}_k]|\Psi_0\rangle = \omega_k\mathcal{R}_k|\Psi_0\rangle, \quad (85)$$

where  $\omega_k = \Delta E_k - \Delta E_0$  is the excitation energy.

Since they both consist entirely of excitation operators,  $e^T$  and  $\mathcal{R}_k$  commute. Multiplying Eq. (85) by  $e^{-T}$  gives

$$[(e^{-T}H_Ne^T), \mathcal{R}_k]|0\rangle = \omega_k\mathcal{R}_k|0\rangle.$$

The similarity transformed Hamiltonian,  $\bar{H}_N$ , has been discussed above in Secs. 2 and 3. It is manifestly connected, and exactly terminates after four  $T$  operators regardless of the number of electrons. The only terms that can survive in the commutator are the contractions between  $\bar{H}_N$  and  $\mathcal{R}_k$ , or  $(\bar{H}_N\mathcal{R}_k)_C$ , so we have

$$(\bar{H}_N\mathcal{R}_k)_C|0\rangle = \omega_k\mathcal{R}_k|0\rangle. \quad (86)$$

In this way, the open part of  $\bar{H}_N$  (the closed part is just  $\Delta E$ , which disappears from the commutator) is treated as a generalized, second-quantized operator that can be written as a sum of one-body, two-body, and higher interactions:

$$\begin{aligned} \bar{H}_N = & \sum_{p,q} \bar{f}_{pq} \{p^\dagger q\} + \frac{1}{2!} \sum_{\substack{p,q \\ r,s}} \langle \overline{pq||rs} \rangle \{p^\dagger q^\dagger sr\} \\ & + \frac{1}{3!} \sum_{\substack{p,q,r \\ s,t,u}} \langle \overline{pqr||stu} \rangle \{p^\dagger q^\dagger r^\dagger uts\} + \dots \end{aligned} \quad (87)$$



The  $\bar{f}$  and  $\langle \bar{\parallel} \rangle$  integrals are modified or “dressed” versions of ordinary Fock matrix elements and two-electron integrals,<sup>70,75,79</sup> whose specific expressions in terms of intermediates composed of two-electron integrals and  $T$  amplitudes taken from the reference state CC calculation are presented elsewhere.<sup>72</sup> The “three-body” form is similarly indicated. For calculations limited to single and double excitations, i.e., EOM-CCSD, nothing contributes beyond the three-body terms.

From the definition, it is clear that  $\bar{H}_N$  is a non-Hermitian operator, so it has left  $\mathcal{L}$  and  $\mathcal{R}$  eigenvectors,<sup>80</sup>

$$\langle 0 | \mathcal{L}_k \bar{H}_N = \omega_k \langle 0 | \mathcal{L}_k, \quad (88)$$

with the same eigenvalues.  $\{\mathcal{L}_k\}$  and  $\{\mathcal{R}_k\}$  form a set of biorthogonal eigenvectors  $\langle \mathcal{L}_k | \mathcal{R}_l \rangle = \lambda_k \delta_{kl}$  and we are free to choose  $\lambda_k = 1$ . Both  $\{\mathcal{L}_k\}$  and  $\{\mathcal{R}_k\}$  are required to evaluate transition moments and other properties.<sup>72</sup>

Equations (86) and (88) can be converted to a non-Hermitian CI-like eigenvalue problem

$$\bar{H}_N \mathbf{R}_k = \omega_k \mathbf{R}_k,$$

$$\mathbf{L}_k \bar{H}_N = \mathbf{L}_k \omega_k.$$

$\mathbf{R}_k$  and  $\mathbf{L}_k$  represent the vectors of coefficients for the chosen excitations. Eigenvalues and eigenvectors of  $\bar{H}_N$  can be determined using a non-Hermitian modification of Davidson’s method.<sup>81</sup>

Since the CC amplitudes are solutions,  $(\bar{H}_N)_{QP} = 0$ , the first column of  $\bar{H}_N$  consists of zeroes, which means the excited state solutions do not interact with the ground state, permitting the excitation energies to be directly evaluated from the sub-matrix  $(\bar{H}_N)_{QQ}$ . Notice  $r_0(k)$  is irrelevant for the energy determination. The left eigenvector for the reference state is  $\mathcal{L}_0 = 1 + \Lambda$ , which is exactly that from CC analytical gradient theory as previously discussed, while  $\mathcal{L}_k = \Lambda_k$ ,  $k > 0$ . Consequently, EOM-CC excited states can be obtained as a by-product of a CC analytical gradient program.<sup>71,96</sup> The connection with gradients becomes more evident when considering the response to a time (frequency) dependent oscillating electric field via the time-dependent Schrödinger equation.<sup>74,77,82</sup>

EOM-CCSD is clearly exact (i.e., the full CI) for two electrons, but as will be pointed out in the numerical section, results are much better for states dominated by single excitations.

### 9.1. Comparison with Exact Results

Beryllium provides a useful test case because excited state full CI numbers are available for comparison.<sup>83</sup> We previously reported EOM-CCSD excited state results for Be, singlets and triplets, as a test for a partitioned form of the full EOM-CCSD equations and with Fock space MRCCSD.<sup>70</sup> See Refs. 79 and 84 for a description of the MRCCSD theory. Others have considered the EOM-CCSD = CCSDLR singlet excitations, but in a slightly different (6 *d*-functions with no *s*-virtual dropped) basis<sup>77</sup> and the corresponding FCI.<sup>85</sup> The singlet and triplet excitation energies are compared with the full CI in Tables 18 and 19.

The comparison between the EOM-CC and full CI numbers seen in Tables 18 and 19 is remarkable, though Be with only two valence electrons is not the most challenging example. With the exception of the double excitation  $2s^2 \rightarrow 2p^2$ , the EOM-CCSD energies are all within 0.03 eV from the full CI values. Most excitations are within 0.01 eV. Even the double excitation value is within 0.1 eV.

**Table 18.** Be singlet excitation energies (in eV).<sup>a</sup>

	CISD	MR-CCSD <sup>b</sup>	EOM-CCSD	Full CI <sup>c</sup>	Expt.
$2s2p \ ^1P^0$		5.40	5.323	5.318	5.277
$2s3s \ ^1S$	7.383	6.87	6.773	6.765	6.779
$2p^2 \ ^1D$	7.710	—	7.139	7.089	7.05
$2s3p \ ^1P^0$		7.50	7.465	7.462	7.462
$2s3d \ ^1D$	8.658	7.80	8.059	8.034	7.988
$2s4s \ ^1S$	8.697	8.12	8.078	8.076	8.089
$2s4p \ ^1P^0$		8.34	8.309	8.302	8.311
$2s4d \ ^1D$	9.159	8.48	8.547	8.536	8.527
$2s5s \ ^1S$	9.221	8.62	8.583	8.600	8.595
$2s5p \ ^1P^0$		8.72	8.700	8.693	8.694
average deviation	0.621 <sup>d</sup>	0.07	0.016	0.000	0.018

<sup>a</sup>[9s 9p 5d] basis set. Used five components of *d* functions.

<sup>b</sup>Ref. 70. MRCCSD is the Fock space multi-reference method.<sup>84</sup>

<sup>c</sup>Ref. 83.

<sup>d</sup>The large error is due to the lack of adequate core correlation in the excited states.<sup>86</sup> If the core 1s is frozen, this error nearly vanishes, as only a two-electron system is being described. Note that EOM-CCSD does not have this problem.

Table 19. Be triplet excitation energies (in eV).

	MR-CCSD <sup>a</sup>	"Closed-shell" EOM-CCSD <sup>b</sup>	Open-shell EOM-CCSD <sup>c</sup>	Full CI <sup>e</sup>	Expt. <sup>e</sup>
$2s2p\ ^3P^0$	2.80	2.729	2.723 <sup>d</sup>	2.733	2.725
$2s3s\ ^3S$	6.49	6.447	6.433 <sup>d</sup>	6.444	6.457
$2s3p\ ^3P^0$	7.35	7.301	7.290	7.295	7.303
$2p^2\ ^3P^e$	—	7.510	7.414	7.423	7.401
$2s3d\ ^3D$	7.78	7.748	7.730	7.741	7.694
$2s4s\ ^3S$	8.01	7.991	7.973	7.985	7.998
$2s4p\ ^3P^0$	8.34	8.278	8.267	8.272	8.283
$2s4d\ ^3D$	8.47	8.456	8.437	8.449	8.423
$2s5s\ ^3S$	8.58	8.566	8.548	8.560	8.556
$2s5p\ ^3P^0$	8.70	8.691	8.681	8.686	8.688
$2s6s\ ^3S$	8.92	8.893	8.874	8.886	8.823
average deviation	0.038	0.013	0.009	0.000	0.023

<sup>a</sup>Ref. 70.

<sup>b</sup>Used  $2s^2\ ^1S$  ground state reference.

<sup>c</sup>For  $^3S$  and  $^3D$  states, used  $2s3s\ ^3S$  reference. For  $^3P$  states, used  $2s2p\ ^3P^0$  reference.

<sup>d</sup>Difference between coupled-cluster energy for the listed state and coupled-cluster ground state energy.

<sup>e</sup>Ref. 83.

Despite ground state Be being a closed-shell atom, to demonstrate application to open shells we can still calculate "excitation" energies using an excited state as the reference. Excitation energies using the  $2s2p\ ^3P^0$  and  $2s3s\ ^3S$  excited states as the coupled-cluster reference states relative to a UHF single reference (an ROHF reference causes only a slight difference) appear in Table 19 in the column labeled "open-shell EOM-CC." These numbers compare very well with the ordinary "closed-shell EOM-CC" results. On average, the "open-shell" numbers show a slightly smaller average error (0.009) that is primarily caused by the superior description of the  $2p^2\ ^3P^e$  double excitation state, as it is a single excitation relative to the  $2s2p\ ^3P^0$  reference. Clearly, the energies calculated from different reference states are consistent, providing great flexibility in their choice.

EOM-CCSD describes the excited states in a CI-like expansion. Once the expansion is truncated, just like for ground states, certain categories of unlinked diagrams can remain in the CI-like excited states.<sup>86</sup> On the

other hand, the (Fock space) MRCCSD results come from a fully linked theory. The latter has advantages for larger molecules due to its entirely linked diagram structure,<sup>86</sup> as it is a completely exponential-operator-based method, but the multi-reference space consists of only single excitations with the double excitation effects being introduced via the wave operator. EOM-CCSD has the advantage that all double excitations are explicitly introduced so they can be more properly weighted in the final excited state wave function. Generalization to a multi-reference space that contains singles and doubles (i.e., through the (2,2) sector of Fock space) would have similar flexibility and a fully linked structure.

For situations like  $AB \rightarrow A + B$ , excited states of  $AB$  go smoothly into excited states on  $A$  or on  $B$ . This is a size-consistency property that has also been called size-intensive.<sup>77</sup> However, for all excited states to correspond to a purely linked expression, which is the definition of (size)-extensivity, there must also be a smooth transition to charge transfer states, and these require excitations that correspond to those on  $A^+$  and  $B^-$  in the limit. These are not necessarily correct in the non-interacting limit in EOM-CC = CCLR theory.<sup>86</sup>

Below, we will also consider approximate excitation levels (AEL) that act as a measure of the number of electrons that are excited from the CCSD ground state (i.e., not the SCF orbitals). The AEL is defined by the equation

$$\text{AEL} = \frac{1}{2} \sum_p |\gamma_{pp}^k - \gamma_{pp}^o|, \quad (89)$$

where both the ground ( $o$ ) and excited ( $k$ ) reduced density matrices are expressed in the quasiparticle approximate natural orbital basis that diagonalizes the ground state CC density.<sup>73</sup> The AEL would be exactly one for a state that is described by only single excitations. Hence, AEL values significantly larger than unity should be regarded with a certain amount of suspicion since the parametrization of the excited state wave function is constrained for states with significant double replacement character. This is due to the nature of the double-excitation component of the  $\mathcal{L}$  and  $\mathcal{R}$  vectors, which acts to expand the space available to the wave function beyond that spanned by the singly excited quasiparticle states

$$a^\dagger i \exp(T) |\Psi_o\rangle. \quad (90)$$

This provides important flexibility for describing transitions that are well described by single excitations. However, within the singles and doubles

implementation of the EOM-CC methods studied here, no such flexibility is available for describing doubly excited states, since triple-excitation operators in  $\mathcal{L}$  and  $\mathcal{R}$  would be required for this purpose, and have been.<sup>93,97</sup>

## 9.2. EOM-CC for Properties and Oscillator Strengths

With the aid of EOM-CC ideas, one can offer an alternative treatment of second-order properties,<sup>55</sup> like the polarizability results presented in Table 16. Since the CC energy functional, Eq. (57), is

$$\Delta\mathcal{E} = P(1 + \Lambda)\bar{H}_N P, \quad (91)$$

its energy derivative with respect to  $\alpha$  is

$$\Delta E^\alpha = P(1 + \Lambda)\bar{H}_N^\alpha P, \quad (92)$$

where  $\bar{H}_N^\alpha = e^{-T} H_N^\alpha e^T$ , and  $H_N^\alpha$  is the derivative of the second-quantized Hamiltonian.

The second derivative  $E^{\alpha\beta}$  depends upon  $\Lambda^\alpha$  and  $T^\alpha$ , as well as  $H_N^{\alpha\beta}$ . For the dipole polarizability, e.g., where  $h^\alpha = \sum_i r_{\alpha i}$ , and  $h^\beta = \sum_i r_{\beta i}$ , there is no  $h^{\alpha\beta}$  term. There would be an  $H_N^{\alpha\beta}$  term deriving from MO changes, however. Hence,

$$\Delta E^{\alpha\beta} P = P\Lambda^\beta \bar{H}_N^\alpha P + P(1 + \Lambda)[\bar{H}_N^\alpha, T^\beta] P + P(1 + \Lambda)\bar{H}_N^{\alpha\beta} P. \quad (93)$$

Using the  $\Lambda$  equation, Eq. (60), and the  $T$  equation  $Q\bar{H}_N P = 0$ , differentiation plus liberal use of the resolution of the identity  $1 = P + Q$ , provides

$$QT^\beta P = Q(\Delta E - Q\bar{H}_N Q)^{-1} Q\bar{H}_N^\beta P = R_0 \bar{H}_N^\beta P, \quad (94)$$

$$P\Lambda^\beta Q = P(1 + \Lambda)Q\{[\bar{H}_N, T^\beta] + \bar{H}_N^\beta - \Delta E^\beta\} R_0. \quad (95)$$

Insertion into Eq. (93) and substantial further simplification<sup>56a</sup> leads to

$$\begin{aligned} \Delta E^{\alpha\beta} P &= P(1 + \Lambda)(\bar{H}_N^\alpha - \Delta E^\alpha)T^\beta P \\ &\quad + P(1 + \Lambda)(\bar{H}_N^\beta - \Delta E^\beta)T^\alpha P \\ &\quad + P(1 + \Lambda)Q(\bar{H}_N - \Delta E)T^\alpha T^\beta P. \end{aligned} \quad (96)$$

If we choose to ignore MO (and AO, if any) relaxation, in the limit of a complete space, the quadratic  $T^\alpha T^\beta$  term disappears, since Eq. (60) for  $\Lambda$

is satisfied, and we can exclude that term. Then, introducing  $R_0$  in terms of our left and right EOM ground  $\Psi_0$  and excited  $\Psi_k$  states,

$$\Delta E^{\alpha\beta} = \left\{ \sum_{k \neq 0} (\langle \tilde{\Psi}_0 | h^\alpha | \Psi_k \rangle \langle \tilde{\Psi}_k | h^\beta | \Psi_0 \rangle + \langle \tilde{\Psi}_0 | h^\beta | \Psi_k \rangle \langle \tilde{\Psi}_k | h^\alpha | \Psi_0 \rangle) / \omega_{k0} \right\}.$$

In this way, we obtain the familiar sum over state (SOS) expression for second-order properties for which  $\alpha_{xy} = 2\Delta E^{xy}$ , for example. The analogous time-dependent development will similarly lead to the dynamic polarizability, which introduces a frequency,  $\pm\omega$ , to the denominator, to obtain the frequency-dependent polarizability, e.g.,

$$\alpha_{xy}(\omega) = 2 \left\{ \sum_{k \neq 0} \left( \frac{\langle \tilde{\Psi}_0 | x | \Psi_k \rangle \langle \tilde{\Psi}_k | y | \Psi_0 \rangle}{\omega_{k0} + \omega} + \frac{\langle \tilde{\Psi}_0 | y | \Psi_k \rangle \langle \tilde{\Psi}_k | x | \Psi_0 \rangle}{\omega_{k0} - \omega} \right) \right\}. \quad (97)$$

It is well known that the proper definition of the oscillator strength is the residue when  $\omega = \omega_{k0}$ . Hence, from Eq. (97) we have the definition of the dipole strength as

$$D_{k0} = \langle \tilde{\Psi}_0 | \mathbf{r} | \Psi_k \rangle \langle \tilde{\Psi}_k | \mathbf{r} | \Psi_0 \rangle, \quad (98)$$

from which the oscillator strength is

$$f_L = \frac{2}{3} \omega_{k0} D_{k0}.$$

Note that the transition moment is not well defined, although the actual observable, the dipole strength, is. In this way, Eq. (98) provides a CI-like approximation for oscillator strengths. In practice, the space of configurations is not complete. Consequently, the quadratic  $T^\alpha T^\beta$  term in Eq. (96) cannot be ignored. As all derivatives of the CC functional manifest proper linkedness, polarizabilities and oscillator strengths from Eq. (96) are properly extensive and intensive, respectively. However, this is not shared by the CI-like approximation, although for a *single* molecule the results are close numerically. Similar considerations apply to ordinary (non-transition) properties evaluated in EOM-CC theory.<sup>98</sup>

As a test of the accuracy of oscillator strengths obtained within the framework presented here, calculations are presented in Table 3 for the two

systems for which full configuration interaction (FCI) results are available — the beryllium atom and the  $\text{CH}^+$  molecule. The two values shown are based on the CI-like approximation to Eq. (96) and including the quadratic term.<sup>87</sup>

For beryllium, excitation energies and dipole transition strengths obtained in the present calculations are in nearly perfect agreement with the FCI results, and there is little difference between the two results.

A more difficult test is provided by the  $\text{CH}^+$  molecule, which contains more electrons and exhibits strong nondynamical electron correlation effects in its ground electronic state via interaction of the  $1\sigma^2 2\sigma^2 3\sigma^2$  and  $1\sigma^2 2\sigma^2 1\pi^2$  electronic configurations. Due to this important configuration mixing, one expects some of the low-lying electronic states to have appreciable double-excitation character, as confirmed by the AEL values listed in the rightmost column of Table 20. It can be seen that the closest coincidence of FCI and EOM-CCSD results for excitation energies and oscillator strengths occurs for the transitions near 3.2 and 13.5 eV, which both have associated AEL values below 1.1. Differences between FCI and EOM-CCSD dipole strengths for transitions to the third  $^1\Sigma^+$  and second  $^1\Pi$  state are larger (error of 5.26% (AEL = 1.13) and 17.69% (AEL = 1.24), respectively). The quantitative agreement between FCI and EOM-CCSD

**Table 20.** EOM-CCSD and full configuration interaction excitation energies and dipole strengths for the lowest optically allowed transitions in  $\text{CH}^+$  and the beryllium atom.<sup>72</sup> Also listed are the approximate excitation levels (AEL) for each process. The basis sets used in these calculations are discussed in Ref. 72.

Final state	Excitation energy (eV)		Dipole strength (a.u.)			AEL <sup>b</sup>
	EOM-CCSD	FCI	CI-Approx.	Derivative Value <sup>d</sup>	FCI	
Be <sup>b</sup>	$1^1P(2s2p)$	5.318	5.314	3.564	3.549	1.07
	$2^1P(2s3p)$	7.465	7.460	0.021	0.022	1.06
	$3^1P(2s4p)$	8.306	8.300	0.000 102	0.000 121	1.05
CH <sup>+</sup> <sup>c</sup>	$1^1\Sigma^+$	9.109	8.549	0.025	0.025	1.96
	$2^1\Sigma^+$	13.580	13.525	1.073	1.075	1.03
	$3^1\Sigma^+$	17.315	17.217	0.720	0.719	1.13
	$1^1\Pi$	3.261	3.230	0.095	0.094	1.03
	$2^1\Pi$	14.454	14.127	0.692	0.687	1.24

<sup>a</sup>Approximate excitation level.

<sup>b</sup>FCI results from Ref. 85.

<sup>c</sup>FCI results from J. Olsen, A. M. Sanchez de Meas, H. J. Aa. Jensen and P. Jørgensen, *Chem. Phys. Lett.* **54**, 380 (1989).

<sup>d</sup>Ref. 87.

for the dipole strength of the nearly pure double excitation at 8.549 eV is fortuitous. Again, the oscillator strengths with either approximation are quite similar. Lesser approximations for  $\text{CH}^+$ , like the Tamm-Dancoff or CI singles (CIS) or the random phase approximation (RPA), give ridiculous results for  $\text{CH}^+$  (Ref. 5), as the  $2^1\Sigma^+$  state and several other low-lying states are not properly described.

While the limited body of FCI excitation energies and oscillator strengths in the literature prevents us from drawing many conclusions from the present set of calculations, it appears that the EOM-CCSD method gives reliable values for dipole strengths and excitation energies (and, therefore, oscillator strengths) for electronic transitions dominated by single excitations.

### 9.3. Excited States of Ethylene

For another example, consider the ethylene molecule,  $\text{C}_2\text{H}_4$ .<sup>90</sup> This is probably the best studied example for excited states, yet it is still a demanding case. The  $\pi \rightarrow \pi^*$  transition in ethylene leads to the so-called valence ( $V$ ) state ( $^1A_1 \rightarrow ^1B_2$ ). In addition, there is a Rydberg ( $N$ ) series that corresponds to  $\pi \rightarrow 3s, 3p, 3d$ , etc. transitions. In poor methods, the  $V$ -state is found to have a dimension  $\langle V|x^2|V \rangle$  that is much greater than the size of the ground state  $\langle o|x^2|o \rangle$ , which is about 18 a.u., implying that the  $V$ -state is Rydberg-like rather than a valence state. Comparison with experiment is further complicated by the nonadiabatic effects associated with the  $\pi \rightarrow \pi^*$  transition, which cause the maximum of the band to occur at 7.65 eV, making it difficult to identify the correct vertical excitation energy.

Consider the Rydberg states first, whose EOM-CCSD excitation energies and oscillator strengths are shown in Table 21,<sup>90</sup> compared to multi-reference CI results and to complete-active-space (CAS) second-order perturbation theory (CASPT2) results. The Rydberg states are exceptionally well described, having only a 0.06 eV average absolute error. Rydberg states are sensitive to having sufficient diffuse functions in the basis, and, to offer nearly definitive results, here we are using an unnecessarily large 252-function atomic natural orbital basis. There would be little difference in these results with even a DZP + diffuse basis of about 60 functions, for example. Clearly, with an adequate basis, EOM-CCSD would appear to be highly accurate for the  $n = 3$  Rydberg states.

For the more demanding  $V$ -state, we see the convergence with basis in Table 22. Again, there is relative insensitivity, converging nicely to



Table 21. Low-lying Rydberg states of ethylene.

State	Description	Excitation Energy ( $\Delta E$ )				Oscillator Strength ( $f$ )		
		MD <sup>a</sup>	SA <sup>b</sup>	EOM-CCSD	Expt.	MD <sup>a</sup>	SA <sup>a</sup>	EOM CI-Approx.
<sup>1</sup> B <sub>3u</sub>	$\pi \rightarrow 3s$	7.26	7.17	7.21	7.11	0.06	0.07	0.09
<sup>1</sup> B <sub>1g</sub>	$\pi \rightarrow 3p_y$	7.93	7.85	7.86	7.83	—	—	—
<sup>1</sup> B <sub>2g</sub>	$\pi \rightarrow 3p_\sigma$	8.01	7.95	7.92	7.83	—	—	—
<sup>1</sup> A <sub>g</sub>	$\pi \rightarrow 3p_\pi$	8.36	8.40	8.26	8.26	—	—	—
<sup>1</sup> B <sub>3u</sub>	$\pi \rightarrow 3d_\sigma$	8.80	8.66	8.76	8.62	0.0005	0.0009	0.0004
<sup>1</sup> A <sub>u</sub>	$\pi \rightarrow 3d_{yz}$	8.99	8.94	8.96	8.90	—	—	—
<sup>1</sup> B <sub>1u</sub>	$\pi \rightarrow 3d_{xz}$	9.31	9.31	9.39	9.36	0.05	0.078	0.058
Average Error		0.12	0.07	0.06	—			

<sup>a</sup>L. E. McMurchie and E. R. Davidson, *J. Chem. Phys.* **67**, 5613 (1977).

<sup>b</sup>L. Serrano-Andres, M. Merchán, I. Nebot-Gil, R. Lindh and B. O. Roos, *J. Chem. Phys.* **98**, 3151 (1993). This is a complete active space, second-order perturbation theory (CASPT2) approximation.

Table 22. EOM-CCSD: V-state of ethylene.

<sup>1</sup> B <sub>1u</sub>	$\pi \rightarrow \pi^*$	$f$	$\langle x^2 \rangle$	Experiment	
	$\Delta E$			$\Delta E$	$f$
DZP + <i>sp</i>	8.15	0.34	17.8	7.65	0.34
DZP + 2 <i>s2p</i>	8.15	0.35	20.8		
DZP + 2 <i>s2p1d</i>	8.09	0.34	19.7		
WMR1 <sup>a</sup>	8.01	0.37	16.4		
WMR2 <sup>b</sup>	7.98	0.35	18.4		

<sup>a</sup>[4*s 3p 2d*] basis; P. O. Widmark, P. A. Malmqvist, B. O. Roos, *Theoret. Chem. Acta* **77**, 291 (1990).

<sup>b</sup>[5*s 4p 3d*] basis; P. O. Widmark, P. A. Malmqvist, B. O. Roos, *Theoret. Chim. Acta* **77**, 291 (1990).

7.98 eV, as the *vertical* excitation energy. Similarly, the oscillator strength is in excellent agreement with experiment in any of the bases considered. Once again, we observe excellent agreement with the MRCI of McMurchie and Davidson, including the oscillator strength and the valence character of the state, as  $\langle x^2 \rangle = 18$  a.u. However, there is less agreement with the CASPT2 results. The latter excitation energy is 8.40 eV and, worse, the  $\langle x^2 \rangle$  value of 44 a.u. is strongly Rydberg in character. Furthermore, the oscillator strength is off by a factor of 2. Ethylene does not seem to be typical as, for most systems, CASPT2 has offered excellent results.<sup>88</sup>

In Table 23, we report the timings for the 252-basis EOM-CCSD calculations. Though this is the largest-basis, highly correlated study of excited states that has been attempted, the timings are quite reasonable.

**Table 23.** CRAY-YMP Timings (sec) for WMR2 basis EOM-CCSD calculation (252 basis functions).

Integrals	820
SCF	58
Transformation	900
MO Integral Processing	350
CCSD	235
$\Lambda$ equations + $\bar{H}$	393
EOM/root	180

Many other EOM-CCSD studies of excited states have recently been reported, including those for ketene,<sup>5</sup> ozone,<sup>71</sup> the series formaldehyde, acetaldehyde, and acetone,<sup>89</sup> the dienes butadiene, cyclopentadiene, and norbornadiene,<sup>90</sup> chlorine peroxide,<sup>91</sup> and iron tetrachloride anion.<sup>92</sup> Furthermore, analytical gradients have been developed from EOM-CCSD by Stanton and Gauss<sup>99,101</sup> and applied to a variety of excited states. Comparison with vertical excitation energies, where available, suggest that for AEL values < 1.1 eV, the average error is about 0.1 eV. Similar or even better agreement is possible for Rydberg states. When doubly excited states are described, or when they mix significantly with singly excited states of the same symmetry, much greater errors, some > 1 eV, can be encountered. Much of the resolution of this latter problem lies in the inclusion of triple excitations, as has been demonstrated.<sup>93,94</sup> Besides EE-EOM-CC, the electron attached (EA-EOM-CC)<sup>102</sup> and ionization potential (IP-EOM-CC)<sup>105</sup> methods have been developed and applied.<sup>5</sup>

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Note, all three parts of the triple excitation vertex are entirely equivalent even though this designation does not make that explicit.

With the aid of diagrams we have for the energy expression immediately, as we require de-excitation parts of  $H_N$  to get closed diagrams,

$$\Delta E = \underbrace{\bigcirc}^{--x} + \underbrace{\bigcirc} \underbrace{\bigcirc} + \underbrace{\bigcirc \bigcirc} \quad . \quad (1')$$

The rules for closed diagrams are listed in Table A1. Interpreting the diagrams algebraically results in Eq. (26).

These diagrams are closed since they correspond to no net excitation.

### A1.2. Amplitude Diagrams

To illustrate the diagrammatic derivation of the CC amplitude equations, consider the simplest, CCD case, Eq. (20). We have

$$\langle \phi_{ij}^{ab} | [H_N(1 + T_2 + T_2^2/2)]_C | 0 \rangle = 0 \quad (2')$$

for all  $a, b, i, j$  excitations. The  $a, b, i, j$  will “label” the amplitude diagram. We want to draw all possible antisymmetrized diagrams that correspond to a net double excitation, but, unlike the energy expression, there are several more possibilities. However, we have developed very simple and unambiguous procedures for their generation, as illustrated in Table A2. We identify the vertex combinations, which together with the net excitation level specifies one of the excitation levels of  $H_N$ . Then we obtain the simple combinations that are possible.

Using the additional rules for open diagrams (Table A3), we can readily interpret the diagrams to give explicit expressions in terms of integrals and amplitudes. Many more examples including all the diagrams in CCSDT and their algebraic equivalents are presented elsewhere,<sup>20,25</sup> and we will depend upon these sources for more details of the explicit equations, as most of our objectives in this chapter can be achieved without them.

Table A1. Rules for closed diagrams.

$$\text{Diagram 1} = +\frac{1}{4} \sum_{\substack{i,j \\ a,b}} \langle ij || ab \rangle t_{ij}^{ab}$$

$$\text{Diagram 2} = + \sum_{i,a} f_{ia} t_i^a$$

$$\text{Diagram 3} = +\frac{1}{2} \sum_{i,j,a,b} \langle ij || ab \rangle t_i^a t_j^b$$

- 1) label diagram with particle ( $a, b, c, \dots$ ) or hole ( $i, j, k, \dots$ ) labels as appropriate
- 2) Associate with every two-particle vertex,  $|- -| \langle \text{left out right out} || \text{left in right in} \rangle$

- 3) Associate with every one-particle vertex  $|- - x f_{\text{out}, \text{in}}$

- 4) Associate with  $i \swarrow a$  amplitude  $t_i^a$ . Associate with  $i \swarrow a \quad j \swarrow b$  an amplitude  $t_{ij}^{ab}$ , and with  $i \swarrow a \quad j \swarrow b \quad k \swarrow c = t_{ijk}^{abc}$ .

- 5) Sum over all internal line labels.

- 6) Associate factor of 1/2 with each pair of equivalent lines. (A pair of equivalent lines is defined as two lines beginning on one vertex, and ending on another, but going in the same direction.)

- 7) In the event of two equivalent vertices as in  $\text{Diagram 4}$ , a 1/2 is required.

- 8) The sign is  $(-1)^{h+l}$ , where  $h$  is the number of "hole" lines and  $l$  is the number of loops. (The diagram



has two loops, while if it

were drawn as it would

have one, and, consequently, a sign

change.)

Table A2. Excitation level =  $z$ .

Vertices	Perturbation	Combination	Diagram	Interpretation
$++--$ 	$++$ 	$++$		$+\frac{1}{2}\sum_{c,d}\langle ab  cd\rangle t_{ij}^{cd}$
	$--$ 	$--$		$+\frac{1}{2}\sum_{k,l}\langle kl  ij\rangle t_{ki}^{ab}$
	$+-$ 	$+-$		$-\sum_{c,k}(-1)^P P(ab/ij)\langle ak  cj\rangle t_{ik}^{cb}$
Vertices	Perturbation	Combination	Diagram	Interpretation
$+++-- ++--$ 	$+++--$ 	$+++-- 0$		Disconnected Not Allowed
		$++- -$		$-\frac{1}{2}\sum(-1)^P P(ij)\langle kl  cd\rangle t_{ki}^{cd} t_{ij}^{ab}$
		$+-- +$		$-\frac{1}{2}\sum(-1)^P P(ab)\langle kl  cd\rangle t_{ki}^{ca} t_{ij}^{db}$
		(Note: $+ +-- = +-- +$ and $++- - = - ++-$ )		
		$++ --$		$\frac{1}{4}\sum\langle kl  cd\rangle t_{ij}^{cd} t_{kl}^{ab}$
		$+ -   + -$		$\frac{1}{2}\sum(-1)^P P(ab/ij)\langle kl  cd\rangle t_{ik}^{ac} t_{jl}^{bd}$

**Table A3.** Additional rules for open diagrams.

1. Label *external* lines in order with the hole-particle labels,  $a, i; b, j; c, k$ .
2. Sum over all *distinct* permutations of external line labels, with parity factor  $\sum_P (-1)^P P$ . When lines are quasi-equivalent (i.e., lines that would be equivalent if the diagram were closed by a final iteration) there are no distinct permutations. Hence there is no  $P(ab)$  in the first, second or fifth diagram, but it occurs in the third and sixth. In the last diagram, the  $1/2$  occurs for two equivalent vertices and *all* open line permutations.
3. External, fictitious loops connecting  $a$  with  $i$ ,  $b$  with  $j$  and  $c$  with  $k$ , etc. are counted as loops for sign determination.

## Appendix B. Quadratic Configuration Interaction

What is QCI? To answer this question, we need to consider the relationship between CI and CC theory a little more. In operator form, the CISD equations are (canonical SCF case)

$$\langle \Phi_i^a | H_N (\hat{C}_1 + \hat{C}_2) | \Phi_0 \rangle = \Delta E \langle \Phi_i^a | \hat{C}_1 | \Phi_0 \rangle, \quad (3')$$

$$\langle \Phi_{ij}^{ab} | H_N (1 + \hat{C}_1 + \hat{C}_2) | \Phi_0 \rangle = \Delta E \langle \Phi_{ij}^{ab} | \hat{C}_2 | \Phi_0 \rangle, \quad (4')$$

$$\Delta E = \langle \Phi_0 | H_N \hat{C}_2 | \Phi_0 \rangle. \quad (5')$$

In contrast, in terms of  $\hat{C}_p$ , the CCSD equations are

$$\langle \Phi_i^a | H_N (\hat{C}_1 + \hat{C}_2 + \hat{C}_3') | \Phi_0 \rangle = \Delta E \langle \Phi_i^a | \hat{C}_1 | \Phi_0 \rangle, \quad (6')$$

$$\langle \Phi_{ij}^{ab} | H_N (1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3' + \hat{C}_4') | \Phi_0 \rangle = \Delta E \langle \Phi_{ij}^{ab} | \hat{C}_2 | \Phi_0 \rangle, \quad (7')$$

$$\Delta E = \langle \Phi_0 | H_N \hat{C}_2 | \Phi_0 \rangle, \quad (8')$$

where  $\hat{C}_3' = C_3 - T_3$  and  $\hat{C}_4' = C_4 - \hat{T}_4 - \hat{T}_1 \hat{T}_3$ . Remember, while the  $\Delta E$  remains in CI, it has to disappear from extensive methods. Algebraic analysis shows that  $\Delta E \langle \Phi_i^a | \hat{C}_1 | \Phi_0 \rangle$  (which is an unlinked term) is equal to a term derived from  $\hat{T}_1 \hat{T}_2$  in  $C_3'$  in Eq. (6'). Similarly,  $\Delta E \langle \Phi_{ij}^{ab} | \hat{C}_2 | \Phi_0 \rangle$  equals

a term arising from the  $\hat{T}_2^2/2 + \hat{T}_1^2\hat{T}_2/2$  terms in  $C'_4$  in Eq. (7'). Eliminating the corresponding terms from the equations eliminates  $\Delta E$ , making the CCSD method extensive.

The idea of QCI is to replace these essential terms by the closest *CI coefficient* analog. Namely,  $\hat{C}_1\hat{C}_2 = \hat{T}_1\hat{T}_2 + \hat{T}_1^3/2$  and  $\hat{C}_2^2/2 = \hat{T}_2^2/2 + \hat{T}_1^2\hat{T}_2/2 + \hat{T}_1^4/4$ . Hence, the QCISD equations are

$$\langle \Phi_i^a | H_N (\hat{C}_1 + \hat{C}_2 + \hat{C}_1\hat{C}_2) | \Phi_0 \rangle = \Delta E \langle \Phi_i^a | \hat{C}_1 | \Phi_0 \rangle, \quad (9')$$

$$\langle \Phi_{ij}^{ab} | H_N (1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_2^2/2) | \Phi_0 \rangle = \Delta E \langle \Phi_{ij}^{ab} | \hat{C}_2 | \Phi_0 \rangle, \quad (10')$$

$$\Delta E = \langle \Phi_0 | H_N \hat{C}_2 | \Phi_0 \rangle. \quad (11')$$

These differ from CCSD via the  $C'_3$  term in the double excitation equation and the different numerical factors in the  $\hat{T}_1^3$  and  $\hat{T}_1^4$  terms, but none of these terms are required to cancel unlinked terms. Also, none of these terms contribute before the fifth-order energy in the canonical SCF case. So usually QCISD  $\simeq$  CCSD (see Table B1). QCISD's mean error of 6.41 mhartrees compares with 7.06 for CCSD. Also, since non-linear  $T$  terms tend to raise the correlation energy, their neglect in QCISD will usually cause  $E(\text{QCISD}) < E(\text{CCSD})$  slightly. If we restrict ourselves to just CCD, then QCID = CCD. Also, it is apparent from the above derivation that, despite the CF designation, QCISD is an extensive, i.e., *many-body* method. It is also clear that for two electrons, CISD = QCISD = CCSD. Unlike CCSD, QCISD is only defined in the canonical SCF case. Besides keeping the effects of  $\hat{T}_1$  small because of the Brillouin theorem, this is necessary to maintain the extensive property of the method, since otherwise  $\Delta E = \langle \Phi_0 | H_N (\hat{C}_1 + \hat{C}_2) | \Phi_0 \rangle$  and adding the additional  $C_1C_2$  term to Eq. (10') and  $\hat{C}_1^2/2$  in the single-triple excitation equation can lead to residual unlinked terms in the wave function. This is also why there is no extensive QCISDT method.<sup>e</sup>

Non-iterative  $T_3$  contributions can be added to QCISD just as in the CCSD case. The contribution from double excitations to  $T_3$  is formally exactly the same  $T(\text{CCSD})$  term, except, it is evaluated using QCISD coefficients, i.e.,  $T(\text{QCISD})$ ; while the single-triple excitation term  $\Delta E_{\text{ST}}$  needs

<sup>e</sup>J. Paldus, J. Čížek and B. Jeziorski, *J. Chem. Phys.* **90**, 4356 (1989).



**Table B1.** Differences between QCI and full CI energies (DZP: mhartrees).

	BH			FH			H <sub>2</sub> O			Mean abs. error
	<i>R<sub>e</sub></i>	1.5 <i>R<sub>e</sub></i>	2.0 <i>R<sub>e</sub></i>	<i>R<sub>e</sub></i>	1.5 <i>R<sub>e</sub></i>	2.0 <i>R<sub>e</sub></i>	<i>R<sub>e</sub></i>	1.5 <i>R<sub>e</sub></i>	2.0 <i>R<sub>e</sub></i>	
QCISD	1.75	2.35	3.84	2.57	4.14	8.40	3.88	9.37	21.38	6.41
QCISD(T)	0.40	0.41	0.12	0.24	0.66	1.38	0.62	1.81	-1.26	0.77
QCISD[TQ*] <sup>a</sup>	0.05	-0.09	-0.85	0.17	0.34	0.87	0.09	-0.13	-1.08	0.41

<sup>a</sup>QCISD[TQ\*] = QCISD + TQ\*(QCISD), from R. J. Bartlett, J. D. Watts, S. A. Kucharski and J. Noga, *Chem. Phys. Lett.* **165**, 513 (1990).

to be multiplied by two compared to CCSD, as explained in the text. Unlike CI, where  $\Psi_{\text{CISD}} = (1 + \hat{C}_1 + \hat{C}_2)\Phi_0$  and CCSD,  $\Psi_{\text{CCSD}} = \exp(\hat{T}_1 + \hat{T}_2)\Phi_0$ , the  $\Psi_{\text{QCISD}}$  wave function cannot be simply represented like the CI or CC solution. It is an approximate truncation of  $\exp(\hat{T}_1 + \hat{T}_2)\Phi_0$  that is different for the single and double excitation projection. The QCISD(T) mean error of 0.77 compares to 1.15 for CCSD(T). Also adding  $T_4$  effects gives QCISD(TQ\*), whose mean error of 0.41 is close to that of CC5SD[TQ\*], 0.44. As QCISD and QCISD(T) are simply approximate versions of the CCSD and CCSD(T) equations, all the analytical gradient and other methods for CC in ACES II contain QCI as a special case.

The neglect of higher  $T_1$  product terms can cause QCISD(T) to fail when  $T_1$  is large. A dramatic example is obtained by BeO (Ref. 94). For the  $\alpha_{zz}$  polarizability, QCISD(T) differs by an order of magnitude from CCSD(T) and by three orders of magnitude for the IR intensity.<sup>94</sup>

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- calculations. Elements of this package are: the SCF, integral transformation, CC/MBPT correlation energies and gradients, equation-of-motion EOM-CC and Hilbert and Fock space multi-reference (MR-CC) for excited states and excited state properties, programs written by J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, P. Szalay, A. Balková, H. Sekino and R. J. Bartlett. ACES II uses the VMOL integral and VPROPS property integral programs written by J. Almlöf and P. R. Taylor, a modified version of the integral derivative program ABACUS written by T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, and P. R. Taylor, and a geometry optimization and vibrational analysis package written by J. F. Stanton and D. E. Bernholdt.
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