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NEW DEVELOPMENTS IN MANY BODY PERTURBATION THEORY AND COUPLED CLUSTER THEORY

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1. Introduction

Many body perturbation theory (MBPT) methods using the Møller-Plesset (MP) perturbation operator [1] are the most popular correlation corrected ab initio methods in Quantum Chemistry for calculating dynamic electron correlation effects. [2-9] The popularity of MP methods results from several reasons: (a) MP theory leads to a hierarchy of well-defined methods, which provide increasing accuracy with increasing order n. (b) Correlation effects are included stepwise in a systematic manner that facilitates their analysis and the understanding of the correlation problem. (c) Most important is the fact that all MP methods are size-extensive. [3,10] (d) Up to fourth order, MP energies can be calculated at relatively small computational cost since calculations involve just single, noniterative evaluation steps.

There are also some disadvantages of MP theory, which have to be mentioned. (a) MP methods are not variational. (b) At a given order n of MP perturbation theory, there exists not a well-defined wave function. (c) One observes often an oscillatory or erratic rather than monotonic convergence behaviour of calculated MPn energies. [11-14] The first two problems are of just minor consequence. For example, it is more important to use a size-extensive rather than a variational method for calculating electron correlation effects. Also, one can calculate molecular properties in form of response properties using analytical energy derivatives without ever referring to a wave function. [11,15] However, the third problem is more serious: One has early observed that the MPn energy can strongly oscillate

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for small values of n before it converges to the full CI (FCI) energy value, which is identical with the infinite order MP energy. [11-14] Oscillations are also found for other properties such as the internal coordinates of molecular geometries, dipole moments, vibrational frequencies or infrared intensities. [11]

Clearly, these oscillations make the use of MP methods less attractive, which is one of the major reasons why Coupled Cluster (CC) methods have replaced MP method more and more in the nineties. [10,16-21] CC methods are related to MP methods in so far as they are also size-extensive and non-variational. Of course, CC methods are more expensive than MP methods since the CC wave function and, by this, the CC energy has to be calculated iteratively. The gain from the extra cost is increased accuracy that results from the fact that due to the exponential ansatz CC contrary to MP includes infinite order effects. By this, it is guaranteed that oscillations in the CC energy series are excluded and CC energies can effectively compete with those of other high-accuracy ab initio methods. Since the infinite order effects, it is much more difficult to keep track which correlation effects are covered by a given CC method and which not. A solution to this problem can be found by using MP theory to analyze the correlation contributions covered by a given CC method. [22,23]

The last ten years have seen many attempts to improve the repertoire of MP and CC methods for their effective use in Quantum Chemistry. The present account of MP and CC theory does not intend to present a summary of this work. Instead it exclusively concentrates on research carried out at Theoretical Chemistry of the University of Göteborg to develop techniques for including higher order correlation effects into MP or CC theory. [22-32] There is reason to believe that higher order correlation effects will make it possible to successfully apply single determinant theory even in the case of a typical multi-reference problem. Apart from this, the analysis of higher order correlation effects provides a basis for the understanding of the convergence behaviour of the MPn series and, by this, of the electron correlation problem in general. Once the convergence behaviour of the MPn series is well understood, the prediction of reliable FCI energies from MPn energies for low n becomes possible. [27-29]

Knowledge about the MPn methods and their coverage of electron correlation effects can directly be used to predict performance and accuracy of CC methods since it is possible to express correlation contributions covered by CC in terms of MP correlation effects. [22,23] For example, it is one of the key questions of the last years whether approximate CC methods, which do not include all cluster operators or handle part of the correlation problem by perturbation theory, can replace full CC methods. [30-32] We will deal with these questions in this work, which is structured in the following way.

In chapter 2, we will present a procedure, by which MP perturbation methods can be developed to higher orders. This procedure is a combination of the two traditional approaches in perturbation theory, namely the algebraic development procedure applied at lower orders and the diagrammatic development procedure applied at fourth and fifth order MP perturbation theory. We will show that by the combination of the two traditional approaches one avoids their disadvantages and is able to derive fourth order MP (MP4) [6,7] and fifth order MP (MP5) theory [8,9] in a compact form expressed in terms of cluster operators of first and second order. The cluster operator equations can easily be converted into a two-electron integral equations and programmed for use on a computer.

In addition to the discussion of how to develop MPn methods, we will shortly review cost requirements of MP methods where we will use the two-electron integral equations. We will stress the importance of the use of intermediate arrays in the computation of MPn correlation energies since this is the best way of cutting down computational cost for MPn methods. We will also discuss the various correlation effects covered by MP theory at low orders to get a better understanding of the accuracy of MPn methods presently used. [28,29]

In chapter 3, sixth order MP (MP6) perturbation theory [24-29,33] will be developed along the lines discussed in chapter 2, i.e. the development will start from the general MP energy formula, then partition the principal term in connected and disconnected cluster operator contributions, and, finally, extract all those terms that represent linked diagram contributions [34] to the MP6 correlation energy. The final cluster operator equations of the MP6 energy will be transformed term by term into two-electron integral formulas. It will be shown that the most costly terms are those that result from disconnected cluster operators. However, the computational cost of the disconnected cluster operator terms can systematically be reduced by using intermediate arrays. In this way, we will be able to give final two-electron integral formulas that lead to a minimum of computational cost for calculating the MP6 correlation energy. [24,25]

Also in chapter 3, the implementation of the first MP6 computer program for routine calculations will be discussed where special emphasis will be laid on the various ways of testing such a complicated program for programming errors. Some applications of MP6 will be discussed. [25]

In chapter 4, a short summary of CC theory is given. The projection equations of CC theory with single and double excitations (CCSD) [19] will be derived in their connected form and compared with those of the corresponding quadratic CI (QCI) approach, QCISD [35], which represents an approximation to the more complete CCSD theory. It will be pointed out that the QCI approach as developed

by Pople and co-workers [35] can not be extended to the triple (T) excitation level because at this level it looses the property of size-extensivity.

In chapter 5, we will analyse CC and QCI methods on the basis of perturbation theory. [22,23] A graphical method will be presented to assess the infinite order effects of CC theory. It will be shown that high accuracy can be expected from CC methods that include in some way T excitations that describe three-electron correlation effects. Clearly, the best method in terms of accuracy is CCSDT [20] while satisfactory results can also be expected from CCSD(T) [36] that includes T effects in a perturbative way. Compared to the corresponding CC methods, QCISD and QCISD(T) lack many energy contributions and, therefore, they are unable to describe T effects in a balanced way. This will be clearly shown on the basis of the perturbation analysis. [23]

In chapter 6, we will use the work on MP and CC methods to develop a hierarchy of size-extensive QCI methods. [30] For this purpose, a systematic procedure of converting the non-size-extensive CI methods into extended CI methods, which are size-extensive. [30] We will show that, if correctly applied, the original QCI concept of Pople and co-workers [35] leads to just two size-extensive extended CI (ECI) methods, namely QCISD = ECISD and ECISDT. [30] At the quadruple (Q) excitation level as well as any higher excitation level, ECI methods merge with the corresponding CC methods, which means that the original QCI concept does not lead to a hierarchy of approximate CC methods. [30] However, using the linked diagram theorem the ECI equations can be converted into a connected form and, then, systematically simplified to projection equations with linear and quadratic cluster operator terms. In this way, a hierarchy of size-extensive QCI methods is developed that are parallel to the CC methods, but have the advantage of a rather simple form that can easily be converted into a computer program. [30]

We will discuss in chapter 6, the development of the first size-extensive QCISDT method and its application to simple electron systems for which FCI results are known. [31,32] We will show that QCISDT leads to the same accuracy as CCSDT, but has the advantage of being much easier to implement on a computer. In addition, QCISDT converges in many cases faster than CCSDT, which leads to time savings. [32]

Finally, in chapter 7 we will summarize the most important aspects of this review and shortly discuss the future of MBPT and CC theory.

2. Møller-Plesset Perturbation Theory

There are two different ways of developing MP methods for use in quantum chemical calculations. The first way can be called the algebraic approach since it is based on an algebraic derivation of matrix elements from general perturbation theory formulas. It works very well for low order perturbation theory [4,5,7], however becomes problematic for higher orders. In the latter case, one can distinguish between a principal term and one or several renormalization terms in the general perturbation theory formula. The linked diagram theorem [34] shows that it is superfluous to evaluate the renormalization terms since these are all cancelled by appropriate parts of the principal term. One realizes this by writing principal and renormalization terms in form of diagrams. The renormalization terms correspond to unlinked diagram contributions to the energy, which are cancelled by the unlinked diagram contributions of the principal term. Only the linked diagram contributions of the principal term determine the nth order MP correlation energy.

Because of the linked diagram theorem it is of advantage to derive the MP energy formulas by diagrammatic techniques which immediately identify those terms that really contribute to the correlation energy. Accordingly, diagrammatic derivations of the third, fourth and even fifth order MP energy have been made, which clearly demonstrated superiority over the algebraic approach. [6,8,37] However, the diagrammatic approach has also its disadvantages. This becomes obvious when considering the increase in linked diagrams contributing to the correlation energy. If one uses Brandow diagrams, there are 1, 3, 39, 840, and 28300 antisymmetrized diagrams at second, third, fourth, fifth, and sixth order, respectively. This means that it is hardly possible to derive the sixth order correlation energy in terms of linked diagrams.

Therefore, we have proposed a third approach for developing higher order perturbation theory formulas. [24] This third approach is based on a combination of algebraic and diagrammatic techniques and comprises the following steps.

1) Principal term and renormalization terms are derived from the general perturbation theory formula.

2) Since it is clear that all renormalization terms will be cancelled by parts of the principal term, derivation of the MPn equations concentrates just on the principal term. This will be dissected into various parts according to the excitations involved at the corresponding order of perturbation theory. The various parts will be written in a cluster operator form.

3) Each part of the principal term characterized by S, D, T, Q, P, H, etc. excitations can be described as representing connected or disconnected energy

diagrams according to the nature of the cluster operators appearing in the energy formula.

4) All connected (closed) energy terms correspond to linked diagram contributions and enter the formula for the correlation energy while the disconnected energy terms represent unlinked diagram contributions which according to the linked diagram theorem can be discarded.

5) The final cluster operator form of the linked diagram contributions is transformed into two-electron integral formulas. This is facilitated by the fact that all those terms that originally involved disconnected cluster parts can be simplified by using intermediate arrays.

The advantages of this approach are that

a) superfluous energy contributions are never determined within the algebraic derivation and

b) a tedious analysis of all linked diagram terms is not necessary.

The latter point will become clear if step 3 as the key step of the procedure 1)-5) is described in more detail. Each cluster operator $\hat{T}$ can be described in terms of simplified Brandow diagrams. [8] Combination of the $\hat{T}$ diagrams with the diagrams of the perturbation operator $\hat{V}$ may lead to closed connected or closed disconnected diagrams, which means that the corresponding matrix elements represent linked or unlinked energy contributions. It is also possible that the combination of $\hat{T}$ and $\hat{V}$ diagrams leads to disconnected open diagrams. In this case, the diagrams correspond to the wave operator and cover both linked and unlinked contributions. One has to combine the wave operator part with further parts of the energy formula to get a separation into connected closed (= linked) and disconnected closed (= unlinked) energy diagrams. In any case, it is possible to identify for each part of the principal term whether it contains just linked or in addition unlinked diagram contributions. The diagrams one has to use for this purpose are rather simple because they correspond to some basic operators and need not to be specified with regard to hole and particle lines. [8]

2.1 DERIVATION OF THE MØLLER-PLESSET CORRELATION ENERGY AT LOWER ORDERS

Using the procedure outlined above, we will derive in the following MP2, MP3, MP4, and MP5 energy formula. For the perturbation expansion, the Hartree-Fock (HF) wave function is used as zeroth order function.

$$\hat{H}_0|\Phi_0\rangle = E_0|\Phi_0\rangle \tag{2.1}$$

with

$$\hat{H}_0 = \sum_p \hat{F}_p = \sum_p (\hat{h}_p + \hat{g}_p) \ , \tag{2.2}$$

In Eq. (2.2), $\hat{h}$ denotes the one-electron part of the Hamiltonian and $\hat{g}$ covers the sum over Coulomb operators $\hat{J}_q$ and exchange operators $\hat{K}_q$, which describe two-electron interactions between electrons p and q.

With these definitions, the eigen value E_0 of Eq. (2.1) and HF energy E_{HF} are given by

$$E_0 = \langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle \tag{2.3a}$$

$$E_{HF} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \tag{2.3b}$$

In the following the HF spin orbitals are denoted by ψ_p. It is assumed that they are eigen functions of the Fock operator $\hat{F}_p$ with eigen value ϵ_p. Following a widespread convention we will use indices $i, j, k, \ldots$ to label occupied spin orbitals and indices $a, b, c, \ldots$ to label unoccupied (virtual) spin orbitals. In cases where the formulas hold for both type of spin orbitals indices $p, q, r, \ldots$ are used.

To solve the non-relativistic electronic Schrödinger equation

$$\hat{H}\Psi = E\Psi \tag{2.4}$$

one considers the true Hamiltonian $\hat{H}$ and the true wave function Ψ as related to the HF Hamiltonian and HF wave function by a perturbation, i.e. $\hat{H}$ splits into unperturbed Hamiltonian $\hat{H}_0$ and perturbation operator $\hat{V}$: [1]

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{2.5}$$

Hence, the perturbation operator $\hat{V}$ is given as the difference between the exact Hamiltonian $\hat{H}$ and the zeroth order Hamiltonian $\hat{H}_0$:

$$\hat{V} = \sum_{p<q} \hat{r}_{pq}^{-1} - \sum_p \hat{g}_p \ . \tag{2.6}$$

The energy E of Eq. (2.4) can be expanded in a perturbation series

$$E = E_{HF} + E_{MP}^{(2)} + E_{MP}^{(3)} + E_{MP}^{(4)} + E_{MP}^{(5)} + \ldots \tag{2.7a}$$

or

$$E = E_0 + E_{MP}^{(1)} + E_{MP}^{(2)} + E_{MP}^{(3)} + E_{MP}^{(4)} + E_{MP}^{(5)} + \ldots \tag{2.7b}$$

The energy difference $\Delta E = E - E_{HF}$ represents the correlation energy

$$\Delta E = E - E_{HF} = \sum_{n=2} E_{MP}^{(n)} \tag{2.8}$$

that is calculated as the sum of the Møller-Plessent (MP) perturbation contributions at order n.

The MP energy $E_{MP}^{(n)}$ at nth order can be written as

$$E_{MP}^{(n)} = \langle \Phi_0 | \hat{V} \hat{\Omega}^{(n-1)} | \Phi_0 \rangle, \tag{2.9}$$

where the wave operator $\hat{\Omega}$ at nth order is given by Eq. (2.10):

$$\hat{\Omega}^{(n)} = \hat{G}_0 \left[\hat{V} \hat{\Omega}^{(n-1)} - \sum_{m=1}^{n-1} E_{MP}^{(m)} \hat{\Omega}^{(n-m)} \right] \tag{2.10}$$

with $\hat{G}_0$ being the reduced resolvent:

$$\hat{G}_0 = \sum_{k=1}^{\infty} \frac{|\Phi_k\rangle\langle\Phi_k|}{E_0 - E_k}. \tag{2.11}$$

For a given order n, the correlation energy contribution $E_{MP}^{(n)}$ takes the form of Eq. (2.12)

$$E_{MP}^{(n)} = \langle \Phi_0 | \hat{V} (\hat{G}_0 \bar{V})^{n-1} | \Phi_0 \rangle + \textit{ renormalization terms} \qquad (n \geq 2) \tag{2.12}$$

with $\bar{V}$ being

$$\bar{V} = \hat{V} - \langle \Phi_0 | \hat{V} | \Phi_0 \rangle \tag{2.13}$$

The first term of Eq. (2.12) is the principal term while all additional terms are renormalization terms. The number of renormalization terms increases rapidly with order n and , therefore, it is rather difficult algebraically to derive the energy formula for increasing order n.

However, in this situation the linked diagram theorem [34] helps, which states that only the linked diagram terms of Eq. (2.12) contribute to the correlation energy. All linked diagram contributions to the energy are contained in the principal term while the renormalization terms represent just unlinked diagram contributions, which are cancelled by the corresponding unlinked diagram contributions of the principal term. Therefore, Eq.(2.12) can be simplified to give Eq. (2.14):

$$E_{MP}^{(n)} = \langle \Phi_0 | \hat{V} (\hat{G}_0 \bar{V})^{n-1} | \Phi_0 \rangle_L \tag{2.14}$$

where the L indicates limitation to "linked" diagrams. This means that a derivation of the energy formula can focus just on the linked diagram contributions of the principal term. Linked diagram contributions to the energy can easily be identified by considering that they have to be closed and connected. If diagrams are not closed, they represent wave operator diagrams. In this case, a linked diagram can be either connected or disconnected, which makes it advisable to close the diagram first to an energy diagram and then to decide whether it is of linked or unlinked nature.

At second order MP (MP2) perturbation theory, there are no unlinked diagram contributions in Eq. (2.12). The energy $E_{MP}^{(2)}$ can be written as

$$E_{MP}^{(2)} = \langle \Phi_0 | \hat{V} \hat{G}_0 \hat{V} | \Phi_0 \rangle \tag{2.15a}$$

$$= \sum_{d}^{D} \langle \Phi_0 | \hat{V} | \Phi_d \rangle (E_0 - E_d)^{-1} \langle \Phi_d | \hat{V} | \Phi_0 \rangle \tag{2.15b}$$

in which d corresponds to double (D) excitations. In the following, we will denote single (S), triple (T), quadruple (Q), pentuple (P), and hextuple (H) excitations by subscripts s, t, q, p and h. For general excitations X, Y, etc., we will use subscripts x, y, etc.

In Eq. (2.15b), energies E_d are (in the same way as E_0) eigen values of the zeroth-order Hamiltonian $\hat{H}_0$ corresponding to the eigen functions $|\Phi_d\rangle$ ($|\Phi_0\rangle$).

We can rewrite Eq. (2.15b) by defining a D excitation cluster operator $\hat{T}_2^{(1)}$ at first order according to Eq. (2.16)

$$\hat{T}_2^{(1)} |\Phi_0\rangle = \sum_{d}^{D} a_d |\Phi_d\rangle \tag{2.16}$$

where the first order D excitation amplitudes a_d are given by

$$a_d = (E_0 - E_d)^{-1} \langle \Phi_d | \hat{V} | \Phi_0 \rangle \tag{2.17}$$

With the cluster operator $\hat{T}_2^{(1)}$ of Eq. (2.16), the second order energy adopts the simple form of Eq. (2.18):

$$E_{MP}^{(2)} = \langle \Phi_0 | \hat{V} \hat{T}_2^{(1)} | \Phi_0 \rangle \tag{2.18}$$

The analogous expression for the third order energy $E_{MP}^{(3)}$ can be easily obtained:

$$E_{MP}^{(3)} = \langle \Phi_0 | \hat{V} \hat{G}_0 \bar{V} \hat{G}_0 \hat{V} | \Phi_0 \rangle \tag{2.19a}$$

$$= \sum_{d_1, d_2}^{D} \langle \Phi_0 | \hat{V} | \Phi_{d_1} \rangle (E_0 - E_{d_1})^{-1} \langle \Phi_{d_1} | \bar{V} | \Phi_{d_2} \rangle$$

$$\times (E_0 - E_{d_2})^{-1} \langle \Phi_{d_2} | \hat{V} | \Phi_0 \rangle \tag{2.19b}$$

$$= \langle \Phi_0 | \hat{V} \hat{T}_2^{(2)} | \Phi_0 \rangle \tag{2.19c}$$

The second order D excitation cluster operator $\hat{T}_2^{(2)}$ is given by

$$\hat{T}_2^{(2)}|\Phi_0\rangle = \sum_d^D b_d|\Phi_d\rangle \tag{2.20}$$

with the second order amplitude b_d being

$$b_d = (E_0 - E_d)^{-1}\langle\Phi_d|\bar{V}\hat{T}_2^{(1)}|\Phi_0\rangle \tag{2.21}$$

At fourth order MP theory, one encounters for the first time beside the principal term also a renormalization term. Using Eq. (2.14), the contribution $E_{MP}^{(4)}$ is given by

$$E_{MP}^{(4)} = \langle\Phi_0|\hat{V}\hat{G}_0\bar{V}\hat{G}_0\bar{V}\hat{G}_0\hat{V}|\Phi_0\rangle_L \tag{2.22a}$$

$$= \sum_x^{S,D,T,Q} \left(\langle\Phi_0|(\hat{T}_2^{(1)})^\dagger\bar{V}|\Phi_x\rangle(E_0 - E_x)^{-1}\langle\Phi_x|\bar{V}\hat{T}_2^{(1)}|\Phi_0\rangle\right)_L$$

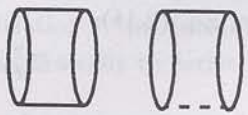
$$= \sum_{i=1,2,3} \langle\Phi_0|(\hat{T}_2^{(1)})^\dagger\bar{V}\hat{T}_i^{(2)}|\Phi_0\rangle + \langle\Phi_0|(\hat{T}_2^{(1)})^\dagger\left[\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2\right]_C|\Phi_0\rangle \tag{2.22b}$$

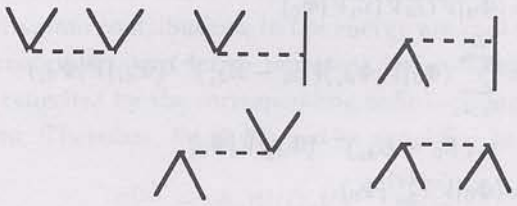
$$= E_S^{(4)} + E_D^{(4)} + E_T^{(4)} + E_Q^{(4)} \tag{2.23}$$

The renormalization term is associated with the disconnected cluster operator $(\hat{T}_2^{(1)})^2$:

$$\langle\Phi_0|(\hat{T}_2^{(1)})^\dagger\left[\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2\right]_D|\Phi_0\rangle = \langle\Phi_0|(\hat{T}_2^{(1)})^\dagger\hat{T}_2^{(1)}(\bar{V}\hat{T}_2^{(1)})_C|\Phi_0\rangle \tag{2.24a}$$

$$= \langle\Phi_0|(\hat{T}_2^{(1)})^\dagger\hat{T}_2^{(1)}|\Phi_0\rangle E_{MP}^{(2)} \tag{2.24b}$$

$=$  (2.24c)

$\bar{V}$:  (2.25a)

$\hat{T}_1^{(n)}$:  (2.25b)

$\hat{T}_2^{(n)}$:  (2.25c)

$\hat{T}_3^{(n)}$:  (2.25d)

This is an unlinked diagram term, which can be disregarded in the MP4 calculation. In Eq.s (2.22) and (2.24) the subscripts C and D denote restriction to connected and disconnected diagrams. Simplified graphical representations of perturbation operator $\bar{V}$ and cluster operators $\hat{T}_i^{(n)}$ (i = 1,2,3) at nth order perturbation theory, are given in (2.25a)-(2.25d). [24] Obviously, unlinked diagram terms result from a disconnected cluster operator and, therefore, terms involving disconnected cluster operators such as $\hat{T}_2^2$, $\hat{T}_1\hat{T}_2$, etc., have to be analyzed.

In Eq. (2.22b), the S and T excitation cluster operators $\hat{T}_1^{(2)}$ and $\hat{T}_3^{(2)}$ are defined by

$$\hat{T}_1^{(2)}|\Phi_0\rangle = \sum_s^S b_s|\Phi_s\rangle \tag{2.26}$$

and

$$\hat{T}_3^{(2)}|\Phi_0\rangle = \sum_t^T b_t|\Phi_t\rangle \tag{2.27}$$

where the corresponding amplitudes b_s and b_t are given by

$$b_s = (E_0 - E_s)^{-1}\langle\Phi_s|\bar{V}\hat{T}_2^{(1)}|\Phi_0\rangle \tag{2.28}$$

and

$$b_t = (E_0 - E_t)^{-1}\langle\Phi_t|\bar{V}\hat{T}_2^{(1)}|\Phi_0\rangle \tag{2.29}$$

At fifth order, the MP correlation energy contribution $E_{MP}^{(5)}$ can be expressed according to Eq. (2.30):

$$E_{MP}^{(5)} = \langle\Phi_0|\hat{V}\hat{G}_0\bar{V}\hat{G}_0\bar{V}\hat{G}_0\bar{V}\hat{G}_0\bar{V}\hat{G}_0\hat{V}|\Phi_0\rangle_L \tag{2.30}$$

Using the expression for $\hat{G}_0$ (Eq.(2.11)) and the cluster operators $\hat{T}_2^{(1)}$ and $\hat{T}_i^{(2)}$ (i = 1, 2, 3), one obtains

$$\begin{aligned} E_{MP}^{(5)} = & \sum_{x_1,x_2}^{S,D,T,Q} \Big(\langle\Phi_0|(\hat{T}_2^{(1)})^\dagger \bar{V}|\Phi_{x_1}\rangle (E_0 - E_{x_1})^{-1} \langle\Phi_{x_1}|\bar{V}|\Phi_{x_2}\rangle \\ & \times (E_0 - E_{x_2})^{-1} \langle\Phi_{x_2}|\bar{V}\hat{T}_2^{(1)}|\Phi_0\rangle \Big)_L \\ = & \sum_{i,j=1,2,3} \langle\Phi_0|(\hat{T}_i^{(2)})^\dagger \bar{V}\hat{T}_j^{(2)}|\Phi_0\rangle + 2\sum_{i=2,3} \langle\Phi_0|(\hat{T}_i^{(2)})^\dagger \bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2|\Phi_0\rangle_C \\ & + \langle\Phi_0|\frac{1}{2}((\hat{T}_2^{(1)})^\dagger)^2 \bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2|\Phi_0\rangle_C \qquad (2.31) \\ = & E_{SS}^{(5)} + 2E_{SD}^{(5)} + E_{DD}^{(5)} + 2E_{ST}^{(5)} \\ & + 2E_{DT}^{(5)} + E_{TT}^{(5)} + 2E_{DQ}^{(5)} + 2E_{TQ}^{(5)} + E_{QQ}^{(5)} \qquad (2.32) \end{aligned}$$

The 14 terms of MP5 can be reduced to 9 unique terms by considering that $E_{SD}^{(5)} = E_{DS}^{(5)}$, etc., and weighting each term by appropriate factors of one and two in Eq. (2.32). The last three terms of Eq. (2.32), namely $E_{DQ}^{(5)}$, $E_{TQ}^{(5)}$, and $E_{QQ}^{(5)}$, contain the disconnected cluster operator $(\hat{T}_2^{(1)})^2$. In addition, the term $E_{TS}^{(5)} (= E_{ST}^{(5)})$ contains the open disconnected diagram part (2.33):

$\langle\Phi_t|\bar{V}\hat{T}_1^{(2)}|\Phi_0\rangle$:

(2.33)

which contributes a linked energy diagram to $E_{MP}^{(5)}$ when closed by the triple cluster operator $(\hat{T}_3^{(2)})^\dagger$. However, it is relevant for the derivation of the MP6 method discussed in chapter 3 that term (2.33) can lead to unlinked diagram contributions at higher orders of perturbation theory and, therefore, it is reasonable to place the term E_{TS} in a separate class, which at higher orders will be associated with disconnected T contributions. In this way, $E_{MP}^{(5)}$ is partitioned into $E(MP5)_1$, $E(MP5)_2$, and $E(MP5)_3$:

$$E_{MP}^{(5)} = E(MP5)_1 + E(MP5)_2 + E(MP5)_3 \qquad (2.34)$$

where

$$\begin{aligned} E(MP5)_1 = & E_{SS}^{(5)} + 2E_{SD}^{(5)} + E_{DD}^{(5)} + 2E_{DT}^{(5)} + E_{TT}^{(5)} \\ = & \sum_{i=1,2} (2 - \delta_{1,i}) \langle\Phi_0|(\hat{T}_1^{(2)})^\dagger \bar{V}\hat{T}_i^{(2)}|\Phi_0\rangle \\ & + \sum_{i=2,3} (2 - \delta_{2,i}) \langle\Phi_0|(\hat{T}_2^{(2)})^\dagger \bar{V}\hat{T}_i^{(2)}|\Phi_0\rangle \\ & + \langle\Phi_0|(\hat{T}_3^{(2)})^\dagger \bar{V}\hat{T}_3^{(2)}|\Phi_0\rangle \qquad (2.35) \end{aligned}$$

represents the contributions of the connected cluster operators,

$$E(MP5)_2 = 2E^{(5)}_{DQ} + 2E^{(5)}_{TQ} + E^{(5)}_{QQ} \tag{2.36}$$

the contributions from the disconnected Q cluster operators, and

$$E(MP5)_3 = 2E^{(5)}_{TS} \tag{2.37}$$

a contribution, which at higher orders results from disconnected T cluster operators. It is straightforward to evaluate the contributions covered by $E(MP5)_1$, however care has to be taken with regard to all terms associated with disconnected cluster operators since they lead to both linked and unlinked diagrams. For example, in the Q terms of $E(MP5)_2$, one has to identify those disconnected parts of the wave operator that upon closure lead to unlinked diagrams, which can be eliminated.

$$\begin{aligned} E^{(5)}_{DQ} =& \langle\Phi_0|(\hat{T}^{(2)}_2)^\dagger \bar{V}\frac{1}{2}(\hat{T}^{(1)}_2)^2|\Phi_0\rangle_C \\ =& \langle\Phi_0|(\hat{T}^{(2)}_2)^\dagger \left[\bar{V}\frac{1}{2}(\hat{T}^{(1)}_2)^2\right]_C|\Phi_0\rangle \end{aligned} \tag{2.38}$$

As also found for the Q term of MP4, the disconnected diagram part $\left[\bar{V}\frac{1}{2}(\hat{T}^{(1)}_2)^2\right]_D$ solely leads to unlinked diagram contributions so that $E^{(5)}_{DQ}$ is determined just by the connected diagram part $\left[\bar{V}\frac{1}{2}(\hat{T}^{(1)}_2)^2\right]_C$ as shown in Eq.(2.38).

The second Q term of Eq. (2.36) can also be partitioned into two parts according to the splitting into $\left[\bar{V}\frac{1}{2}(\hat{T}^{(1)}_2)^2\right]_C$ and $\left[\bar{V}\frac{1}{2}(\hat{T}^{(1)}_2)^2\right]_D$. However, closure of the disconnected cluster part by the $\hat{T}^{(2)}_3$ operator leads to a connected contribution.

$$\begin{aligned} E^{(5)}_{TQ} =& \langle\Phi_0|(\hat{T}^{(2)}_3)^\dagger \bar{V}\frac{1}{2}(\hat{T}^{(1)}_2)^2|\Phi_0\rangle_C \\ =& \langle\Phi_0|(\hat{T}^{(2)}_3)^\dagger \left[\bar{V}\frac{1}{2}(\hat{T}^{(1)}_2)^2\right]_D|\Phi_0\rangle_C + \langle\Phi_0|(\hat{T}^{(2)}_3)^\dagger \left[\bar{V}\frac{1}{2}(\hat{T}^{(1)}_2)^2\right]_C|\Phi_0\rangle \\ =& E^{(5)}_{TQ}(I) + E^{(5)}_{TQ}(II) \end{aligned} \tag{2.39}$$

By combining $E^{(5)}_{TQ}(I)$ with $E^{(5)}_{TS}$ of $E(MP5)_3$, one can get rid of the triple cluster operator $\hat{T}^{(2)}_3$ according to

$$E^{(5)}_{TS} + E^{(5)}_{TQ}(I) = \langle\Phi_0|(\hat{T}^{(2)}_3)^\dagger \bar{V}\hat{T}^{(2)}_1|\Phi_0\rangle + \langle\Phi_0|(\hat{T}^{(2)}_3)^\dagger \hat{T}^{(1)}_2(\bar{V}\hat{T}^{(1)}_2)_C|\Phi_0\rangle_C \tag{2.40}$$

$$= \langle\Phi_0|(\hat{T}^{(1)}_2)^\dagger (\bar{V}\hat{T}^{(2)}_1\hat{T}^{(1)}_2)_C|\Phi_0\rangle \tag{2.41}$$

where we have used the fact that [38]

$$\langle\Phi_y|(\bar{V}\hat{T}_m\hat{T}_n)_D|\Phi_0\rangle = \langle\Phi_y|\hat{T}_m(\bar{V}\hat{T}_n)_C|\Phi_0\rangle + \langle\Phi_y|\hat{T}_n(\bar{V}\hat{T}_m)_C|\Phi_0\rangle \tag{2.42}$$

and have applied the factorization theorem [34],

$$(xy)^{-1} = (x+y)^{-1}(x^{-1}+y^{-1}). \tag{2.43}$$

The combination of $E_{TS}^{(5)}$ and $E_{TQ}^{(5)}(I)$ leads to a reduction of computational cost from $O(M^7)$ to $O(M^6)$ since the computational requirements for triple amplitudes b_t involve an $O(M^7)$ dependence while the calculation of $E_{TS}^{(5)} + E_{TQ}^{(5)}(I)$ in Eq. (2.41) requires only $O(M^6)$ steps.

The last Q term of Eq. (2.36) can also be split into two parts, which have to be evaluated separately.

$$\begin{aligned} E_{QQ}^{(5)} =& \langle\Phi_0|\frac{1}{2}((\hat{T}_2^{(1)})^\dagger)^2\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2|\Phi_0\rangle_C \\ =& \langle\Phi_0|\frac{1}{2}((\hat{T}_2^{(1)})^\dagger)^2\left[\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2\right]_D|\Phi_0\rangle_C \\ &+ \langle\Phi_0|\frac{1}{2}((\hat{T}_2^{(1)})^\dagger)^2\left[\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2\right]_C|\Phi_0\rangle \\ =& E_{QQ}^{(5)}(I) + E_{QQ}^{(5)}(II) \end{aligned} \tag{2.44}$$

In this way, each of the nine terms of $E_{MP}^{(5)}$ (see Eq.2.32) is expressed in a cluster operator form, which can easily be transformed into appropriate two-electron integral formulas. Any computer program for the calculation of MP2, MP3, MP4 or MP5 correlation energies is based on the two-electron integral equations and, therefore, the transformation into the latter has to be done in the most economic way. This aspect will be discussed in the next section.

2.2 DERIVATION OF MØLLER-PLESSET CORRELATION ENERGIES IN TERMS OF TWO-ELECTRON INTEGRAL FORMULAS

MP methods are practical up to fourth order and become more difficult to apply at higher orders. This becomes obvious when inspecting the two-electron integral formulas of MP2, MP3, MP4, etc. For example, the appropriate expression for the MP2 energy is given by [3,4]

$$E_{MP}^{(2)} = \frac{1}{4}\sum_{ij}\sum_{ab}\langle ij||ab\rangle a_{ij}^{ab} \tag{2.45}$$

where a_{ij}^{ab} are the D amplitudes that are defined by

$$a_{ij}^{ab} = (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1} \langle ab||ij\rangle \tag{2.46}$$

The double-bar integrals $\langle ij||ab\rangle$ are antisymmetrized two-electron integrals of the general type $\langle pq||rs\rangle$:

$$\langle pq||rs\rangle = \int\int \psi_p^*(1)\psi_q^*(2)\frac{1}{r_{12}}[\psi_r(1)\psi_s(2) - \psi_s(1)\psi_r(2)]d\tau_1 d\tau_2$$

Eq. (2.45) is obtained by transformation of Eq.s (2.16) and (2.18), respectively, using Slater rules for matrix elements over orthonormal spin orbitals ψ_p. The computational cost for the evaluation of the MP2 energy results just from the transformation of two-electron integrals over basis functions χ_μ into two-electron integrals over spin orbitals ψ_p, which is proportional to $O(M^5)$ where M denotes the number of basis functions. This cost factor is actually much lower than the cost suggested by the transformation Eq. (2.47).

$$\langle ij|kl\rangle = \sum_\mu \sum_\nu \sum_\lambda \sum_\sigma \langle \mu\nu|\lambda\sigma\rangle c_{\mu i} c_{\nu j} c_{\lambda k} c_{\sigma l} \tag{2.47}$$

If one would carry out the one-step transformation of (2.47), then the computational work would be proportional to $O(M^8)$. This can be seen by realizing that about M^4 two-electron integrals over basis functions χ_μ have to be calculated at the SCF level (this the reason why the cost of a HF calculation is proportional to $O(M^4)$), which are transformed into M^4 two-electron integrals over spin orbitals. Yoshimine and co-workers [39] realized that the M^8 transformation could be dissected into a sequence of four M^5 transformations by calculating intermediate arrays $\langle \mu\nu|\lambda l\rangle$, $\langle \mu\nu|kl\rangle$, and $\langle \mu j|kl\rangle$ which represent partially transformed two-electron integrals:

$$\langle \mu\nu|\lambda l\rangle = \sum_\sigma \langle \mu\nu|\lambda\sigma\rangle c_{\sigma l} \tag{2.48}$$

$$\langle \mu\nu|kl\rangle = \sum_\lambda \langle \mu\nu|\lambda l\rangle c_{\lambda k} \tag{2.49}$$

$$\langle \mu j|kl\rangle = \sum_\nu \langle \mu\nu|kl\rangle c_{\nu j} \tag{2.50}$$

$$\langle ij|kl\rangle = \sum_\mu \langle \mu j|kl\rangle c_{\mu i} \tag{2.51}$$

In this way, the integral transformation can be carried out at a cost level which is not so much higher than that of a HF calculation. On the other hand, it is clear that any correlation corrected ab initio calculation involves at least $O(M^5)$ computational steps because of (2.48) - (2.51).

The computational cost for the calculation of the MP3 correlation energy can be determined from the appropriate two-electron integral formula given in Eq. (2.52): [5]

$$E_{MP}^{(3)} = \frac{1}{4}\sum_{ij}\sum_{ab}\langle ij||ab\rangle b_{ij}^{ab} \tag{2.52}$$

where the second order D excitation amplitudes are defined in Eq. (2.53):

$$b_{ij}^{ab} = (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1}\left[\frac{1}{2}(\sum_{ef}\langle ab||ef\rangle a_{ij}^{ef} + \sum_{mn}\langle mn||ij\rangle a_{mn}^{ab}) - \sum_{me}\sum_{P}(-1)^P P(i/j|a/b)\langle mb||je\rangle a_{im}^{ae}\right] \tag{2.53}$$

The calculation of the b_{ij}^{ab} amplitudes requires $O(M^6)$ steps and, accordingly, the calculation of the MP3 correlation energy is an $O(M^6)$ operation.

One could expect that the calculation of the MP4 energy is an $O(M^8)$ procedure because one has to loop over occupied spin orbitals i,j,k,l and virtual spin orbitals a,b,c,d to get the Q term. However, the idea of using intermediate arrays becomes important when calculating $E_Q^{(4)}$. To calculate $E_{MP}^{(4)}$, one has to define first the second order amplitudes for S and T excitations, respectively:

$$b_i^a = -(\epsilon_i - \epsilon_a)^{-1}\left[\frac{1}{2}\sum_{m,ef}\langle ma||ef\rangle a_{im}^{ef} + \frac{1}{2}\sum_{mn,e}\langle mn||ie\rangle a_{mn}^{ae}\right] \tag{2.54}$$

$$b_{ijk}^{abc} = (\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c)^{-1}\sum_{P}(-1)^P P(i/jk|a/bc)\left[\sum_{e}\langle bc||ei\rangle a_{jk}^{ae} - \sum_{m}\langle ma||jk\rangle a_{im}^{bc}\right]. \tag{2.55}$$

Then, one can simply transform matrix elements such as $\langle\Phi_d|\bar{V}\hat{T}_i^{(2)}|\Phi_0\rangle$ (i = 1, 2, 3) and $\langle\Phi_d|\left[\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2\right]_C|\Phi_0\rangle$ of the cluster operator Eq. (2.22) into two-electron integral formulas using the auxiliary arrays $vn(ij..,ab..)$ shown in Table 2.1.

TABLE 2.1. Definition of auxiliary arrays v1 - v9 for use in MP4 and MP5 calculations.

Array	Matrix element	Two-electron integral formula	Cost
v1(ij,ab)	$\langle\Phi_{ij}^{ab}\|\bar{V}\hat{T}_1^{(2)}\|\Phi_0\rangle$	$\sum_e \sum_P (-1)^P P(i/j)\langle ab\|\|ej\rangle b_i^e \quad + \quad \sum_m \sum_P (-1)^P P(a/b)\langle ma\|\|ij\rangle b_m^b$	$O(M^5)$
v2(ij,ab)	$\langle\Phi_{ij}^{ab}\|\bar{V}\hat{T}_2^{(2)}\|\Phi_0\rangle$	$\frac{1}{2}\left[\sum_{ef}\langle ab\|\|ef\rangle b_{ij}^{ef} + \sum_{mn}\langle mn\|\|ij\rangle b_{mn}^{ab}\right]$ $-\sum_{me}\sum_P (-1)^P P(i/j\|a/b)\langle mb\|\|je\rangle b_{im}^{ae}$	$O(M^6)$
v3(ij,ab)	$\langle\Phi_{ij}^{ab}\|\bar{V}\hat{T}_3^{(2)}\|\Phi_0\rangle$	$\frac{1}{2}\left[\sum_{mef}\sum_P (-1)^P P(a/b)\langle bm\|\|ef\rangle b_{ijm}^{aef}\right.$ $\left.+\sum_{mne}\sum_P (-1)^P P(i/j)\langle mn\|\|ej\rangle b_{imn}^{abe}\right]$	$O(M^7)$
v4(ij,ab)	$\langle\Phi_{ij}^{ab}\|[\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2]_C\|\Phi_0\rangle$	$\frac{1}{2}\sum_{mn} x1(ij,mn)a_{mn}^{ab} \quad - \quad \sum_e \sum_P (-1)^P P(a/b)x2(b,e)a_{ij}^{ae}$ $-\sum_m \sum_P (-1)^P P(i/j)x3(j,m)a_{im}^{ab} \quad + \quad \sum_{nf}\sum_P (-1)^P P(i/j)x4(ia,nf)a_{jn}^{bf}$	$O(M^6)$
v5(ij,ab)	$\langle\Phi_{ij}^{ab}\|[\bar{V}\hat{T}_1^{(2)}\hat{T}_2^{(1)}]_C\|\Phi_0\rangle$	$\sum_P (-1)^P P(i/j)\left[\sum_n y1(n,j)a_{in}^{ab} + \sum_{n,e}\sum_{P'}(-1)^{P'}P'(a/b)y2(a,n,j,e)a_{in}^{be}\right]$ $+\sum_p (-1)^P P(a/b)\left[\sum_f y3(a,f)a_{ij}^{bf} + \sum_{m,f}\sum_{P'}(-1)^{P'}P'(i/j)y4(a,m,i,f)a_{jm}^{bf}\right]$ $-\frac{1}{2}\sum_{mn} y5(mn,ij)a_{mn}^{ab} \quad - \quad \frac{1}{2}\sum_{ef} y6(ab,ef)a_{ij}^{ef}$	$O(M^6)$
v6(i,a)	$\langle\Phi_i^a\|\bar{V}\hat{T}_1^{(2)}\|\Phi_0\rangle$	$-\sum_{me}\langle ma\|\|ie\rangle b_m^e$	$O(M^5)$
v7(ijk,abc)	$\langle\Phi_{ijk}^{abc}\|\bar{V}\hat{T}_3^{(2)}\|\Phi_0\rangle$	$\frac{1}{2}\left[\sum_{ef}\sum_P (-1)^P P(a/bc)\langle bc\|\|ef\rangle b_{ijk}^{aef}\right.$ $\left.+\sum_{mn}\sum_P (-1)^P P(i/jk)\langle mn\|\|jk\rangle b_{imn}^{abc}\right]$ $-\sum_{me}\sum_P (-1)^P P(i/jk\|a/bc)\langle ma\|\|ie\rangle b_{jkm}^{bce}$	$O(M^8)$
v8(ijk,abc)	$\langle\Phi_{ijk}^{abc}\|(\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2)_C\|\Phi_0\rangle$	$\sum_P (-1)^P P(i/jk\|a/bc)\left[\sum_f y7(i,bc,f)a_{jk}^{af} + \sum_m y8(jk,m,a)a_{im}^{bc}\right]$	$O(M^7)$
v9(ijkl,abcd)	$a_{ij}^{ab}a_{kl}^{cd}\langle\Phi_{ijkl}^{abcd}\|\left[\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2\right]_C\|\Phi_0\rangle$	$-a_{ij}^{ab}a_{kl}^{cd}\sum_m\sum_P (-1)^P P(i/jkl\|ab/cd)\left\{\sum_{P'}(-1)^{P'}P'(j/kl)\left[\frac{1}{2}\sum_n\langle kl\|\|mn\rangle a_{jn}^{cd}\right.\right.$ $\left.\left.-\sum_e\sum_{P''}(-1)^{P''}P''(c/d)\langle mc\|\|je\rangle a_{kl}^{de}\right]\right\}a_{im}^{ab}$	
		$-\frac{1}{2}a_{ij}^{ab}a_{kl}^{cd}\sum_{ef}\sum_P (-1)^P P(ij/kl\|a/bcd)\left[\sum_{P'}(-1)^{P'}P'(b/cd)\langle cd\|\|ef\rangle a_{kl}^{bf}\right]a_{ij}^{ae}$	$O(M^{10})$

TABLE 2.2. Definition of intermediate arrays xi and yj used in MP4 and MP5 calculations to reduce cost.

Arrays xi and yj	Array vk	Tow-electron integral formula	Cost
x1(ij,mn)	v4(ij,ab)	$\frac{1}{2}\sum_{ef}\langle mn\|\|ef\rangle a_{ij}^{ef}$	$O(M^6)$
x2(b,e), x3(j,m)	v4(ij,ab)	$\frac{1}{2}\sum_{mn,f}\langle mn\|\|ef\rangle a_{mn}^{bf}$, $\frac{1}{2}\sum_{n,ef}\langle mn\|\|ef\rangle a_{jn}^{ef}$	$O(M^5)$
x4(ia,nf)	v4(ij,ab)	$\sum_{m,e}\langle mn\|\|ef\rangle a_{im}^{ae}$	$O(M^6)$
y1(n,j), y3(a,f)	v5(ij,ab)	$\sum_{m,e}\langle mn\|\|je\rangle b_m^e$, $\sum_{m,e}\langle am\|\|ef\rangle b_m^e$	$O(M^5)$
y2(a,n,j,e), y4(a,m,i,f)	v5(ij,ab)	$\sum_m\langle mn\|\|je\rangle b_m^a$, $\sum_e\langle am\|\|ef\rangle b_i^e$	$O(M^5)$
y5(mn,ij)	v5(ij,ab)	$\sum_e\sum_P(-1)^P P(i/j)\langle mn\|\|je\rangle b_i^e$	$O(M^5)$
y6(ab,ef)	v5(ij,ab)	$\sum_m\sum_P(-1)^P P(a/b)\langle am\|\|ef\rangle b_m^b$	$O(M^5)$
y7(i,bc,f)	v8(ijk,abc)	$\sum_{me}\sum_P(-1)^P P(b/c)\langle mb\|\|ef\rangle a_{im}^{ce} - \frac{1}{2}\sum_{mn}\langle mn\|\|if\rangle a_{mn}^{bc}$	$O(M^6)$
y8(jk,m,a)	v8(ijk,abc)	$\frac{1}{2}\sum_{ef}\langle am\|\|ef\rangle a_{jk}^{ef} + \sum_{ne}\sum_P(-1)^P P(j/k)\langle mn\|\|ej\rangle a_{kn}^{ae}$	$O(M^6)$
y9(b,e), y10(j,m)	v9(ijkl,abcd)	$\sum_{ij,a} a_{ij}^{ab}a_{ij}^{ae}$, $\sum_{iab} a_{ij}^{ab}a_{im}^{ab}$	$O(M^5)$
y11(j,b,m,c), y12(i,j,k,n)	v9(ijkl,abcd)	$\sum_{ia} a_{ij}^{ab}a_{im}^{ac}$, $\sum_{ab} a_{ij}^{ab}a_{kn}^{ab}$	$O(M^6)$
y13(a,b,c,f), y14(k,l,e,f)	v9(ijkl,abcd)	$\sum_{ij} a_{ij}^{ab}a_{ij}^{cf}$, $\sum_{cd} a_{kl}^{cd}\langle cd\|\|ef\rangle$	$O(M^6)$
y15(c,d,m,n) , y16(k,c,m,e)	v9(ijkl,abcd)	$\sum_{kl} a_{kl}^{cd}\langle mn\|\|kl\rangle$, $\sum_{ld} a_{kl}^{cd}\langle md\|\|le\rangle$	$O(M^6)$
y17(k,l,e,f)	v9(ijkl,abcd)	$-\frac{1}{8}\sum_b y9(b,e)a_{kl}^{bf} + \frac{1}{4}\sum_{jb} y11(j,b,k,e)a_{jl}^{bf}$	$O(M^6)$
y18(b,d,e,f)	v9(ijkl,abcd)	$\frac{1}{8}y9(b,e)y9(d,f) + \frac{1}{8}\sum_{ac} y13(a,b,c,f)y13(c,d,a,e)$ $-\frac{1}{2}\sum_{jk} y11(j,b,k,e)y11(k,d,j,f)$	$O(M^6)$
y19(c,d,m,n)	v9(ijkl,abcd)	$-\frac{1}{8}\sum_j y10(j,m)a_{jn}^{cd} + \frac{1}{4}\sum_{jb} y11(j,b,m,c)a_{jn}^{bd}$	$O(M^6)$
y20(m,n,j,l)	v9(ijkl,abcd)	$\frac{1}{8}y10(j,m)y10(l,n) + \frac{1}{8}\sum_{ik} y12(i,j,k,n)y12(k,l,i,m)$ $-\frac{1}{2}\sum_{bc} y11(j,b,m,c)y11(l,c,n,b)$	$O(M^6)$
y21(k,c,m,e)	v9(ijkl,abcd)	$\sum_{ja} y11(j,a,m,c)a_{jk}^{ae} - \frac{1}{2}\sum_j y10(j,m)a_{jk}^{ce}$ $-\frac{1}{2}\sum_b y9(b,e)a_{km}^{bc} - \frac{1}{4}\sum_{ij} y12(i,j,k,m)a_{ij}^{ce}$	$O(M^6)$
y22(m,b,l,e)	v9(ijkl,abcd)	$\frac{1}{2}\sum_{ik} y11(i,b,k,e)y12(k,l,i,m) - \sum_{jc} y11(j,b,m,c)y11(l,c,j,e)$ $-\frac{1}{4}y9(b,c)y10(l,m) + \frac{1}{2}\sum_{ad} y13(a,b,d,c)y11(l,d,m,a)$	$O(M^6)$

This leads to the MP4 energy of Eq. (2.56):

$$E_{MP}^{(4)} = \frac{1}{4}\sum_{ij}\sum_{ab} a_{ij}^{ab}\,(v1(ij,ab) + v2(ij,ab) + v3(ij,ab) + v4(ij,ab)) \qquad (2.56)$$

in which the array $v4(ij,ab)$ is calculated with the help of the intermediate arrays $x1(ij,mn), x2(b,e), x3(j,m)$ and $x4(ia,nf)$ listed in Table 2.2. For the calculation of the intermediate arrays, one needs $O(M^6)$ or less costly computational steps, which means that the calculation of the Q term of $E_{MP}^{(4)}$ is actually not more costly than calculating the S or D term of MP4. According to Table 2.1, the cost for calculating the MP4 correlation energy is determined by the array $v3(ij,ab)$ associated with the T term. Since this is an $O(M^7)$ operation, full MP4 is just one power of M more costly than MP3 while MP4(SDQ) and MP3 are comparable in cost. [5-7]

At MP5 and higher levels of MP perturbation theory, the development of an efficient computer program is directly connected with the derivation of suitable intermediate arrays. By defining the right intermediate arrays, the mathematical algorithms for MP5, MP6, etc. can be executed on a computer in a minimum of time. This is indicated in Table 2.3 for MP5 and MP6, which are reduced from $O(M^{10})$ to $O(M^8)$ and $O(M^{12})$ to $O(M^9)$ procedures by using series of intermediate arrays. One can say that the development of such electron correlation methods focuses a) on how to get rid of unwanted unlinked diagram contributions and b) on how to set up the right intermediate arrays in the two-electron integral equations.

In a similar way as for $E_{MP}^{(4)}$, one can derive two-electron integral formulas for $E(MP5)_1$, $E(MP5)_2$ and $E(MP5)_3$ of $E_{MP}^{(5)}$. The following equations are obtained.

$$\begin{aligned} E(MP5)_1 =& E_{SS}^{(5)} + 2E_{DS}^{(5)} + E_{DD}^{(5)} + 2E_{DT}^{(5)} + E_{TT}^{(5)} \\ =& \sum_{i,a} b_i^a v6(i,a) + \frac{1}{4}\sum_{ij}\sum_{ab} b_{ij}^{ab}\,[2v1(ij,ab) + v2(ij,ab) + 2v3(ij,ab)] \\ &+ \frac{1}{36}\sum_{ijk}\sum_{abc} b_{ijk}^{abc} v7(ijk,abc) \end{aligned} \qquad (2.57)$$

$$E_{DQ}^{(5)} = \frac{1}{4}\sum_{ij}\sum_{ab} b_{ij}^{ab} v4(ij,ab) \qquad (2.58)$$

$$E_{TS}^{(5)} + E_{TQ}^{(5)}(I) = \frac{1}{4}\sum_{ij}\sum_{ab}[a_{ij}^{ab} v5(ij,ab) + \langle ij||ab\rangle(b_i^a b_j^b - b_i^b b_j^a)] \qquad (2.59)$$

TABLE 2.3. Comparison of MPn methods.

MPn	Number of total terms	Number of unique terms	Cost (without intermediate arrays)	Most expensive term	Cost (intermediate arrays included)	Most expensive terms
MP2	1	1	$O(M^5)$		$O(M^5)$	$\langle ij\|\|ab\rangle$
MP3	1	1	$O(M^6)$		$O(M^6)$	b_{ij}^{ab}
MP4	4	4	$O(M^8)$	$E_Q^{(4)}$	$O(M^7)$	$E_T^{(4)}$
MP5	14	9	$O(M^{10})$	$E_{QQ}^{(5)}$	$O(M^8)$	$E_{TT}^{(5)}$
MP6	55	36	$O(M^{12})$	$E_{QHQ}^{(6)}$	$O(M^9)$	$E_{TQT}^{(6)}$, $E_{QQQ}^{(6)}(II)$ and $E_{TQQ}^{(6)}(II)$
MP7	221	141	$O(M^{14})$	$E_{QHHQ}^{(7)}$	$O(M^{10})$	$E_{TQQT}^{(7)}$, etc.
MP8	915	583	$O(M^{16})$	$E_{QHOHQ}^{(8)}$	$O(M^{11})$	$E_{TQS_7QT}^{(8)}$, etc.

$$E_{TQ}^{(5)}(II) = \frac{1}{36}\sum_{ijk}\sum_{abc} b_{ijk}^{abc} v8(ijk,abc) \tag{2.60}$$

$$E_{QQ}^{(5)}(I) = \frac{1}{4}\sum_{mn}\sum_{ef} a_{mn}^{ef} Q_{mn}^{ef}(\tilde{b}_d, a\times a) \tag{2.61}$$

$$E_{QQ}^{(5)}(II) = \frac{1}{32}\sum_{ij}\sum_{ab}\sum_{kl}\sum_{cd} v9(ijkl,abcd) \tag{2.62}$$

in which $v5(ij,ab)$, $v6(i,a)$, $v7(ijk,abc)$, $v8(ijk,abc)$, and $v9(ijkl,abcd)$ are taken from Table 2.1 and the array $Q_{ij}^{ab}(\tilde{b}_d, a\times a)$ is defined in Eq. (2.63).

$$\begin{aligned} Q_{ij}^{ab}(\tilde{b}_d, a\times a) = &\frac{1}{4}\sum_{mn}\sum_{ef}\tilde{b}_{mn}^{ef}\Big[a_{ij}^{ef}a_{mn}^{ab} - 2\sum_{P}(-1)^P P(a/b)a_{ij}^{ae}a_{mn}^{bf} \\ &-2\sum_{P}(-1)^P P(i/j)a_{im}^{ab}a_{jn}^{ef} \\ &+4\sum_{P}(-1)^P P(i/j)a_{im}^{ae}a_{jn}^{bf}\Big] \end{aligned} \tag{2.63}$$

with

$$\tilde{b}_{mn}^{ef} = (\epsilon_m + \epsilon_n - \epsilon_e - \epsilon_f)b_{mn}^{ef} \tag{2.64}$$

As can be seen from Table 2.1, arrays $v5$, and $v8$ are build up using intermediate arrays $y1, y2, y3, y4, y5, y6, y7$, and $y8$ of Table 2.2. The calculation of each of these arrays does not require more than $O(M^6)$ operations. Hence, the determination of DQ requires just $O(M^6)$ steps, that of TS+TQ(I) also just $O(M^6)$ steps, that of TQ(II) is determined by the cost of evaluating the second order triple amplitudes, which requires $O(M^7)$ steps. If one would not use intermediate arrays, the QQ term would lead to a cost factor of $O(M^{10})$ (Table 2.3), however this is reduced to $O(M^6)$ by using intermediate arrays $y9$ - $y22$, as shown in Eq.(2.65)

$$\begin{aligned} E_{QQ}^{(5)}(II) = &\sum_{kl,ef} y17(k,l,e,f)y14(k,l,e,f) + \sum_{bdef} y18(b,d,e,f)\langle bd||ef\rangle \\ &+\sum_{mncd} y19(c,d,m,n)y15(c,d,m,n) + \sum_{mnjl} y20(m,n,j,l)\langle mn||jl\rangle \\ &+\sum_{kmce} y21(k,c,m,e)y16(k,c,m,e) \\ &+\sum_{lmbe} y22(m,b,l,e)\langle mb||le\rangle \end{aligned} \tag{2.65}$$

Table 2.3 gives an impression on how computational cost increase with the order of MP perturbation theory. Clearly, the reduction of cost by the use of intermediate arrays increases with order n. Accordingly, MP6 is an $O(M^9)$ rather than

an $O(M^{12})$ method, MP7 an $O(M^{10})$ rather than an $O(M^{14})$ method, etc. This indicates that higher order perturbation theory methods are no longer feasible for routine calculations, however MP5, MP6, and even MP7 are suitable for important test calculations or investigations of small molecules. For example, there are $O(M^{10})$ methods such as CISDTQ [40] or CCSDTQ [21], which are nowadays available for expert calculations. Accordingly, the development of MP6 or even MP7 is desirable since these methods provide direct information on higher correlation effects and the convergence behaviour of the MPn series.

Inspection of Table 2.3 reveals that it will almost be impossible with the strategies presently available to derive equations for the 141 energy terms of MP7. The MP6 correlation energy is built up from 36 energy contributions, which also requires an enormous amount of work if one follows either the algebraic or the diagrammatic development procedure, however which becomes feasible when using the strategy described at the beginning of this chapter (see also chapter 3 and references 24, 25).

2.3 CORRELATION EFFECTS COVERED AT VARIOUS ORDERS OF MØLLER-PLESSET PERTURBATION THEORY

Second order MP (MP2) theory covers D excitations and, accordingly, describes pair correlation effects. [3,4] There is no coupling between the D excitations at second order and, therefore, each pair correlation correction is determined as if no other electron pairs are present in the molecule. This leads to an overestimation of pair correlation effects, which has been documented in the literature. [11,28,29] At third order MP (MP3) theory, coupling between D excitations is introduced and in this way, an exaggeration of pair correlation effects at MP2 is partially corrected. [5,11,28,29]

At fourth order MP (MP4) theory, D excitations are complemented by single (S), triple (T) and quadruple (Q) excitations. [6,7] Single excitations describe orbital relaxation effects, which are needed to adjust orbitals to the correlated movement of the electrons. This leads to some limited improvements of the spin orbitals, however, these changes cannot be compared with the systematic self-consistent-field type of adjustment of orbitals within a MCSCF calculation.

The (connected) triple excitations cover three-electron correlation effects that are smaller than the pair correlation effects. For a given electronic system, one can normally distinguish a number of core electron pairs, bond electron pairs, and lone electron pairs. [41] Each of these pairs can correlate with any of the other

electrons in a three-electron situation, which means that the number of three-electron combinations is much larger than the number of core, bond, and lone pairs. Although the T correlation effects are usually quite small their large number leads to sizeable contributions to the correlation energy. [11,28,29] These T contributions may become even rather large if electron pairs are packed close together in a particular area of a molecule. This occurs for multiple bonds in the bonding region, for atoms with two or more lone pairs in the lone pair region or in the valence region of strongly electronegative atoms. In these cases, T excitations help to keep the electron pairs more separated and, therefore, T correlation corrections increase in magnitude.

Quadruple effects in a MP4 calculation correspond to disconnected quadruples [6,7], i.e. they do not describe the correlation of four electrons, but the simultaneous correlation of two independent electron pairs. These pair-pair correlations essentially represent positive correction terms to the pair correlation energy calculated at MP2. They are quite important to get a balanced description of pair correlation. Of course, in large molecules the simultaneous correlation of 3, 4, etc. electron pairs is also important, but these effects are not introduced to MP theory before sixth order (3 electron pairs), eighth order (4 electron pairs), etc.

Three-electron correlation effects can be exaggerated at MP4 for the same reason pair correlation effects are exaggerated at MP2. [11,28,29] MP5 introduces the coupling between S, D, T, and Q excitations in form of SS, SD, ST, DD, DT, DQ, TT, TQ, and QQ correlation effects and, therefore, MP5 gives a better account of T and Q effects. New correlation effects are introduced at sixth order in form of connected Q, disconnected pentuple (P) and disconnected hextuple (H) excitations, i.e. MP6 introduces for the first time four-electron correlation effects. The latter are important in all those situations, in which electrons cluster in a confined region of atomic space as has been demonstrated by MP6 calculations. [28,29] Again, connected Q and disconnected P or H effects can be exaggerated at MP6 because QQ, PP or HH couplings are introduced not before seventh order. In this way, the MPn series continues by introducing new effects at even orders and correcting them via the appropriate couplings at odd orders.

One can compare MP perturbation theory with a car that is fuelled at even orders but slowed down at odd orders. Cremer and co-workers have considered this basic nature of MP perturbation theory as the reason for an erratic or oscillatory behaviour of the MPn series. [11,15,28,29] Energy and other molecular properties do not converge smoothly to an infinite order limit but very often oscillate in the range n = 1 (HF) to n = 5 (MP5). This oscillatory behaviour of results becomes apparent when comparing MP2 and MP4 with MP1 (= HF),

MP3, and MP5 results. It represents a major drawback of perturbation theory, which can fully be understood when MP6 results are included into the comparison. [28,29] Therefore, we will discuss in the following chapter MP6 theory.

3. Møller-Plesset Perturbation Theory at Sixth Order

The MP6 correlation energy comprises 55 energy contributions of the type $E^{(6)}_{ABC}$, which reduce to 36 terms because of symmetry. These energy terms are given in Figure 3.1 in a graphical way as paths connecting excitations S, D, T, and Q at order n with excitations S, D, T, and Q at order 4 under the constraint that Slater rules for the corresponding matrix terms are obeyed. [22,23] For example, one obtains 14 fifth order paths in this way, namely the SS, SD, ST, DS, DD, DT, DQ, TS, TD, TT, TQ, QD, QT, and the QQ path. At sixth order, one has to consider that T and Q excitations can couple with P and H excitations. Therefore, the diagram extends to the right when the paths go down to levels n-1, etc. However, any allowed path can only start and end at A = S, D, T, Q, which is indicated by (wiggled) separation lines for the starting level n in Figure 3.1.

In the lower half of Figure 3.1 all 55 energy paths of MP6 are listed, 19 of which are equivalent because of symmetry. Hence, there remain 36 unique paths corresponding to 36 unique energy terms $E^{(6)}_{ABC}$, which have to be calculated to determine the MP6 correlation energy.

Our work on a MP6 method for routine calculations was triggered by several reasons.

(1) MP6 is after MP2 and MP4 the next even order method that should be of interest because of the introduction of new correlation effects described by connected Q or disconnected P and H excitations.

(2) With MP6 one has three energies (MP2, MP4, MP6) in the class of even order methods and three in the class of odd order methods (MP1 = HF, MP3, MP5). In this way, one gets a somewhat more realistic basis to test the initial convergence behaviour of the MPn series.

(3) Inspection of Table 2.3 and Figure 3.1 reveals that MP6 is actually the last method that can be developed using traditional techniques. MP7 has already a total of 221 terms, 141 of which are unique. Therefore, setting up MP7 or even higher MPn methods will require some form of automated method development strategy based on computer algebra languages.

(4) The cost of a MP6 calculation is proportional to $O(M^9)$ (see Table 2.3). This is too expensive for calculations on larger molecules, but still gives a chance for systematic studies on small molecules.

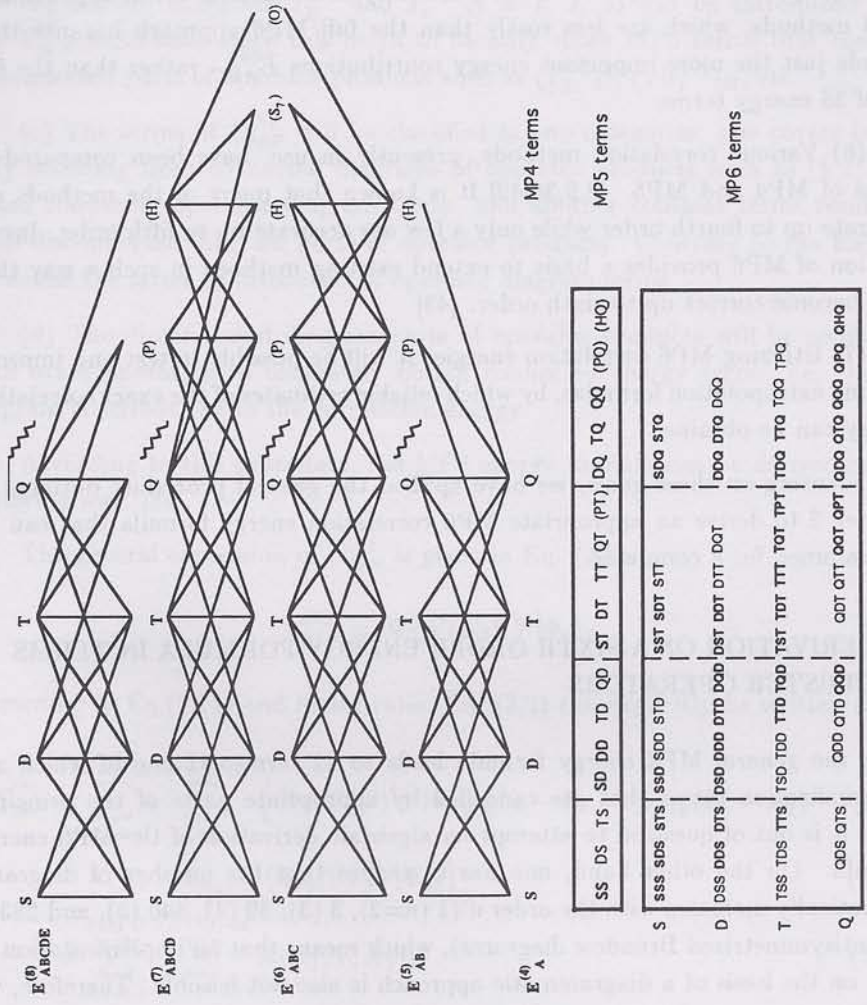


Figure 3.1. Graphical representation of energy contributions $E^{(n)}_{ABC..}$ at nth order many-body perturbation theory (n = 4, 5, 6, 7, 8) (upper part of the figure). A particular energy contribution $E^{(n)}_{ABC..}$ is given by the solid line that starts at A = S, D, T or Q in row $E^{(n)}$ and connects B, C, etc. at row n-1, n-2, etc. until n = 4 is reached. Note that at the n-1, n-2, .., n = 5 level also those excitations are included that can couple with A = S, D, T, Q at level n and level 4 according to Slater rules. They are given in parentheses after a separator (downward directed wiggles) to the right of the S, D, T, Q excitations. - At the bottom of the diagram, 5th order and 6th order energy terms $E^{(5)}_{AB}$ and $E^{(6)}_{ABC}$ respectively, are listed in correspondence to the energy paths shown in the upper half of the diagram. Unique terms are given in bold print. *Reprinted with permission from Z. He and D. Cremer, Int. J. Quant. Chem (1996) 59, 15. Copyright (1996) J. Wiley, Inc.*

(5) Apart from this, there is the possibility of developing useful approximate MP6 methods, which are less costly than the full MP6 approach because they include just the more important energy contributions $E_{ABC}^{(6)}$ rather than the full set of 36 energy terms.

(6) Various correlation methods, presently in use, have been compared in terms of MP4 and MP5. [8,9,36,42] It is known that many of the methods are accurate up to fourth order while only a few are accurate up to fifth order. Investigation of MP6 provides a basis to extend existing methods in such a way that they become correct up to sixth order. [43]

(7) Utilizing MP6 correlation energies it will be possible to test and improve existing extrapolation formulas, by which reliable estimates of the exact correlation energy can be obtained.

Focusing on these goals, we have applied the general procedure outlined in chapter 2 to derive an appropriate MP6 correlation energy formula that can be programmed for a computer.

3.1 DERIVATION OF A SIXTH ORDER ENERGY FORMULA IN TERMS OF CLUSTER OPERATORS

Since the general MP6 energy formula leads to 42 terms, 41 one of which are renormalization terms that are cancelled by appropriate parts of the principal term, it is out of question to attempt an algebraic derivation of the MP6 energy formula. On the other hand, one has to realize that the number of diagrams dramatically increases with the order n (1 (n=2), 3 (3), 39 (4), 840 (5), and 28300 (6) antisymmetrized Brandow diagrams), which means that an implementation of MP6 on the basis of a diagrammatic approach is also not feasible. Therefore, we avoid to derive the MP6 energy formula in a diagram-by-diagram manner or in an algebraic fashion. Instead, we use the procedure outlined in chapter 2, which represents a balanced mixture of diagrammatic and algebraic approach. This procedure comprises for MP6 the following steps.

(a) Starting from the general formula

$$E_{MP}^{(n)} = \langle \Phi_0 | \hat{V} (\hat{G}_0 \bar{V})^{n-1} | \Phi_0 \rangle_L \tag{3.1}$$

and the expression for the reduced resolvent $\hat{G}_0$ (Eq.(2.11), we will develop the MP6 energy equation in terms of S, D, T, Q, P, and H contributions. Contributions of higher excitations will be truncated according to Slater rules.

(b) Cluster operators $\hat{T}_2^{(1)}$ and $\hat{T}_i^{(2)}$ (i = 1, 2, 3) will be introduced into the $E_{MP}^{(6)}$ expression since this helps to identify those MP6 terms that contain disconnected parts of operator products such as $(\hat{T}_2^{(1)})^2$, $(\bar{V}\hat{T}_i^{(2)})_D$, etc.

(c) The terms of $E_{MP}^{(6)}$ will be classified in two categories: one covers terms only resulting from connected diagrams of operator products such as $(\bar{V}\hat{T}_i^{(2)})_C$ called connected operator diagram terms; and another contains terms resulting from disconnected diagram parts of operator products. Contrary to the former, we define the latter as disconnected operator diagram terms.

(d) The disconnected diagram parts of operator products will be combined with other operators to ultimately obtain connected energy terms, i.e. linked diagram contributions to the correlation energy.

According to this procedure, the MP6 energy formula can be derived in the following way. [24].

The general expression of $E_{MP}^{(6)}$ is given in Eq. (3.2):

$$E_{MP}^{(6)} = \langle\Phi_0|\bar{V}(\hat{G}_0\bar{V})^5|\Phi_0\rangle_L \tag{3.2}$$

According to Eq.(2.11) and Slater rules, Eq. (3.2) can explicitly be written as

$$E_{MP}^{(6)} = \sum_{x_1,x_2}^{SDTQ}\sum_{y}^{SDTQPH}\Big(\langle\Phi_0|(\hat{T}_2^{(1)})^\dagger\bar{V}|\Phi_{x_1}\rangle(E_0-E_{x_1})^{-1}\bar{V}_{x_1y}(E_0-E_y)^{-1}\bar{V}_{yx_2}$$
$$\times(E_0-E_{x_2})^{-1}\langle\Phi_{x_2}|\bar{V}\hat{T}_2^{(1)}|\Phi_0\rangle\Big)_L \tag{3.3a}$$
$$= \sum_{X_1,X_2}^{SDTQ}\sum_{Y}^{SDTQPH}\mathcal{A}(X_1,Y,X_2)_L \tag{3.3b}$$

with $\mathcal{A}(X_1,Y,X_2)$ being

$$\mathcal{A}(X_1,Y,X_2) = \sum_{x_1}^{X_1}\sum_{x_2}^{X_2}\sum_{y}^{Y}\langle\Phi_0|(\hat{T}_2^{(1)})^\dagger\bar{V}|\Phi_{x_1}\rangle(E_0-E_{x_1})^{-1}\bar{V}_{x_1y}(E_0-E_y)^{-1}$$
$$\times\bar{V}_{yx_2}(E_0-E_{x_2})^{-1}\langle\Phi_{x_2}|\bar{V}\hat{T}_2^{(1)}|\Phi_0\rangle \tag{3.4}$$

By using the cluster operators $\hat{T}_2^{(1)}$ and $\hat{T}_i^{(2)}$ (i = 1, 2, 3), one can partition the MP6 energy into three different $\mathcal{A}(X_1,Y,X_2)$ terms:

$$E_{MP}^{(6)} = \mathcal{A}_1[(\bar{V}\hat{T}_i^{(2)})_C] + \mathcal{A}_2[(\hat{T}_2^{(1)})^2]_L + \mathcal{A}_3[(\bar{V}\hat{T}_i^{(2)})_D]_L \quad (i=1,2,3) \tag{3.5}$$

The first part, $\mathcal{A}_1$, covers all connected cluster operator diagrams resulting from $(\bar{V}\hat{T}_i^{(2)})_C$ and fully contributes to to $E_{MP}^{(6)}$ in form of $E(MP6)_1$:

$$\begin{aligned}\mathcal{A}_1[(\bar{V}\hat{T}_i^{(2)})_C] =& E(MP6)_1 \\ =& \sum_{i,j=1,2,3}\sum_{y}^{S,D}\langle\Phi_0|[(\hat{T}_i^{(2)})^\dagger\bar{V}]_C|\Phi_y\rangle(E_0-E_y)^{-1}\langle\Phi_y|(\bar{V}\hat{T}_j^{(2)})_C|\Phi_0\rangle \\ &+\sum_{i,j=2,3}\sum_{t}^{T}\langle\Phi_0|[(\hat{T}_i^{(2)})^\dagger\bar{V}]_C|\Phi_t\rangle(E_0-E_t)^{-1}\langle\Phi_t|(\bar{V}\hat{T}_j^{(2)})_C|\Phi_0\rangle \\ &+\sum_{q}^{Q}\langle\Phi_0|[(\hat{T}_3^{(2)})^\dagger\bar{V}]_C|\Phi_q\rangle(E_0-E_q)^{-1}\langle\Phi_q|(\bar{V}\hat{T}_3^{(2)})_C|\Phi_0\rangle \qquad (3.6) \\ =& E_{SSS}^{(6)}+2E_{SSD}^{(6)}+2E_{SST}^{(6)}+E_{SDS}^{(6)}+2E_{SDD}^{(6)} \\ &+2E_{SDT}^{(6)}+E_{DSD}^{(6)}+2E_{DST}^{(6)}+E_{DDD}^{(6)}+2E_{DDT}^{(6)}+E_{TST}^{(6)} \\ &+E_{TDT}^{(6)}+E_{DTD}^{(6)}+2E_{DTT}^{(6)}+E_{TTT}^{(6)}+E_{TQT}^{(6)} \qquad (3.7)\end{aligned}$$

The second and the third part, $\mathcal{A}_2$ and $\mathcal{A}_3$, cover all disconnected cluster operator diagram terms resulting from $(\hat{T}_2^{(1)})^2$ or various combinations of $\hat{T}_i^{(2)}$ with $\bar{V}$ as illustrated in Figure 3.2.

$$\begin{aligned}\mathcal{A}_2[(\hat{T}_2^{(1)})^2]_L = \sum_{X_1}^{S,D,T,Q}\sum_{Y}^{D,T,Q,P,H} & (2-\delta_{X_1,Q}-\delta_{X_1,S}\delta_{Y,T}-\delta_{X_1,D}\delta_{Y,Q} \\ & -\delta_{X_1,T}\delta_{Y,P})\mathcal{A}(X_1,Y,Q)_L \qquad (3.8)\end{aligned}$$

where

$$\mathcal{A}(X_1,Y,Q)=\sum_{y}^{Y}\langle\Phi_0|(\hat{T}_i^{(2)})^\dagger\bar{V}|\Phi_y\rangle(E_0-E_y)^{-1}\langle\Phi_y|\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2|\Phi_0\rangle$$
$$(i=1,2,3\ for\ X_1=S,D,T) \qquad (3.9)$$

or

$$\mathcal{A}(Q,Y,Q)=\sum_{y}^{Y}\langle\Phi_0|\frac{1}{2}((\hat{T}_2^{(1)})^\dagger)^2\bar{V}|\Phi_y\rangle(E_0-E_y)^{-1}\langle\Phi_y|\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2|\Phi_0\rangle \qquad (3.10)$$

As indicated in Figure 3.2, the disconnected Q cluster operator $(\hat{T}_2^{(1)})^2$ in $\mathcal{A}_2[(\hat{T}_2^{(1)})^2]_L$ couples with the perturbation operator $\bar{V}$. This leads to disconnected and connected cluster operator diagram parts, which in turn lead to the energy contributions $\mathcal{A}(X_1,Y,Q_D)_L$ and $\mathcal{A}(X_1,Y,Q_C)_L$ of Eq.s (3.11) - (3.14).

$$\mathcal{A}(X_1,Y,Q_D)_L=\sum_{y}^{Y}\left(\langle\Phi_0|(\hat{T}_i^{(2)})^\dagger\bar{V}|\Phi_y\rangle(E_0-E_y)^{-1}\langle\Phi_y|\hat{T}_2^{(1)}(\bar{V}\hat{T}_2^{(1)})_C|\Phi_0\rangle\right)_L$$
$$(i=1,2,3\ when\ X_1=S,D,T;Y=T,Q,P) \qquad (3.11)$$

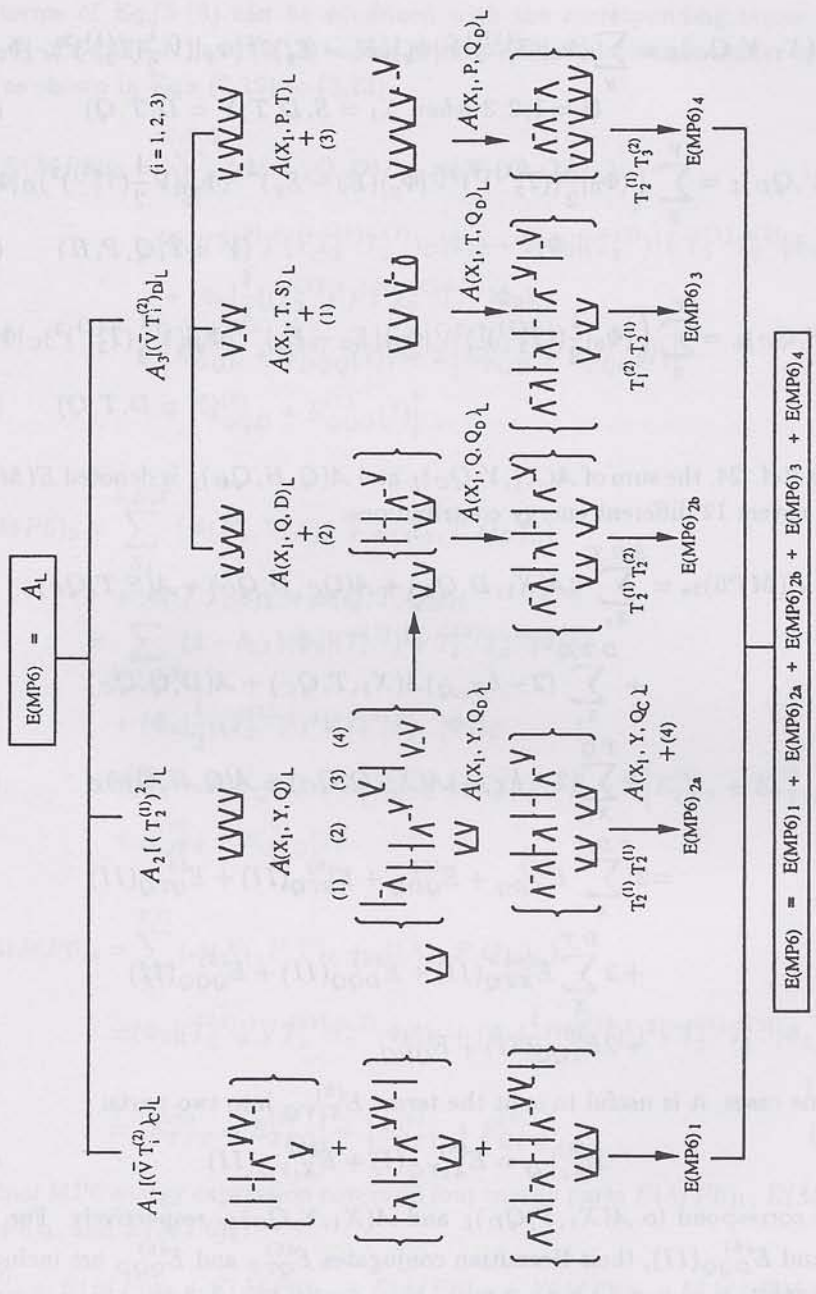


Figure 3.2. Derivation of the MP6 energy formula. For the perturbation operator and the cluster operators simplified Brandow diagrams are used. For more details, see text. *Reprinted with permission from D. Cremer and Z. He, J. Phys. Chem., (1996) 100, 6173. Copyright (1996) American Chemical Society.*

$$\mathcal{A}(X_1,Y,Q_C)_L=\sum_y^Y\langle\Phi_0|(\hat{T}_i^{(2)})^\dagger\bar{V}|\Phi_y\rangle(E_0-E_y)^{-1}\langle\Phi_y|(\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2)_C|\Phi_0\rangle$$
$$(i=1,2,3\ when\ X_1=S,D,T;Y=D,T,Q) \tag{3.12}$$

$$\mathcal{A}(Q,Y,Q_D)_L=\sum_y^Y\left(\langle\Phi_0|\frac{1}{2}((\hat{T}_2^{(1)})^\dagger)^2\bar{V}|\Phi_y\rangle(E_0-E_y)^{-1}\langle\Phi_y|(\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2)_D|\Phi_0\rangle\right)_L$$
$$(Y=T,Q,P,H) \tag{3.13}$$

$$\mathcal{A}(Q,Y,Q_C)_L=\sum_y^Y\left(\langle\Phi_0|\frac{1}{2}((\hat{T}_2^{(1)})^\dagger)^2\bar{V}|\Phi_y\rangle(E_0-E_y)^{-1}\langle\Phi_y|(\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2)_C|\Phi_0\rangle\right)_L$$
$$(Y=D,T,Q) \tag{3.14}$$

In Ref. 24, the sum of $\mathcal{A}(X_1,Y,Q_C)_L$ and $\mathcal{A}(Q,H,Q_D)_L$ is denoted $E(MP6)_{2a}$, which covers 12 different energy contributions:

$$\begin{aligned}E(MP6)_{2a}=&\sum_{X_1}^{S,D,T}2\mathcal{A}(X_1,D,Q_C)+\mathcal{A}(Q_C,D,Q_C)+\mathcal{A}(S,T,Q_C)\\&+\sum_{X_1}^{D,T,Q}(2-\delta_{X_1,Q})\mathcal{A}(X_1,T,Q_C)+\mathcal{A}(D,Q,Q_C)\\&+\sum_{X_1}^{T,Q}(2-\delta_{X_1,Q})\mathcal{A}(X_1,Q,Q_C)+\mathcal{A}(Q,H,Q_D)_L \qquad (3.15)\\=&2\sum_X^{S,D,T}E^{(6)}_{XDQ}+E^{(6)}_{QDQ}+E^{(6)}_{STQ}(II)+E^{(6)}_{QTQ}(II)\\&+2\sum_X^{D,T}E^{(6)}_{XTQ}(II)+E^{(6)}_{DQQ}(II)+E^{(6)}_{QQQ}(II)\\&+2E^{(6)}_{TQQ}(II)+E^{(6)}_{QHQ} \qquad (3.16)\end{aligned}$$

In some cases, it is useful to split the terms $E^{(6)}_{X_1YQ}$ into two parts:

$$E^{(6)}_{X_1YQ}=E^{(6)}_{X_1YQ}(I)+E^{(6)}_{X_1YQ}(II) \tag{3.17}$$

which correspond to $\mathcal{A}(X_1,Y,Q_D)_L$ and $\mathcal{A}(X_1,Y,Q_C)_L$, respectively. For $E^{(6)}_{STQ}(II)$ and $E^{(6)}_{DQQ}(II)$, their Hermitian conjugates $E^{(6)}_{QTS}$ and $E^{(6)}_{QQD}$ are included in $\mathcal{A}_3[(\bar{V}\hat{T}_i^{(2)})_D]_L$, which is defined by (compare with Figure 3.2)

$$\mathcal{A}_3[(\bar{V}\hat{T}_i^{(2)})_D]_L=\sum_{X_1}^{D,T,Q}\mathcal{A}(X_1,Q,D)_L+\sum_{X_1}^{S,D,T,Q}\mathcal{A}(X_1,T,S)_L+\sum_{X_1}^{T,Q}\mathcal{A}(X_1,P,T)_L \tag{3.18}$$

The terms of Eq.(3.18) can be combined with the corresponding terms $\mathcal{A}(X_1, Y, Q_D)_L$ of Eq.s (3.11) and (3.13) to lead to simpler formulations in cluster operator form as shown in Eq.s (3.19) to (3.23).

$$E(MP6)_{2b} = \sum_{X_1}^{D,T,Q} (\mathcal{A}(X_1, Q, D)_L + \mathcal{A}(X_1, Q, Q_D)_L)$$

$$= \langle\Phi_0|(\hat{T}_2^{(2)})^\dagger(\bar{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)})_C|\Phi_0\rangle + 2\langle\Phi_0|(\hat{T}_3^{(2)})^\dagger\bar{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)}|\Phi_0\rangle$$
$$+ \langle\Phi_0|\frac{1}{2}((\hat{T}_2^{(1)})^\dagger)^2\bar{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)}|\Phi_0\rangle_C \qquad (3.19)$$

$$= \left[E_{DQD}^{(6)} + E_{DQQ}^{(6)}(I)\right] + 2\left[E_{TQD}^{(6)} + E_{TQQ}^{(6)}(I)\right]$$
$$+ \left[E_{QQD}^{(6)} + E_{QQQ}^{(6)}(I)\right] \; ; \qquad (3.20)$$

$$E(MP6)_3 = \sum_{X_1}^{S,D,T} (\mathcal{A}(X_1, T, S)_L + \mathcal{A}(X_1, T, Q_D)_L)$$
$$+ \mathcal{A}(Q, T, S)_L + \mathcal{A}(Q, T, Q_D)_L$$
$$= \sum_{i=1,2,3} (2 - \delta_{i,1})\langle\Phi_0|(\hat{T}_i^{(2)})^\dagger\bar{V}\hat{T}_1^{(2)}\hat{T}_2^{(1)}|\Phi_0\rangle_C$$
$$+ \langle\Phi_0|\frac{1}{2}((\hat{T}_2^{(1)})^\dagger)^2\bar{V}\hat{T}_1^{(2)}\hat{T}_2^{(1)}|\Phi_0\rangle_C \qquad (3.21)$$

$$= E_{STS}^{(6)} + E_{STQ}^{(6)}(I) + 2\left[E_{DTS}^{(6)} + E_{DTQ}^{(6)}(I)\right] + 2\left[E_{TTS}^{(6)} + E_{TTQ}^{(6)}(I)\right]$$
$$+ E_{QTS}^{(6)} + E_{QTQ}^{(6)}(I) \qquad (3.22)$$

$$E(MP6)_4 = \sum_{X_1}^{T,Q} (\mathcal{A}(X_1, P, T)_L + \mathcal{A}(X_1, P, Q_D)_L)$$

$$= \langle\Phi_0|(\hat{T}_3^{(2)})^\dagger\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)}|\Phi_0\rangle_C + \langle\Phi_0|\frac{1}{2}((\hat{T}_2^{(1)})^\dagger)^2\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)}|\Phi_0\rangle_C \qquad (3.23a)$$

$$= \left[E_{TPT}^{(6)} + E_{TPQ}^{(6)}\right] + \left[E_{QPT}^{(6)} + E_{QPQ}^{(6)}\right] \; . \qquad (3.23b)$$

The final MP6 energy expression covers all four energy parts $E(MP6)_1$, $E(MP6)_2$, $E(MP6)_3$, and $E(MP6)_4$:

$$E_{MP}^{(6)} = E(MP6)_1 + E(MP6)_{2a} + E(MP6)_{2b} + E(MP6)_3 + E(MP6)_4 \qquad (3.24)$$

which correspond to the connected cluster operator part ($E(MP6)_1$), the disconnected Q cluster operator part ($E(MP6)_2$), the disconnected T cluster operator part ($E(MP6)_3$), and the disconnected P cluster operator part ($E(MP6)_4$). [24]

3.2 SETTING UP TWO-ELECTRON INTEGRAL FORMULAS

The development of a MP6 computer program implies the transformation of the MP6 cluster operator equations into two-electron integral formulas. Analogue to the auxiliary arrays vn used in chapter 2 for the derivation of the MP4 and MP5 energy, a series of auxiliary arrays un is derived at the MP6 level of theory. For lower n, these arrays actually correspond to the vn arrays used at the MP4 and MP5 level as is indicated in Table 3.1. Table 3.2 shows how each correlation energy contribution is determined with one of the auxiliary arrays un according to equations which are explicitly listed in Ref. 25. Utilizing the auxiliary arrays un, two-electron integral formulas for all MP6 terms listed in Table 3.2 can be readily obtained. However, the computational cost resulting out of this one-to-one transformation would be, as indicated in Table 3.2, $O(M^{12})$ thus leading to a MP6 method that would not be practical even with today's supercomputers.

TABLE 3.1. Relationship between auxiliary arrays vi in MP5 and auxiliary arrays uj in MP6.

MP5	MP6
v1(ij,ab)	u4(ij,ab)
v2(ij,ab)	u5(ij,ab)
v3(ij,ab)	u6(ij,ab)
v4(ij,ab)	u10(ij,ab)
v5(ij,ab)	u14(ij,ab)
v6(i,a)	u1(i,a)
v7(ijk,abc)	u8(ijk,abc)
v8(ijk,abc)	u11(ijk,abc)
v9(ijkl,abcd)	u12(ijkl,abcd)

As mentioned in section 3.1, all energy contributions of $E(MP6)_2$, $E(MP6)_3$, and $E(MP6)_4$ (#17 to #38 in Table 3.2) result from disconnected cluster operators. In Ref. 25, we have shown that correlation energy contributions associated with disconnected cluster operator diagrams can be expressed with the help of intermediate arrays that significantly reduce computational cost. This is indicated in

TABLE 3.2. Two-electron integral formulas for the energy contributions of MP6. [a]

#	Contribution	Auxiliary arrays	Expected cost
	$\underline{E(MP6)_1}$		
1	$E^{(6)}_{SSS}$	u1(i,a)	$O(M^5)$
2	$E^{(6)}_{SSD}$	u1(i,a),u2(i,a)	$O(M^6)$
3	$E^{(6)}_{SST}$	u1(i,a),u3(i,a)	$O(M^7)$
4	$E^{(6)}_{DSD}$	u2(ij,ab)	$O(M^6)$
5	$E^{(6)}_{DST}$	u2(ij,ab),u3(ij,ab)	$O(M^7)$
6	$E^{(6)}_{TST}$	u3(i,a)	$O(M^7)$
7	$E^{(6)}_{SDS}$	u4(ij,ab)	$O(M^5)$
8	$E^{(6)}_{SDD}$	u4(ij,ab),u5(ij,ab)	$O(M^6)$
9	$E^{(6)}_{SDT}$	u4(ij,ab),u6(ij,ab)	$O(M^7)$
10	$E^{(6)}_{DDD}$	u5(ij,ab)	$O(M^6)$
11	$E^{(6)}_{DDT}$	u5(ij,ab),u6(ij,ab)	$O(M^7)$
12	$E^{(6)}_{TDT}$	u6(ij,ab)	$O(M^7)$
13	$E^{(6)}_{DTD}$	u7(jk,abc)	$O(M^7)$
14	$E^{(6)}_{DTT}$	u7(ijk,abc),u8(ijk,abc)	$O(M^8)$
15	$E^{(6)}_{TTT}$	u8(ijk,abc)	$O(M^8)$
16	$E^{(6)}_{TQT}$	u9(ijkl,abcd)	$O(M^9)$
	$\underline{E(MP6)_2}$		
17	$E^{(6)}_{SDQ}$	u4(ij,ab),u10(ij,ab)	$O(M^8)^*$
18	$E^{(6)}_{DDQ}$	u5(ij,ab),u10(ij,ab)	$O(M^8)^*$
19	$E^{(6)}_{TDQ}$	u6(ij,ab),u10(ij,ab)	$O(M^8)^*$
20	$E^{(6)}_{QDQ}$	u10(ij,ab)	$O(M^8)^*$
21	$E^{(6)}_{STQ}(II) + E^{(6)}_{QTQ}(II)_a$	b_s, a_d, u11(ijk,abc)	$O(M^7)^*$
22	$E^{(6)}_{DQQ}(II) + E^{(6)}_{QQQ}(II)_a$	a_d, b_d, u12(ijkl,abcd)	$O(M^9)^*$
23	$E^{(6)}_{QTQ}(II)_b$	u11(ijk,abc)	$O(M^9)^*$
24	$E^{(6)}_{QQQ}(II)_b$	u12(ijkl,abcd)	$O(M^{10})^*$
25	$E^{(6)}_{DTQ}(II)$	u7(ijk,abcd),u11(ijk,abc)	$O(M^9)^*$
26	$E^{(6)}_{TTQ}(II)$	u8(ijk,abc),u11(ijk,abc)	$O(M^9)^*$
27	$E^{(6)}_{TQQ}(II)$	u9(ijkl,abcd),u12(ijkl,abcd)	$O(M^{10})^*$
28	$E^{(6)}_{QHQ}(I)$	Q^{cd}_{kl},u10(ij,ab)	$O(M^8)^*$
29	$E^{(6)}_{QHQ}(II)$		$O(M^{12})^*$
30	$E^{(6)}_{DQD} + E^{(6)}_{DQQ}(I)$	a_d,b_d,Q^{cd}_{kl}	$O(M^8)^*$
31	$E^{(6)}_{TQD} + E^{(6)}_{TQQ}(I)$	a_d,u9(ijkl,abcd)	$O(M^9)^*$
32	$E^{(6)}_{QQD} + E^{(6)}_{QQQ}(I)$	a_d,b_d,u12(ijkl,abcd)	$O(M^{10})^*$
	$\underline{E(MP6)_3}$		
33	$E^{(6)}_{STS} + E^{(6)}_{STQ}(I)$	b_s,u13(i,a)	$O(M^6)^*$
34	$E^{(6)}_{DTS} + E^{(6)}_{DTQ}(I)$	b_s,b_d,u14(ij,ab)	$O(M^7)^*$
35	$E^{(6)}_{TTS} + E^{(6)}_{TTQ}(I)$	u15(ijk,abc),u16(i,a)	$O(M^8)^*$
36	$E^{(6)}_{QTS} + E^{(6)}_{QTQ}(I)$	Q^{cd}_{kl}, u4(ij,ab), u17(l,d)	$O(M^8)^*$
	$\underline{E(MP6)_4}$		
37	$E^{(6)}_{TPT} + E^{(6)}_{TPQ}$	u3(i,a),u16(i,a),b_t,u18(ijk,abc)	$O(M^{10})^*$
38	$E^{(6)}_{QPT} + E_{QPQ}$	u6(ij,ab),u19(i,a),u20(ijkl,abcd)	$O(M^{10})^*$

[a] Ref. 25. The stars in the column "cost" indicate that the expected cost factor can be reduced by using intermediate arrays. See table 3.3.

Table 3.3 where for each of the disconnected cluster operator terms #17 to #38 of Table 3.2 the intermediate arrays $x1 - x20$, $y1 - y17$, and $z1 - z19$ are given that help to reduce computational cost to a minimum (see Ref. 25, for the definition of all intermediate arrays). This is demonstrated in the following using the term $E^{(6)}_{QHQ}(II)$ (#29 in Tables 3.2 and 3.3) as an appropriate example.

If $E^{(6)}_{QHQ}(II)$ would be calculated according to Eq. (36) of Ref. 25, one would have to determine an auxiliary array $u21(ijkl,abcd)$ according to Eq.s (3.25) and (3.26):

$$E^{(6)}_{QHQ}(II) = \frac{1}{32}\sum_{ij,ab}\sum_{kl,cd} a^{ab}_{ij} a^{cd}_{kl} u21(ijkl,abcd) \tag{3.25}$$

with $u21(ijkl,abcd)$ being defined by

$$\begin{aligned} & u21(ijkl,abcd) \\ &= -\frac{1}{4}\sum_{m}\sum_{PP'}(-1)^{P+P'} P(i/jkl|ab/cd)\left[P'(j/kl)\sum_{n,ef}\langle mn||ef\rangle a^{ef}_{kl} a^{cd}_{jn}\right] a^{ab}_{im} \\ &+ \sum_{f}\sum_{p}(-1)^{P} P(ij/kl|a/bcd)\sum_{mn,e}\langle mn||ef\rangle\left[\sum_{P'}(-1)^{P'} P'(k/l|b/cd) a^{eb}_{mk} a^{cd}_{nl}\right. \\ &\left. -\frac{1}{4}\sum_{P'}(-1)^{P'} P'(b/cd) a^{cd}_{mn} a^{eb}_{kl}\right] a^{af}_{ij} \end{aligned} \tag{3.26}$$

Since $u21$ depends on the eight indices i,j,k,l,a,b,c,d and requires in addition summations over indices m,n,e,f, the cost factor for $u21$ is proportional to $O(M^{12})$. However, this cost factor can be reduced since $u21(ijkl,abcd)$ does not depend on the H energy denominator. This provides the possibility of replacing $u21(ijkl,abcd)$ by a series of much cheaper intermediate arrays such as contractions between double amplitudes and combinations of these contractions (see Eq.s (A5) - (A9) and (A33) -(A42) of Ref. 25). This is outlined in Eq.s (3.27) - (3.36), which start with a dissection of $E^{(6)}_{QHQ}(II)$ into three parts:

$$E^{(6)}_{QHQ}(II) = \sum_{mn}\sum_{ef}\langle mn||ef\rangle\left[\frac{1}{4}w3(mn,ef)_a + w3(mn,ef)_b + \frac{1}{4}w3(mn,ef)_c\right] \tag{3.27}$$

Arrays $w3(mn,ef)_a$, $w3(mn,ef)_b$ and $w3(mn,ef)_c$ are determined with the help of intermediate arrays y12 - y17 according to Eq.s (3.28) - (3.36) (see Ref. 25).

$$w3(mn,ef)_a = -\sum_{kl} a^{ef}_{kl}\, y16(kl,mn) + \sum_{ab} x5(ab,ef) y17(ab,mn) \tag{3.28}$$

$$w3(mn,ef)_b = \sum_{lb} a^{eb}_{ml} y14(nf,lb) + \sum_{jb} x3(jb,me) y15(nf,jb) \tag{3.29}$$

$$w3(mn,ef)_c = -\sum_{kl} x4(kl,mn) y12(kl,ef) + \sum_{ca} a^{ca}_{mn} y13(ca,ef) \tag{3.30}$$

TABLE 3.3. Use of intermediate arrays to reduce the cost of a MP6 calculation. [a]

#	Energy contribution	Auxiliary arrays	Intermediate arrays	Cost
	$\underline{E(MP6)_2}$			
17	$E^{(6)}_{SDQ}$	u4(ij,ab), u10(ij,ab)	z1 - z4	$O(M^6)$
18	$E^{(6)}_{DDQ}$	u5(ij,ab), u10(ij,ab)	z1 - z4	$O(M^6)$
19	$E^{(6)}_{TDQ}$	u6(ij,ab), u10(ij,ab)	z1 - z4	$O(M^7)$
20	$E^{(6)}_{QDQ}$	u10(ij,ab)	z1 - z4	$O(M^6)$
21	$E^{(6)}_{STQ}(II) + E^{(6)}_{QTQ}(II)_a$	b^a_i, w1(i,a)	x1-x5, y1,y2, etc.	$O(M^6)$
22	$E^{(6)}_{DQQ}(II) + E^{(6)}_{QQQ}(II)_a$	b^{ab}_{ij}, w2(ij,ab)	x11-x13, y3 - y11	$O(M^6)$
23	$E^{(6)}_{QTQ}(II)_b$	u11(ijk,abc)	z5, z6	$O(M^7)$
24	$E^{(6)}_{QQQ}(II)_b$	u12(ijk,abc)	z7, z8	$O(M^9)$
25	$E^{(6)}_{DTQ}(II)$	u7(ijk,abc), u11(ijk,abc)	z5, z6	$O(M^7)$
26	$E^{(6)}_{TTQ}(II)$	u8(ijk,abc), u11(ijk,abc)	z5, z6	$O(M^8)$
27	$E^{(6)}_{TQQ}(II)_b$	u9(ijkl,abcd), u12(ijkl,abcd)	z7, z8	$O(M^9)$
28	$E^{(6)}_{QHQ}(I)$	Q^{cd}_{kl}, u10(ij,ab)	z1 - z4	$O(M^6)$
29	$E^{(6)}_{QHQ}(II)$	$w3(mn,ef)_a$, $w3(mn,ef)_b$, $w3(mn,ef)_c$	x1 - x5, y12 - y17	$O(M^6)$
30	$E^{(6)}_{DQD} + E^{(6)}_{DQQ}(I)$	a_d, b_d, Q^{cd}_{kl}	z1 - z4	$O(M^6)$
31	$E^{(6)}_{TQD} + E^{(6)}_{TQQ}(I)$	b_t, w4(ijk,abc)	z5, z6	$O(M^7)$
32	$E^{(6)}_{QQD} + E^{(6)}_{QQQ}(I)$	b_d, w2(ij,ab)	y3 - y11	$O(M^6)$
	$\underline{E(MP6)_3}$			
33	$E^{(6)}_{STS} + E^{(6)}_{STQ}(I)$	b_s, u13(i,a)	$\sum b_s(mn\|\|ef)$	$O(M^5)$
34	$E^{(6)}_{DTS} + E^{(6)}_{DTQ}(I)$	b_s, b_d, u14(ij,ab)	$\sum b_s(mn\|\|je)$, etc.	$O(M^6)$
35	$E^{(6)}_{TTS} + E^{(6)}_{TTQ}(I)$	u15(ijk,abc),u16(i,a)	z9, z10	$O(M^7)$
36	$E^{(6)}_{QTS} + E^{(6)}_{QTQ}(I)$	Q^{cd}_{kl}, u4(ij,ab), u17(l,d)	z1 - z4, x14 - x19	$O(M^6)$
	$\underline{E(MP6)_4}$			
37	$E^{(6)}_{TPT} + E^{(6)}_{TPQ}$	u3(i,a), u16(i,a), b_t, u18(ijk,abc)	z11 - z17	$O(M^8)$
38	$E^{(6)}_{QPT} + E^{(6)}_{QPQ}$	u6(ij,ab), u19(i,a), u20(ijkl,abcd)	z18-z19, x1-x10, x16, x17, x20-x21	$O(M^8)$

[a] Ref 25. Compare with table 3.2. Note that the xn and yn are different from the xn and yn in Table 2.2.

$$y12(kl,ef) = \sum_b a_{kl}^{eb} x1(b,f) - \sum_{jd} a_{lj}^{fd} x3(ke,jd) \tag{3.31}$$

$$\begin{aligned} y13(ca,e,f) = &\sum_{ik} x3(ia,ke)x3(if,kc) - \sum_{bd} x5(ab,fd)x5(eb,cd) \\ &+ x1(a,f)x1(c,e) \end{aligned} \tag{3.32}$$

$$\begin{aligned} y14(nf,lb) = &- \sum_{kj} x4(kl,jn)x3(jb,kf) + x2(l,n)x1(b,f) \\ &- \sum_k x3(lb,kf)x2(k,n) + \sum_{kc} x3(lc,kf)x3(kb,nc) \\ &+ \sum_{ac} x5(ba,cf)x3(lc,na) \end{aligned} \tag{3.33}$$

$$y15(nf,jb) = - \sum_{kc} a_{kj}^{cf} x3(kc,nb) + \frac{1}{2} \sum_{kl} a_{kl}^{fb} x4(kl,nj) - \sum_d a_{nj}^{db} x1(d,f) \tag{3.34}$$

$$\begin{aligned} y16(kl,mn) = &\sum_j x4(kl,jn)x2(j,m) - \sum_{ij} x4(li,mj)x4(kj,ni) \\ &- x2(l,n)x2(k,m) - \sum_{bc} x3(lb,mc)x3(kc,nb) \end{aligned} \tag{3.35}$$

$$y17(ab,mn) = \sum_{kc} a_{mk}^{ac} x3(kc,nb). \tag{3.36}$$

In these equations, the intermediate arrays x1 - x5 appear (see Table 3.3 and Ref. 25), which are contractions of double amplitudes, and the intermediate arrays $y12 - y17$. In total, 11 intermediate arrays are used to reduce the original $O(M^{12})$ dependence of Eq. (3.25). Inspection of Eq.s (3.28) - (3.36) reveals that the calculation of the 11 intermediate arrays involves just $O(M^6)$ computational steps: The total cost of the calculation of $E_{QHQ}^{(6)}(II)$ has been reduced from $O(M^{12})$ to $O(M^6)$, which means a dramatic decrease in needed computer time.

Manipulations as the one described in the case of the $E_{QHQ}^{(6)}(II)$ term have been applied for all terms associated with disconnected cluster operators so that the reduced cost factors listed in Table 3.3 result. Compared to MP4 where just four intermediate arrays are needed (Table 2.1), the number of intermediate arrays for MP6 (57 in total) increases by a factor of 14. This demonstrates that any development of higher order MP methods has to concentrate on those correlation energy contributions which are associated with disconnected cluster operators.

In Ref. 25, each energy contribution of $E(MP6)$ is expressed in terms of two-electron integral formulas, which can directly be programmed for calculation on a computer. Of course, these formulas look rather complicated because of the manifold of double-bar integral terms, the complexity of summations and the large number of arrays to be formed. Therefore, the implementation of the MP6 method in form of a FORTRAN program on a computer requires a carefully worked out strategy.

3.3 IMPLEMENTATION AND TESTING OF A MP6 COMPUTER PROGRAM

As has been discussed in section 3.2, all disconnected cluster operator terms associated with T, Q or P excitations in $E(MP6)_2$, $E(MP6)_3$, and $E(MP6)_4$ can be calculated with the help of intermediate arrays. However, in some cases it is of advantage to combine the calculation of disconnected cluster operator terms with that of related connected cluster operator terms involving a higher cost factor rather than calculating each MP6 term individually. In this way, superfluous I/O operations are suppressed. We have found that in this way the calculation of E(MP6) becomes much more efficient.

A MP6 computer program can be structured in the following way. [25] First, all needed first order and second order amplitudes are collected, which, of course, are available from lower order MP calculations. Then, the loop over T excitations is carried out, which leads to some of the TTA terms as well as the TTT coupling contribution. In the next step, the Q loop is executed, which is the most expensive part of the program. There is a relatively large number of terms, the calculation of which can be based on existing MP5 programs. Finally, terms are collected to give the MP6 correlation energy.

In Ref. 25, a MP6 program has been set up in a way that many (but not all) correlation energy contributions can be determined individually. This gives the chance to analyze these terms, to investigate the importance of the most expensive terms and to develop partial MP6 methods that cover well-defined excitation and correlation effects.

Although the writing of a MP6 program is a time consuming task, even more time consuming is the testing of a new MP6 program. The question whether more than 3000 lines of FORTRAN code are without errors cannot be answered in a simple way. In this work, three testing strategies were developed to search for programming errors. First, a number of benchmark calculations were carried out for which MPn energies ($n \leq 48$) derived from full CI results are available. [12,13]

Then, parts of the program were reprogrammed by using alternative calculation strategies and, finally, MP5 results were used to test MP6 energies.

Testing with the help of FCI calculations could be done for about 30 atoms and molecules with no more than 10 electrons since FCI calculations with reasonable basis sets can be carried out in these cases. The majority of FCI based MP6 correlation energies agrees with our values within 10^{-6} hartree. This difference is also found for many of the lower order correlation contributions if one compares results from FCI-MPn and MPn calculations. Although the agreement between FCI-MP6 and our MP6 data seems to suggest reliability of the new MP6 program, it does not prove that the latter is without any errors. Since all test molecules are rather small possessing just a limited number of electrons, higher excitations such as P or H do not contribute significantly to the final correlation energy. As a consequence, any errors in these terms do not show up in the comparison between FCI-MP6 and MP6 energies. This also holds for any other low value term and has to be considered in the testing.

Therefore, we tested each term of the MP6 program (see list of terms in Table 3.2) individually by extensive reprogramming. For example, in the case of energy terms associated with disconnected cluster operators, we have programmed alternative evaluation procedures that do not take advantage of intermediate arrays. This leads to a rather simple structuring of the FORTRAN code, but also to program versions that can be used only for testing purposes because they are too expensive for normal use. An energy contribution tested in this way was considered to be correct when the difference in energy values obtained by different program versions is smaller or equal to 10^{-10} hartree.

A third way of efficiently searching for errors in the MP6 program was to replace second order amplitudes by the appropriate first order amplitudes to get the corresponding fifth order energy contributions, which can be directly compared with existing MP5 results. [8,9] This procedure is straightforward and can be extended to (partial) third order amplitudes to be replaced by second order amplitudes or products of first order amplitudes. In each case, it was verified that the energy contributions obtained at MP5 did not differ from the corresponding directly calculated MP5 terms by more than 10^{-10} hartree. After checking all MP6 energy contributions listed in Table 3.2 either by reprogramming or by exchanging amplitudes, we concluded that our MP6 program was without errors and could be used for calculating MP6 correlation energies. The MP6 codes were installed on a CRY Y-MP to be run within the ab initio package COLOGNE94. [44]

3.4 COMPARISON OF MP6 AND FULL CI CORRELATION ENERGIES

FCI energies are known for a number of atoms and simple molecules, which accordingly provide an appropriate basis for a comparison with E(MP6) energies obtained with the same basis at the same geometry. The set of reference systems includes charged and uncharged atoms (F and F^-), different states of molecules ($^3B_2$ and $^1A_1$ state of CH_2, $^2B_1$ and $^2A_1$ state of NH_2) as well as AH_n molecules both at their equilibrium geometry (R_e) and in geometries with (symmetrically) stretched AH bonds ($1.5R_e$, $2R_e$: "stretched geometries"). Calculation of the latter represents a critical test on the performance of a correlation method because wave functions of molecules with stretched geometries possess considerable multireference character. In total, 26 energy calculations have been carried out for the comparison. [26]

MP6 correlation energies cover on the average 98 - 99% of the exact (FCI) correlation energy for atoms and molecules at equilibrium geometries. For molecules with stretched geometries ($1.5R_e$ and $2.0R_e$), this coverage can drop to 80 - 85% because of difficulties in describing a problem with relatively high multireference character by a single determinant approach. There are systems, for which the MP6 correlation energy becomes more negative than the FCI correlation energy thus reflecting the non-variational character of MP theory.

We have investigated the mean absolute deviation between FCI and various MPn energies. [26] If just equilibrium geometries are considered, then there is a slight improvement when going from MP4 $\sim$ MP5 energies (mean absolute deviation 2.12 mhartree) to MP6 energies (mean absolute deviation 1.75 mhartree, [26]). If stretched geometries are included in the comparison, then mean absolute deviations become larger by a factor of 3 and decrease more clearly with increasing order n of MPn perturbation theory (MP4: 7.26, MP5: 6.47, MP6: 4.66 mhartree [26]). This suggests that fifth and sixth order corrections become more important with increasing multireference character of a system and that the relative improvement of energies is larger at the MP6 than the MP5 level of theory.

Because of the $O(M^9)$ dependence of MP6 methods, its application is limited to relatively small atoms and molecules. Therefore, it was interesting to test whether deletion of costly MP6 energy terms leads to useful approximate MP6 methods that are more economic and can be applied to larger molecules. We have checked two alternatives. [26] First, we have deleted the three terms $E^{(6)}_{TQT}$, $E^{(6)}_{QQQ}(II)_b$, and $E^{(6)}_{TQQ}(II)$ that require $O(M^9)$ computational steps. In this way, we have obtained an approximate MP6 method (MP6(M8)) with computational requirements $\leq O(M^8)$. In a second step, we have eliminated all terms that

require $O(M^8)$ computational steps. Thus, an approximate $O(M^7)$ method has been obtained (MP6(M7)).

The average errors of MP6(M8) and MP6(M7) are 8 and 13%, respectively, of the total MP6 correlation energy. The difference $\Delta E^{(6)}(M8)$ is with the exception of F^- and the stretched geometry of H_2O considerably smaller than 1 mhartree. This is also true in the case of $\Delta E^{(6)}(M7)$. We have also investigated deviations in relative energies and compared them with those of other MPn methods and FCI. The mean absolute deviation of MP2 relative energies from the corresponding FCI values is rather large (12.5 kcal/mol), which has to do with the fact that the majority of the problems investigated involves systems with multireference character. At MP4, the mean absolute deviation decreases to 8.3 kcal/mol, then to 7.4 at MP5 and, finally, to 5.7 at MP6, i.e. the largest reduction in the mean absolute deviation is obtained at MP4 and MP6, which underlines that MP6 leads to the largest improvements after MP4.

The approximate MP6 methods give about the same mean absolute deviations (5.8 kcal/mol [26]) than MP6, i.e. the three methods MP6, MP6(M8), and MP6(M7) lead to similar relative energies. For example, the singlet-triplet splitting in the case of CH_2 is calculated to be 12.98, 12.99, and 13.06 kcal/mol at MP6, MP6(M8), and MP6(M7), respectively (FCI value 11.97 kcal/mol [26]). A similarly good agreement is obtained for the differences between the $^2A_1$ and the $^2B_1$ state of NH_2 taken at R_e, $1.5R_e$ and $2R_e$ of the NH bond distance. On the other hand, there is a clear improvement of relative energies when going from MP5 to MP6(M8) or MP6(M7). Since the latter method has similar time requirements as MP4, MP6(M7) is an attractive new method for getting higher order correlation corrections for small and medium-sized molecules.

4. Coupled Cluster Theory

Coupled Cluster theory is tightly connected with the Linked Diagram (LD) theorem which states that the exact electronic energy and wave function of the Schrödinger equation can be written as a sum of linked diagrams in field theory language without any contributions from unlinked diagrams. [34] Equivalently, one can say that the wave function is expressed with the help of an exponential of cluster operators, which was first suggested by Coester and Kümmel in physics in the late 1950s [45] and later introduced into Quantum Chemistry by Cizek and Paldus. [16,17] The exponential form of the wave function guarantees correct scaling with the number of electrons, which leads to the important property

of size-extensivity of calculated energies. [10] Sometimes one uses also the term size-consistency in connection with the investigation of dissociation or addition reactions. [5] However, the term size-extensivity is more general than the term size-consistency and, therefore, the former is used throughout this work. Contrary to CI methods, MP and CC methods are all size-extensive. [10]

The major difference between MP and CC methods is that MP theory is used to include all contributions resulting from S, D, T, etc. excitations through some finite order while CC theory covers selected contributions to the MP correlation energy to infinite order. Therefore, it does not lead to the oscillations in correlation energy typical of the MPn series. On the other hand, the cost factor of a given CC method is considerably larger than its MP equivalent (defined by the excitations covered) as we will show in the following.

The use of CC methods in ab initio theory was started on a routine basis in the early 1980s due to the development work of the Pople and the Bartlett group. [18] However, little systematic research with the lower CC methods was done in the first years after CCD [18] and CCSD [19] programs became generally available. This has changed in the last five years when CC methods covering T effects were introduced that provided high-accuracy in calculated energies. As an example for many other investigations the CC study of simple H_2 addition reactions carried out by Kraka and co-workers may be mentioned here. [46] In this work, it was demonstrated that with a CC method that includes T effects, more precise activation barriers and reaction energies could be calculated than previously with MRCI, MCSCF or CI methods. Because of its many advantages, CC theory attracts a lot of research efforts and, therefore, one has investigated how currently used CC methods can be improved to get even higher accuracy. Before this work is discussed, we shortly review the CC projection approach because it is hardly discussed in any of the standard Quantum Chemistry text books.

4.1 THE PROJECTION COUPLED CLUSTER APPROACH

The Coupled Cluster (CC) wave function Ψ_{CC} is expressed in terms of the cluster operator $\hat{T}$ as

$$\Psi_{CC} = e^{\hat{T}}|\Phi_0\rangle \tag{4.1}$$

where $\hat{T}$ is the cluster operator for the n electrons of a given electronic system

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots + \hat{T}_n \tag{4.2}$$

and

$$\hat{T}_n = \frac{1}{(n!)^2} \sum_{i,j\ldots,a,b,\ldots} a_{ij\ldots}^{ab\ldots} \hat{t}_{ij\ldots}^{ab\ldots} \tag{4.3}$$

In Eq. (4.3), the operators $\hat{t}_{ij\ldots}^{ab\cdots}$ represent elementary substitution operators and the amplitudes $a_{ij\ldots}^{ab\cdots}$ are the corresponding cluster amplitudes. With a wave function of the form (4.1) the expectation value ΔE of the Hamiltonian $\bar{H}(= \hat{H} - \langle\Phi_0|\hat{H}|\Phi_0\rangle)$ can be written as

$$\begin{aligned}\Delta E &= \frac{\langle\Phi_0|e^{\hat{T}^\dagger}\bar{H}e^{\hat{T}}|\Phi_0\rangle}{\langle\Phi_0|e^{\hat{T}^\dagger}e^{\hat{T}}|\Phi_0\rangle} \\ &= \langle\Phi_0|\left(e^{\hat{T}^\dagger}\bar{H}e^{\hat{T}}\right)_C|\Phi_0\rangle \end{aligned} \tag{4.4}$$

The expectation value ΔE is obtained by standard variational theory where the variational parameters are the cluster amplitudes $(a_{ij\ldots}^{ab\cdots})^*$. In the first step, one obtains

$$\langle\Phi_{ij\ldots}^{ab\cdots}|(e^{\hat{T}^\dagger}\bar{H}e^{\hat{T}})_C|\Phi_0\rangle = 0 \tag{4.5}$$

By inserting the identity operator $\hat{I} = e^{\hat{T}}e^{-\hat{T}}$ into Eq.(4.5) and using the fact that

$$e^{-\hat{T}}\bar{H}e^{\hat{T}} = (\bar{H}e^{\hat{T}})_C \tag{4.6}$$

Eq.(4.5) becomes

$$\langle\Phi_{ij\ldots}^{ab\cdots}|(e^{\hat{T}^\dagger}e^{\hat{T}})(\bar{H}e^{\hat{T}})_C|\Phi_0\rangle = 0 \tag{4.7}$$

which is equivalent to a set of projection equations:

$$\langle\Phi_i^a|(\bar{H}e^{\hat{T}})_C|\Phi_0\rangle = 0 \tag{4.8a}$$

$$\langle\Phi_{ij}^{ab}|(\bar{H}e^{\hat{T}})_C|\Phi_0\rangle = 0 \tag{4.8b}$$

$$\vdots$$

The correlation energy ΔE of Eq.(4.4) is given by

$$\Delta E = \langle\Phi_0|(\bar{H}e^{\hat{T}})_C|\Phi_0\rangle \tag{4.9}$$

The full CC energy ΔE, which is identical to the full CI correlation energy, is size-extensive and variational according to the derivation given above.

In practice, one has to truncate the cluster operator $\hat{T}$ of Eq. (4.2) at a finite level n to obtain a practical method. This, however, leads to the loss of the variational character of the CC method. For example, when

$$\hat{T} \approx \hat{T}_1 + \hat{T}_2 \tag{4.10}$$

the CCSD wave function is obtained

$$\Psi_{CCSD} = e^{\hat{T}_1+\hat{T}_2}|\Phi_0\rangle \tag{4.11}$$

The CCSD equations are obtained by projecting the Schrödinger equation onto single and double excited determinants:

$$\langle \Phi_i^a | (\bar{H} e^{\hat{T}_1 + \hat{T}_2}) | \Phi_0 \rangle = a_i^a \Delta E_{CCSD} \tag{4.12}$$

$$\langle \Phi_{ij}^{ab} | (\bar{H} e^{\hat{T}_1 + \hat{T}_2}) | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 | \Phi_0 \rangle \Delta E_{CCSD} \tag{4.13}$$

$$\Delta E_{CCSD} = \langle \Phi_0 | \bar{H} (\hat{T}_2 + \frac{1}{2}\hat{T}_1^2) | \Phi_0 \rangle \tag{4.14}$$

The left-hand side of Eq. (4.12) can be split into connected part and disconnected part:

$$\langle \Phi_i^a | (\bar{H} e^{\hat{T}_1 + \hat{T}_2}) | \Phi_0 \rangle = \langle \Phi_i^a | (\bar{H} e^{\hat{T}_1 + \hat{T}_2})_C | \Phi_0 \rangle + \langle \Phi_i^a | (\bar{H} e^{\hat{T}_1 + \hat{T}_2})_D | \Phi_0 \rangle \tag{4.15}$$

The disconnected part of Eq. (4.15) can be rewritten according to (4.16), (4.17) and (4.18):

$$\begin{aligned}
\langle \Phi_i^a | (\bar{H} e^{\hat{T}_1 + \hat{T}_2})_D | \Phi_0 \rangle =& \langle \Phi_i^a | (\bar{H} (\frac{1}{2}\hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \frac{1}{3!}\hat{T}_1^3))_D | \Phi_0 \rangle \\
=& \langle \Phi_i^a | \hat{T}_1 (\bar{H} (\hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2))_C | \Phi_0 \rangle \qquad (4.16) \\
=& \langle \Phi_i^a | \hat{T}_1 | \Phi_0 \rangle \langle \Phi_0 | (\bar{H} (\hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2))_C | \Phi_0 \rangle \qquad (4.17) \\
=& \langle \Phi_i^a | \hat{T}_1 | \Phi_0 \rangle \langle \Phi_0 | (\bar{H} (\hat{T}_2 + \frac{1}{2}\hat{T}_1^2))_C | \Phi_0 \rangle \\
=& a_i^a \Delta E_{CCSD} \qquad (4.18)
\end{aligned}$$

where in Eq. (4.17) the identity operator $\sum_p^\infty |\Phi_p\rangle\langle\Phi_p|$ has been inserted. It becomes clear from Eq. (4.18) that the disconnected part just cancels the term on the right-hand side of Eq. (4.12) so that Eq. (4.12) takes the form of (4.19)

$$\langle \Phi_i^a | (\bar{H} e^{\hat{T}_1 + \hat{T}_2})_C | \Phi_0 \rangle = 0 \tag{4.19}$$

or alternatively

$$\langle \Phi_i^a | \bar{H} (\hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \frac{1}{6}\hat{T}_1^3) | \Phi_0 \rangle_C = 0 \tag{4.20}$$

In a similar way, the disconnected part of the left-hand side of Eq. (4.13) can be rewritten:

$$\begin{aligned}
&\langle \Phi_{ij}^{ab} | (\bar{H} e^{\hat{T}_1 + \hat{T}_2})_D | \Phi_0 \rangle \\
=&\langle \Phi_{ij}^{ab} | \left(\bar{H} (1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{6}\hat{T}_1^3 + \frac{1}{2}\hat{T}_1^2 \hat{T}_2 + \frac{1}{24}\hat{T}_1^4) \right)_D | \Phi_0 \rangle
\end{aligned}$$

$$= \langle \Phi_{ij}^{ab} | \hat{T}_1 \left(\bar{H} (\hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{2}\hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3) \right)_C |\Phi_0\rangle$$
$$+ \langle \Phi_{ij}^{ab} | \hat{T}_2 \left(\bar{H} (\hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2) \right)_C |\Phi_0\rangle$$
$$+ \frac{1}{2} \langle \Phi_{ij}^{ab} | \hat{T}_1^2 \left(\bar{H} (\hat{T}_2 + \frac{1}{2}\hat{T}_1^2) \right)_C |\Phi_0\rangle \quad (4.21)$$

$$= \langle \Phi_{ij}^{ab} | \hat{T}_1 \sum_s^S |\Phi_s\rangle\langle\Phi_s| \left(\bar{H} (\hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{2}\hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3) \right)_C |\Phi_0\rangle$$
$$+ \langle \Phi_{ij}^{ab} | \hat{T}_2 |\Phi_0\rangle\langle\Phi_0| \left(\bar{H} (\hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2) \right)_C |\Phi_0\rangle$$
$$+ \frac{1}{2} \langle \Phi_{ij}^{ab} | \hat{T}_1^2 |\Phi_0\rangle \Delta E_{CCSD} \quad (4.22)$$

$$= \langle \Phi_{ij}^{ab} | (\hat{T}_2 + \frac{1}{2}\hat{T}_1^2) |\Phi_0\rangle\langle\Phi_0| \left(\bar{H} (\hat{T}_2 + \frac{1}{2}\hat{T}_1^2) \right)_C |\Phi_0\rangle \quad (4.23)$$

$$= \langle \Phi_{ij}^{ab} | \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 |\Phi_0\rangle \Delta E_{CCSD} \quad (4.24)$$

where Eq. (4.20) has been used in Eq. (4.22). Hence, the unlinked diagram terms in Eq. (4.13) also mutually cancel. The final D amplitude equations take the form of Eq. (4.25)

$$\langle \Phi_{ij}^{ab} | (\bar{H} e^{\hat{T}_1 + \hat{T}_2})_C |\Phi_0\rangle = 0 \quad (4.25)$$

which can explicitly be written as

$$\langle \Phi_{ij}^{ab} | \bar{H} (1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{6}\hat{T}_1^3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{24}\hat{T}_1^4) |\Phi_0\rangle_C = 0 \quad (4.26)$$

Eq.s (4.20) and (4.26) are the CCSD (Coupled-Cluster Singles and Doubles) projection equations in connected form:

$$\langle \Phi_i^a | \bar{H} (\hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3) |\Phi_0\rangle_C = 0 \quad (4.20)$$

$$\langle \Phi_{ij}^{ab} | \bar{H} (1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{6}\hat{T}_1^3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{24}\hat{T}_1^4) |\Phi_0\rangle_C = 0 \quad (4.26)$$

which have to be solved to obtain ΔE_{CCSD} as an approximation to the true correlation energy.

$$\Delta E_{CCSD} = \langle \Phi_0 | \bar{H} (\hat{T}_2 + \frac{1}{2}\hat{T}_1^2) |\Phi_0\rangle \quad (4.27)$$

Since S and D excitation amplitudes a_i^a and a_{ij}^{ab} of Eq.s (4.20) and (4.26) have to be known to set up and solve the CCSD equations, a solution can only be found by a trial-and-error procedure. Once the amplitudes are known, they can be used to

evaluate the CCSD energy ΔE_{CCSD} according to Eq. (4.27). All CC correlation energies obtained by truncation of $\hat{T}$ similar to (4.10) are still size-extensive, however they are no longer variational. Obviously, truncation of the cluster operator $\hat{T}$ at various excitation levels leads to a hierarchy of Coupled Cluster equations. For example, by truncating at $\hat{T}_3$, the CCSDT projection equations [20], and by truncating at $\hat{T}_4$, the CCSDTQ projection equations [21] are obtained. Since one has to iterate in each case, CCSD requires $N_{iter}O(M^6)$ computational steps, CCSDT $N_{iter}O(M^8)$ computational steps, and CCSDTQ $N_{iter}O(M^{10})$ computational steps. While CCSD computer programs are generally available, only few groups have developed expert programs that can solve the CCSDT [20,47] or even the CCSDTQ projection equations. [21]

4.2 THE QUADRATIC CI APPROACH - AN APPROXIMATE COUPLED CLUSTER METHOD

The quadratic CI (QCI) method was suggested by Pople and co-workers. [35] Although it can be considered as a method that results from a simplification of the corresponding CC equations, Pople and co-workers took a different view and considered QCI as a CI method corrected for the size-extensivity error of CI. [35] To achieve size-extensivity for CI, the authors added new terms to the CI projection equations, which is demonstrated in the following for the case of a truncated CI approach with just S and D excitations (CISD) included. [48]

The CISD wave function can be represented by

$$\Psi_{CISD} = (1 + \hat{T}_1 + \hat{T}_2)|\Phi_0\rangle \tag{4.28}$$

Then, the Schrödinger equation in the CISD approximation takes the form

$$\bar{H}(1 + \hat{T}_1 + \hat{T}_2)|\Phi_0\rangle = \Delta E_{CISD}(1 + \hat{T}_1 + \hat{T}_2)|\Phi_0\rangle \tag{4.29}$$

The projection of Eq. (4.29) on S and D excited determinants as well as the reference wave function (i.e. the HF function) leads to Eq.s (4.30), (4.31), and (4.32):

$$\langle\Phi_i^a|\bar{H}(\hat{T}_1 + \hat{T}_2)|\Phi_0\rangle = a_i^a \Delta E_{CISD} \tag{4.30}$$

$$\langle\Phi_{ij}^{ab}|\bar{H}(1 + \hat{T}_1 + \hat{T}_2)|\Phi_0\rangle = a_{ij}^{ab} \Delta E_{CISD} \tag{4.31}$$

$$\Delta E_{CISD} = \langle\Phi_0|\bar{H}\hat{T}_2|\Phi_0\rangle \tag{4.32}$$

which also can be viewed as resulting from a minimization of the expectation value ΔE_{CISD}. In this and the following, intermediate normalization, i.e. $\langle\Phi_0|\Phi_{CISD}\rangle = 1$, is used throughout.

Since in both Eq. (4.30) and Eq. (4.31) unlinked diagram terms appear, the energy ΔE_{CISD} is not size-extensive, which is a general problem of all truncated CI methods. The simplest way of restoring size-extensivity in the CISD equations is to add $\hat{T}_1\hat{T}_2$ on the left-hand side of Eq. (4.30) and $\frac{1}{2}\hat{T}_2^2$ on the left-hand side of Eq. (4.31). These quadratic terms cancel the unlinked diagram terms of the right-hand side of Eq.s (4.30) and (4.31), namely $a_i^a \Delta E_{CISD}$ and $a_{ij}^{ab} \Delta E_{CISD}$. In this way a size-extensive modified CISD method is obtained, which was coined Quadratic Configuration Interaction with Single and Double excitations (QCISD) by Pople and co-workers. [35] The final QCISD projection equations in connected form are given by

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_1\hat{T}_2)|\Phi_0\rangle_C = 0 \tag{4.33}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2)|\Phi_0\rangle_C = 0 \tag{4.34}$$

$$\Delta E_{QCISD} = \langle \Phi_0 | \bar{H}\hat{T}_2 | \Phi_0 \rangle \tag{4.35}$$

Pople and co-workers have also attempted to develop a QCI method in S, D and T space, which replaces the non-size-extensive CISDT approach. [35] These authors suggested the QCISDT projection equations given in (4.36) - (4.39):

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)|\Phi_0\rangle = a_i^a \Delta E_{QCISDT} \tag{4.36}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \frac{1}{2}\hat{T}_2^2)|\Phi_0\rangle = a_{ij}^{ab} \Delta E_{QCISDT} \tag{4.37}$$

$$\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_2\hat{T}_3)|\Phi_0\rangle = a_{ijk}^{abc} \Delta E_{QCISDT} \tag{4.38}$$

$$\Delta E_{QCISDT} = \langle \Phi_0 | \bar{H}\hat{T}_2 | \Phi_0 \rangle \tag{4.39}$$

However, the two quadratic terms added are not sufficient to cancel the unlinked diagram term $a_i^a \Delta E_{QCISDT}$ in Eq. (4.36) and an unlinked diagram term resulting from $\hat{T}_1$ in Eq. (4.38). In addition, the disconnected diagram part of $\hat{T}_2\hat{T}_3$ in Eq. (4.38) leads to a new unlinked diagram term to the energy ΔE_{QCISDT} so that the QCISDT energy defined by Eq.s (4.36) - (4.39) is not size-extensive. Because of this failure, the QCI concept has been criticized. [49] On the other hand, QCISD was for a long time the most often used (approximate) CC method, which simply had to do with the fact that a) a QCISD program was early available to chemists through Pople's ab initio package GAUSSIAN [50] and b) QCISD results seemed to be superior to CCSD results. The criticism with regard to the QCI concept caused us to analyze QCISD on the basis of perturbation theory (chapter 5) and to look for other ways of restoring size-extensivity at the CISDT level of theory (chapter 6). [22,23,30-32]

5. Analysis of Coupled Cluster Methods in Terms of Perturbation Theory

Since CC methods cover infinite order effects, they are more accurate than MP or CI methods based on the same excitations. In general, it is difficult to say which effects are covered by a given CC method and how it compares with MP or CI methods. [8,9,42] Therefore, one analyzes CC methods in terms of perturbation theory, which is particularly useful since the structure of lower order perturbation contributions to the correlation energy is well-known. As shown in chapter 2, MP4 and MP5 correlation energies can be dissected into contributions from specific excitations according to Eq.s (5.1) and (5.2):

$$E_{MP}^{(4)} = E_{S}^{(4)} + E_{D}^{(4)} + E_{T}^{(4)} + E_{Q}^{(4)} \tag{5.1}$$

$$E_{MP}^{(5)} = E_{SS}^{(5)} + 2E_{SD}^{(5)} + 2E_{ST}^{(5)} + E_{DD}^{(5)} + 2E_{DT}^{(5)} + 2E_{DQ}^{(5)} + E_{TT}^{(5)} + 2E_{TQ}^{(5)} + E_{QQ}^{(5)} \tag{5.2}$$

In a similar way, the MP6 correlation energy can be dissected into 36 contributions:

$$\begin{aligned} E_{MP}^{(6)} =& E_{SSS}^{(6)} + 2E_{SSD}^{(6)} + 2E_{SST}^{(6)} + E_{SDS}^{(6)} + 2E_{SDD}^{(6)} + 2E_{SDT}^{(6)} + 2E_{SDQ}^{(6)} + E_{STS}^{(6)} \\ &+ 2E_{STD}^{(6)} + 2E_{STT}^{(6)} + 2E_{STQ}^{(6)} + E_{DSD}^{(6)} + 2E_{DST}^{(6)} + E_{DDD}^{(6)} + 2E_{DDT}^{(6)} \\ &+ 2E_{DDQ}^{(6)} + E_{DTD}^{(6)} + 2E_{DTT}^{(6)} + 2E_{DTQ}^{(6)} + E_{DQD}^{(6)} + 2E_{DQT}^{(6)} + 2E_{DQQ}^{(6)} \\ &+ E_{TST}^{(6)} + E_{TDT}^{(6)} + 2E_{TDQ}^{(6)} + E_{TTT}^{(6)} + 2E_{TTQ}^{(6)} + E_{TQT}^{(6)} + 2E_{TQQ}^{(6)} \\ &+ E_{TPT}^{(6)} + 2E_{TPQ}^{(6)} + E_{QDQ}^{(6)} + E_{QTQ}^{(6)} + E_{QQQ}^{(6)} + E_{QPQ}^{(6)} + E_{QHQ}^{(6)} \end{aligned} \tag{5.3}$$

Each of these contributions represents a special correlation effect as has been discussed in section 2.3. However, with increasing order n of MP perturbation theory the number of terms increases exponentially and, therefore, it becomes impossible to keep track of each single term and to check whether it is covered by a certain CC method or not. Nevertheless, it will be helpful if one knows that a given CC method is correct up to nth order perturbation theory, which means that all contributions up to this order are contained in the CC approach. In such a case, one can expect that the CC method is as accurate as the corresponding MP perturbation method still contained in the CC method. For example, one has shown that CCSD is correct up to third order and also contains apart from the T contribution all other fourth order terms. One can expect that CCSD calculations are superior to either MP2, MP3 or MP4(SDQ) calculations because

CCSD contains beside the third and fourth order contributions also infinite order contributions not covered by any of the MP methods.

While it is rather easy to compare CC methods with MP methods, the comparison of different CC methods based on the same excitations is much more difficult since it has to be carried to higher orders of perturbation theory. For this purpose, we have developed a graphical method that reveals which contributions to the correlation energy at higher orders of perturbation theory are covered by the CC method in question. [22,23] According to this method, each energy contribution at nth order perturbation theory is described as a path that connects those excitations A, B, C, etc. at orders n, n-1, n-2, etc. down to order 4 that characterize the contribution $E^{(n)}_{ABC\ldots}$. A path can start at one of the excitation levels S, D, T or Q and has to end at one of these levels at order 4. In between, it can leave SDTQ space under the provision that Slater rules for a two-electron operator are fulfilled. [23,24]

For finite MP perturbation theory the possible energy paths form a regular network, which in horizontal direction takes the form of a wedge. This is the direction of increasing excitation levels that can be included for increasing order n. In Figure 5.1, this is shown for MP8. At this level, Q excitations can couple via H excitations to octuple (O) excitations in the sequence QHOHQ according to Slater rules, i.e. MP8 is the first perturbation method that includes correlation effects from septuple (S_7) and O excitations. There are 915 different paths representing the 915 correlation energy contributions $E^{(8)}_{ABCDE}$ of the eighth order MP energy. While it would be very time consuming and of little use to write down all 915 contributions, the diagram in Fig.5.1, gives these contributions in a compact and easy to understand form. With the diagram 5.1, it is straightforward to determine the unique energy paths and to exclude the symmetry equivalent paths so that the 583 unique energy contributions of MP8 can be described. In addition, the diagram makes obvious how the couplings between different excitations grow with the order n forming ladders that stretch in the direction of infinity.

Graphical representations as the one shown for MP8 in Figure 5.1 also have to stop at some finite level. However, even for finite n they give a good impression how the diagram develops for n going to infinity and, therefore, they are well suited to describe the infinite order effects of a CC method. Therefore, they have been used in connection with an algebraic expansion method to analyse the infinite order effects of CC methods.

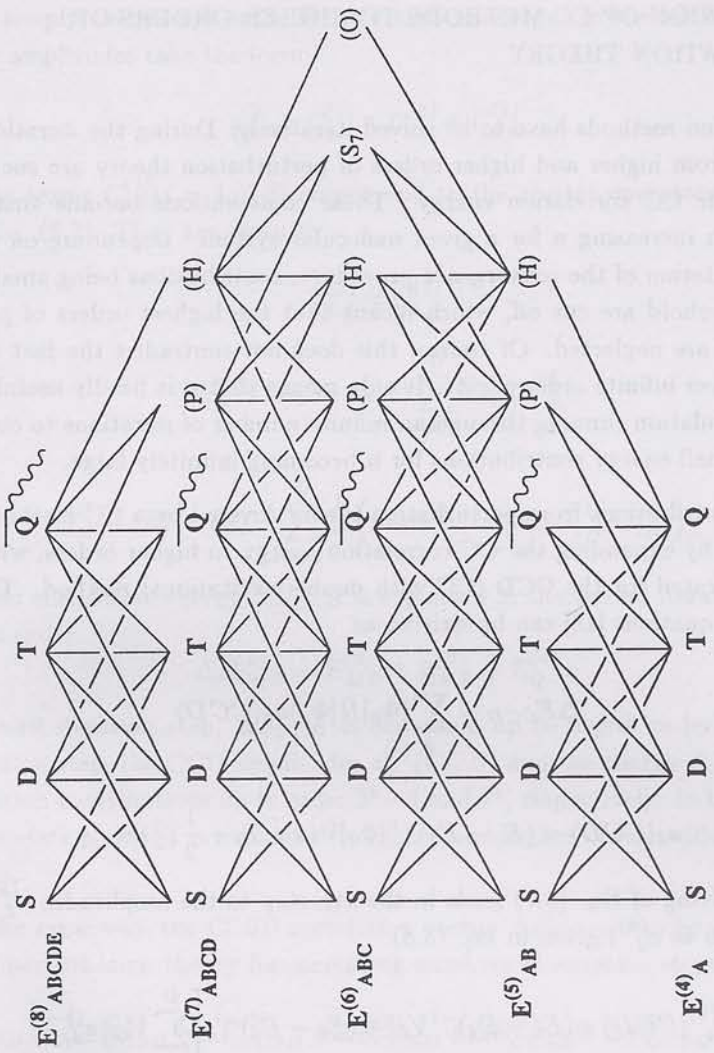


Figure 5.1. Graphical representation of all energy contributions at nth order MP perturbation theory (n= 4, 5, 6, 7, 8). A particular energy contribution $E^{(n)}_{ABC..}$ is given by the solid line that starts at A = S, D, T or Q in the $E^{(n)}$ row and connects B, C, etc. at row n-1, n-2, etc. until n=4 is reached. Note that at the nth order level also those excitations are included that arise from energy terms at higher order levels (m > n). They are given in parentheses after a separator to the right of the scheme. *Reprinted with permission from Z. He and D. Cremer, Int. J. Quant. Chem . Symp. (1991) 25, 43. Copyright (1991) J. Wiley, Inc.*

5.1 EXPANSION OF CC METHODS TO HIGHER ORDERS OF PERTURBATION THEORY

CC projection methods have to be solved iteratively. During the iterations, contributions from higher and higher orders of perturbation theory are successively added to the CC correlation energy. These contributions become smaller and smaller with increasing n for a given molecular system. Depending on the convergence criterion of the convergence procedure, contributions being smaller than a given threshold are cut off, which means that the highest orders of perturbation theory are neglected. Of course, this does not contradict the fact that CC methods cover infinite order effects. It only means that it is hardly useful to have the CC calculation running through an infinite number of iterations to cover even infinitely small energy contributions for n becoming infinitely large.

The contributions from perturbation theory covered by a CC method can be determined by expanding the CC correlation energy to higher orders, which may be demonstrated for the CCD (CC with double excitations) method. The CCD projection equations [18] can be written as

$$\Delta E_{CCD} = \sum_{d}^{D} \langle \Phi_0 | \bar{H} | \Phi_d \rangle a_d(CCD) \tag{5.6}$$

and

$$a_d(CCD) = (E_0 - E_d)^{-1} \langle \Phi_d | \bar{V} (1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle_C \tag{5.7}$$

Iterative solving of Eq. (5.7) leads in the kth step to the amplitudes $a_d^{(k)}(CCD)$ (also written as $a_d^{(k)}$) given in Eq. (5.8):

$$\begin{aligned} a_d^{(k)}(CCD) =& (E_0 - E_d)^{-1} V_{d0} + (E_0 - E_d)^{-1} \left[\sum_{d_1}^{D} \bar{V}_{dd_1} a_{d_1}^{(k-1)} \right. \\ &\left. + \sum_{d_1 d_2}^{D} \frac{1}{2} \left(\langle \Phi_d | \bar{V} \hat{t}_{d_1} \hat{t}_{d_2} | \Phi_0 \rangle a_{d_1}^{(k-1)} a_{d_2}^{(k-1)} \right)_C \right] \end{aligned} \tag{5.8}$$

For k = 1, $a_d^{(1)}$ is given by

$$a_d^{(1)} = (E_0 - E_d)^{-1} V_{d0} = C_{1,d}^{(1)} \tag{5.9}$$

thus leading to the correlation energy $\Delta E_{CCD}^{(1)}$

$$\Delta E_{CCD}^{(1)} = E_{MP}^{(2)} \tag{5.10}$$

which is simply the second order MP correlation energy. In the second iteration step, the amplitudes take the form:

$$a_d^{(2)} = C_{1,d}^{(2)} + C_{2,d}^{(2)} + C_{3,d}^{(2)} \tag{5.11}$$

where the terms $C_{i,d}^{(2)}(i = 1, 2, 3)$ correspond to the cluster operators 1, $\hat{T}_2$, and $\frac{1}{2}\hat{T}_2^2$ of Eq. (5.7). They are given by

$$C_{1,d}^{(2)} = C_{1,d}^{(1)} \tag{5.12}$$

$$C_{2,d}^{(2)} = (E_0 - E_d)^{-1} \sum_{d_1}^{D} \bar{V}_{dd_1} C_{1,d_1}^{(1)} \tag{5.13}$$

and

$$C_{3,d}^{(2)} = (E_0 - E_d)^{-1} \sum_{d_1 d_2}^{D} \frac{1}{2} \left(\langle \Phi_d | \bar{V} \hat{t}_{d_1} \hat{t}_{d_2} | \Phi_0 \rangle C_{1,d_1}^{(1)} C_{1,d_2}^{(1)} \right)_C \tag{5.14}$$

Hence, the correlation energy ΔE_{CCD} is expanded in the second iteration step up to fourth order:

$$\Delta E_{CCD}^{(2)} = E_{MP}^{(2)} + E_{MP}^{(3)} + E_Q^{(4)} \tag{5.15}$$

In the third iteration step, ΔE_{CCD} is expanded up to eighth order and at the kth iteration step, the CCD amplitudes $a_d^{(k)}(CCD)$ and the energy ΔE_{CCD} cover perturbation contributions up to order $2^k - 1$ and 2^k, respectively. In this way, the CCD correlation energy is expanded to higher and higher orders with proceeding iterations.

In the same way, the CCSD correlation energy ΔE_{CCSD} can be expanded in terms of perturbation theory for increasing numbers of iteration steps:

$$\Delta E_{CCSD} = \Delta E_{CCSD}^{(1)} + \Delta E_{CCSD}^{(2)} + \Delta E_{CCSD}^{(3)} + \Delta E_{CCSD}^{(4)} + \Delta E_{CCSD}^{(5)} + \dots \tag{5.16}$$

In the first three iterative steps, CCSD covers the following energy contributions:

$$\Delta E_{CCSD}^{(1)} = E_{MP}^{(2)} \tag{5.17}$$

$$\Delta E_{CCSD}^{(2)} = E_{MP}^{(2)} + E_{MP}^{(3)} + E_S^{(4)} + E_Q^{(4)} \tag{5.18}$$

$$\Delta E_{CCSD}^{(3)} = E_{MP}^{(2)} + E_{MP}^{(3)} + E_S^{(4)} + E_D^{(4)} + E_Q^{(4)} + E_{CCSD}^{(5)} + E_{CCSD}^{(6)} + \dots \tag{5.19}$$

with $E_{CCSD}^{(5)}$ and $E_{CCSD}^{(6)}$ being defined by (5.20) and (5.21)

$$E_{CCSD}^{(5)} = E_{SS}^{(5)} + 2E_{SD}^{(5)} + E_{DD}^{(5)} + E_{DQ}^{(5)} + E_{QD}^{(5)} + E_{QQ}^{(5)}(I) + E_{TS}^{(5)} + E_{TQ}^{(5)}(I) \tag{5.20}$$

$$
\begin{aligned}
E^{(6)}_{CCSD} = & E^{(6)}_{SSS} + 2E^{(6)}_{SSD} + E^{(6)}_{SDS} + 2E^{(6)}_{SDD} + 2E^{(6)}_{SDQ} + E^{(6)}_{STS} + E^{(6)}_{STQ}(I) \\
& + E^{(6)}_{QTS}(I) + E^{(6)}_{DSD} + E^{(6)}_{DDD} + 2E^{(6)}_{DDQ} + E^{(6)}_{DQD} + E^{(6)}_{DQQ}(I) \\
& + E^{(6)}_{QQD}(I) + E^{(6)}_{DTS} + E^{(6)}_{DTQ}(I) + E^{(6)}_{QTQ}(I) + E^{(6)}_{QQQ}(I) + E^{(6)}_{QDQ} \\
& + E^{(6)}_{QHQ}(I) + E^{(6)}_{TSD} + E^{(6)}_{TQD}(I) + E^{(6)}_{TQQ}(I) \\
& + E^{(6)}_{TSS} + E^{(6)}_{TTS}(I) + E^{(6)}_{TTQ}(I) \qquad (5.21)
\end{aligned}
$$

In these equations, the symbol (I) identifies those terms that are only partially contained in the CCSD correlation energy.

Eq.s (5.20) and (5.21) give those MP5 and MP6 energy contributions that are fully or partially covered by CCSD. The energy $\Delta E^{(3)}_{CCSD}$ of Eq. (5.19) added in the third iteration involves at least 8th order MP contributions.

5.2 COMPARISON OF CCSD AND QCISD

A similar expansion as the one described for CCSD in section 5.1 can also be carried out for the QCISD correlation energy. The resulting equations become rather complicated for n = 6 and even higher orders and, therefore, it is of advantage to present results in a graphical way using the same techniques developed for the graphical representation of MPn correlation energy contributions. In Figure 5.2, the corresponding CCSD diagram is shown. [22]

In Figure 5.2 and the following figures, energy contributions that are fully contained at a particular level of perturbation theory are given by solid lines and those, which are only partially contained, have at least in one part of the total path representing an energy contribution a dotted line. The corresponding diagram for QCISD is shown in Figure 5.3. A combination of the CCSD and the QCISD diagrams is given in Figure 5.4 in order to make the differences between the two methods more obvious.

In the combination diagram, terms that are common to both methods are given in thick solid lines and those, which can only be found in CCSD, in thin solid lines. If a term is just partially contained hashed lines are used for common terms and dotted lines for terms that are just covered by CCSD.

CCSD and QCISD are correct up to third order. Figures 5.2 and 5.3 indicate in addition that both CCSD and QCISD are correct at any order of perturbation theory in the truncated configuration space that is made up from S and D excitations, i.e. within this space all infinite-order effects are covered. This, of course, is trivial since it reflects just the nature of the CC ansatz. More important is that

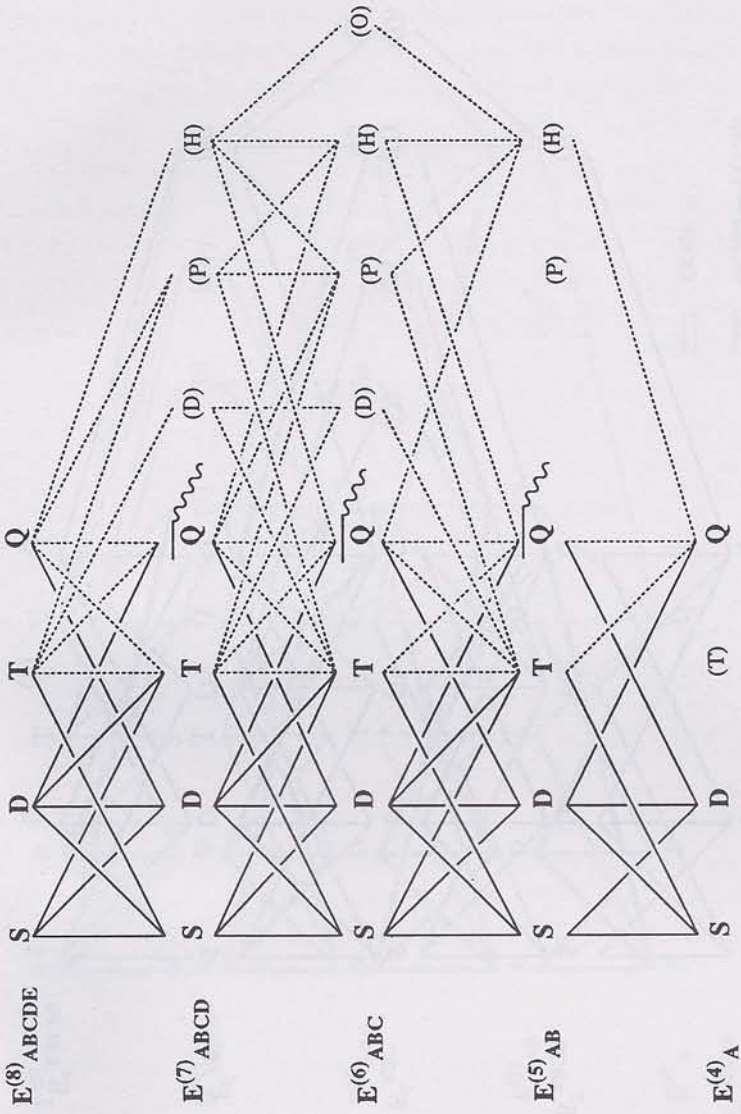


Figure 5.2. Graphical analysis of energy contributions at nth order MP perturbation theory (n= 4, 5, 6, 7, 8) covered by the CCSD correlation energy. See explanations given for Figure 5.1. Note that solid (dashed) lines denote energy terms fully (partially) contained in the CCSD correlation energy. *Reprinted with permission from Z. He and D. Cremer, Int. J. Quant. Chem . Symp. (1991) 25, 43. Copyright (1991) J. Wiley, Inc*

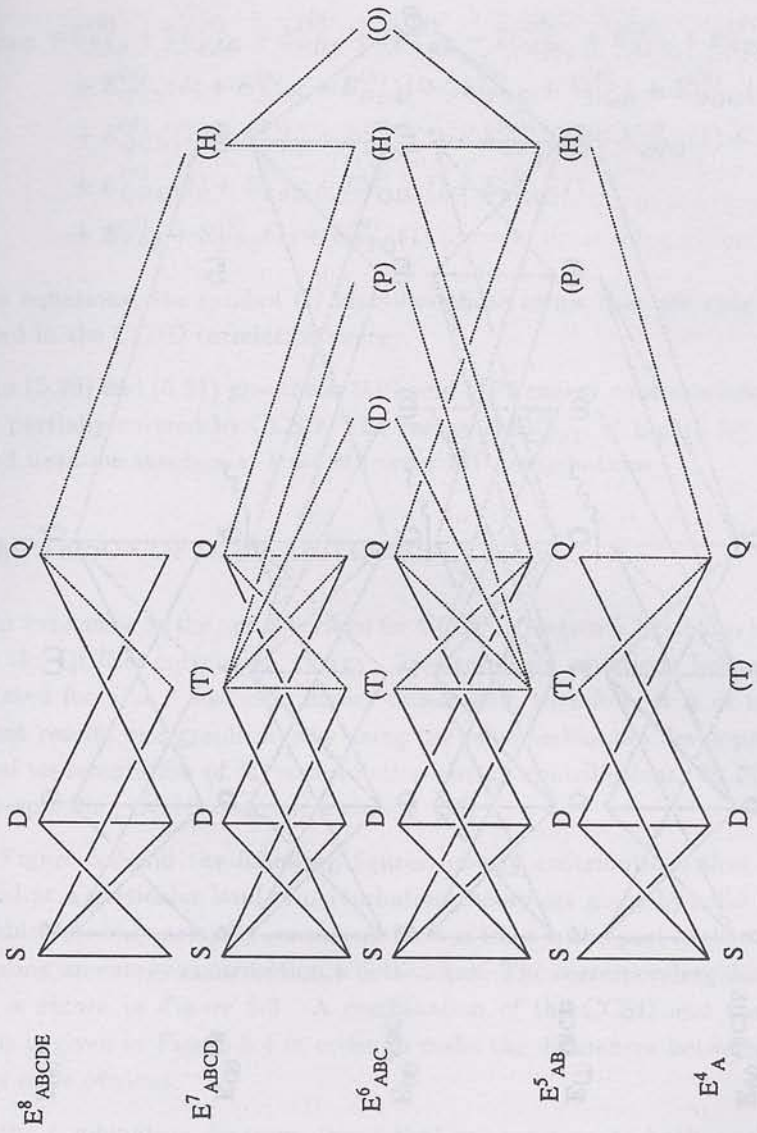


Figure 5.3. Graphical analysis of energy contributions at nth order MP perturbation theory (n= 4, 5, 6, 7, 8) covered by the QCISD correlation energy. See explanations given for Figure 5.1. Note that solid (dashed) lines denote energy terms fully (partially) contained in the QCISD correlation energy. *Reprinted with permission from Z. He and D. Cremer, Int. J. Quant. Chem. Symp. (1991) 25, 43. Copyright (1991) J. Wiley, Inc.*

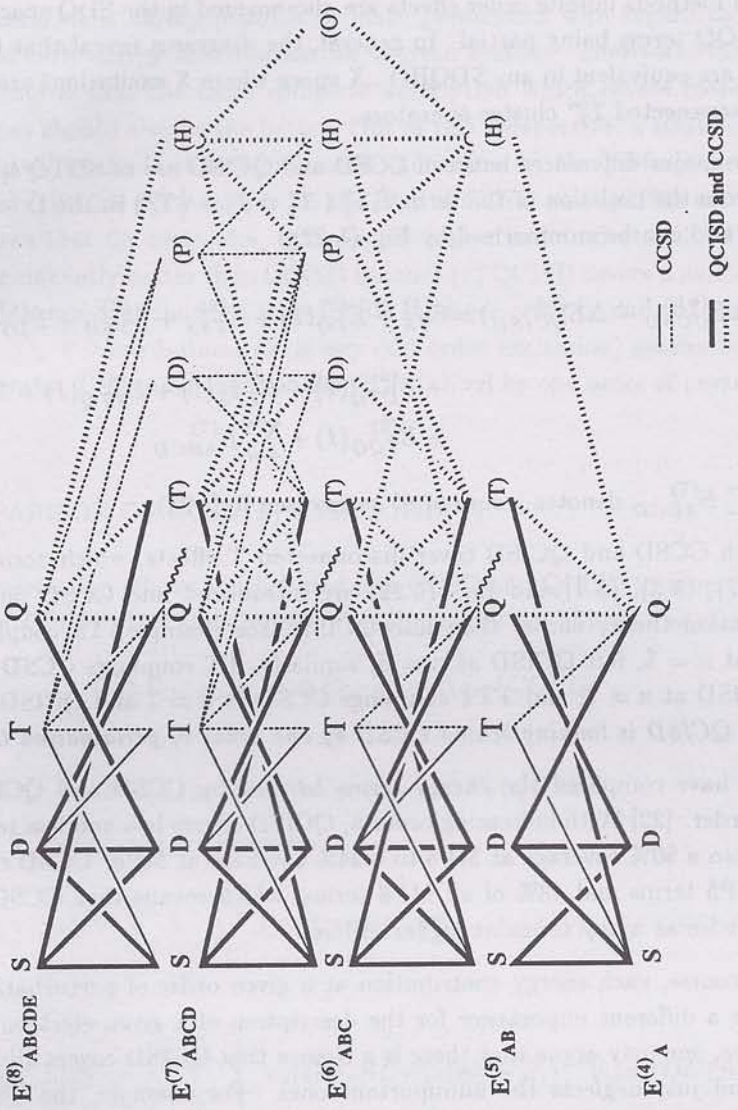


Figure 5.4. Graphical analysis of energy contributions at nth order MP perturbation theory (n= 4, 5, 6, 7, 8) covered by the CCSD and QCISD correlation energy. See explanations given for Figure 5.1. Note that bold solid (hashed) lines denote energy terms that are fully (partially) contained in both the CCSD and the QCISD correlation energy. Those energy terms that are only covered by the CCSD energy terms are denoted by normal solid or dashed lines depending on whether they are fully or partially contained. *Reprinted with permission from Z. He and D. Cremer, Theor. Chim. Acta, (1994) 85, 305. Copyright (1994) Springer Verlag.*

for both methods infinite order effects are also covered in the SDQ space with just the A...QQ terms being partial. In general, the diagrams reveal that CCSD and QCISD are equivalent in any SDQHO...X space where X excitations are generated from disconnected $\hat{T}_2^m$ cluster operators.

The major differences between CCSD and QCISD are in SDTQ space. They result from the omission of the term $\hat{T}_1\hat{T}_2'$ ($\hat{T}_2' = \hat{T}_2 + \frac{1}{2}\hat{T}_1^2$) in the D equations of QCISD and can be summarized by Eq. (5.22):

$$\sum_{n=2}^{7}(\Delta E_{CCSD}^{(n)} - \Delta E_{QCISD}^{(n)}) = E_{TS}^{(5)} + E_{TQ}^{(5)}(I) + E_{TSS}^{(6)} + E_{TSD}^{(6)} + E_{DTS}^{(6)} + E_{DTQ}^{(6)}(I) + E_{TTS}^{(6)}(I) + E_{TTQ}^{(6)}(I) + E_{TQD}^{(6)}(I) + E_{TQQ}^{(6)}(I) + \sum E_{ABCD}^{(7)} \qquad (5.22)$$

where $\sum E_{ABCD}^{(7)}$ denotes a sum of 41 terms (see Ref. 23).

Both CCSD and QCISD cover disconnected T effects, which according Figures (5.2), (5.3), (5.4) and Eq. (5.22) are introduced into CCSD one order of perturbation theory earlier than into QCISD. For example, TS couplings enter CCSD at n = 5, but QCISD at n = 6; similarly, TT couplings CCSD at n = 6, but QCISD at n = 7; and TTT couplings CCSD at n = 7 and QCISD at n = 8. Clearly, *QCISD is limping behind CCSD by one order of perturbation theory.*

We have compared the energy terms covered by CCSD and QCISD up to eighth order. [22] With increasing order n, QCISD covers less and less terms going down from a 50% coverage at MP5 to a 24% coverage at MP8. CCSD covers 64% of all MP5 terms and 43% of all MP8 terms, which means that CCSD contains almost twice as many terms at higher orders.

Of course, each energy contribution at a given order of perturbation theory can have a different importance for the description of a given electronic system. Therefore, one may argue that there is a chance that QCISD covers all important terms and just neglects the unimportant ones. For example, the TS and TQ terms at MP5, that are not covered by QCISD, lead often to positive energy contributions and decrease the absolute magnitude of the correlation energy. As a consequence, QCISD correlation energies are often more negative than CCSD correlation energies, which one could take as indication that the right terms have been neglected in QCISD. On the other hand, the correct description of correlation effects must avoid an exaggeration of certain correlation effects as discussed in chapter 2 in the case of the pair correlation effects. The appearance of positive contributions normally means a correction of correlation effects exaggerated at lower orders and, therefore, these terms should not be neglected.

In general, it is hardly possible to make predictions with regard to the importance of each energy contribution for a given system. Therefore, the simple rule of thumb is that the more complete description which covers more energy contributions should also be the better. Out of this perspective, a statistical comparison of two methods should give some indication on the performance of the two methods. [22,23] For example, in the case of CCSD and QCISD the analysis clearly shows that for molecules, that require higher order effects, CCSD should perform significantly better than QCISD because (a) QCISD covers a much smaller number of energy contributions than CCSD at larger order n; and (b) part of the T, P, $S_7, \ldots,$ Y contributions (Y is any odd order excitation) generated by the cluster operator $\hat{T}_1\hat{T}_2'$ are delayed at the QCISD level by one order of perturbation theory.

5.3 COMPARISON OF CCSD(T) AND QCISD(T)

When T correlation effects are included into CCSD and QCISD in a perturbative way, then CCSD(T) [36] and QCISD(T) [35] energies are obtained according to

$$\Delta E_{CCSD(T)} = \Delta E_{CCSD} + \Delta E_T(CCSD) \tag{5.23}$$

and

$$\Delta E_{QCISD(T)} = \Delta E_{QCISD} + \Delta E_T(QCISD) \tag{5.24}$$

where the T corrections are given by

$$\Delta E_T(CCSD) = \sum_p^{SD} \sum_d^D \sum_t^T a_p(CCSD)\bar{V}_{pt}(E_0 - E_t)^{-1}\hat{V}_{td}a_d(CCSD) \tag{5.25}$$

$$\begin{aligned}\Delta E_T(QCISD) = &\sum_p^{SD} \sum_d^D \sum_t^T a_p(QCISD)\bar{V}_{pt}(E_0 - E_t)^{-1}\hat{V}_{td}a_d(QCISD) \\ &+ \sum_s^S \sum_d^D \sum_t^T a_d(QCISD)\bar{V}_{dt}(E_0 - E_t)^{-1}\hat{V}_{ts}a_s(QCISD)\end{aligned} \tag{5.26}$$

CCSD(T) and QCISD(T) correlation energies were expanded in a similar way as in the case of CCSD and QCISD. [23] Similar methods such as CCSD(TQ) and QCISD(TQ), which were developed to have CC methods that are correct in fifth order perturbation theory [9], were also investigated. We refrain from a lengthy

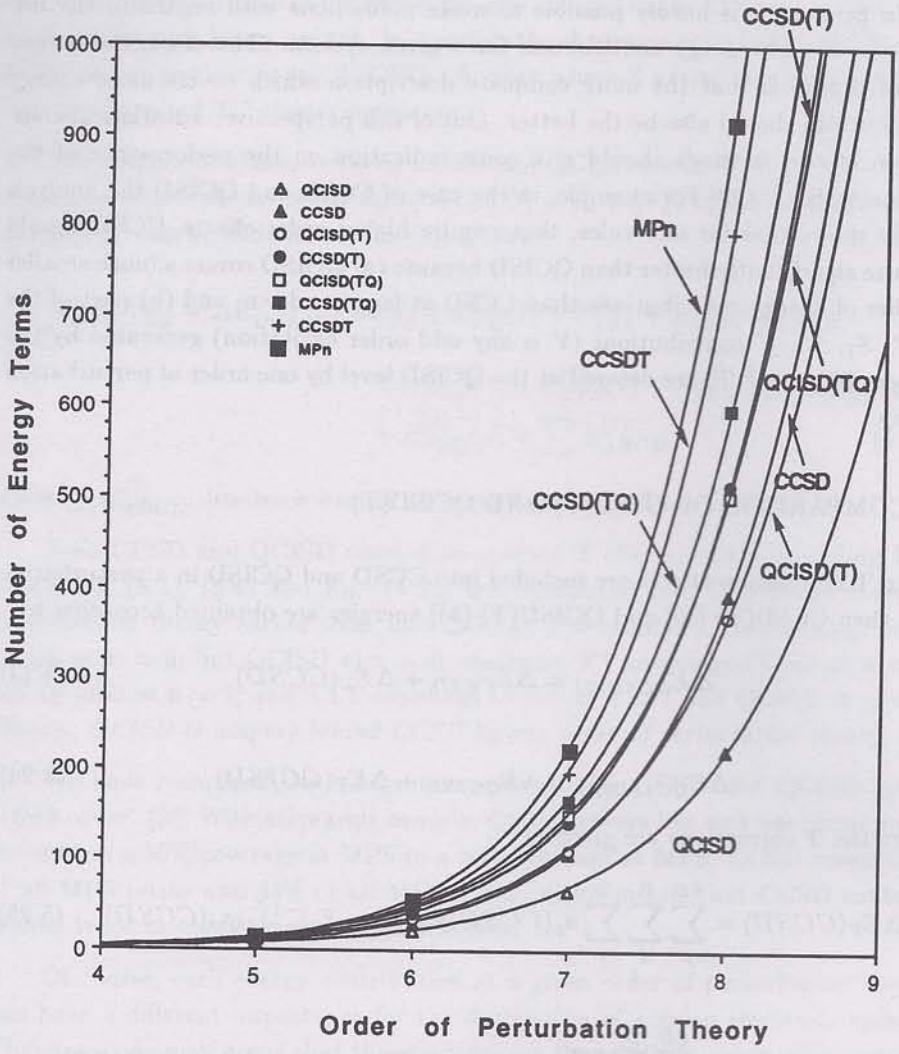


Figure 5.5. Number of energy contributions $E^{(n)}_{ABC..}$ covered by QCISD, CCSD, QCISD(T), CCSD(T), QCISD(TQ), CCSD(TQ), CCSDT, and MPn given as a function of the order n. Numbers are given without considering symmetry. *Reprinted with permission from Z. He and D. Cremer, Theor. Chim. Acta, (1994) 85, 305. Copyright (1994) Springer Verlag.*

discussion of all the results obtained in this work [22,23] and, instead, summarize results in Figure 5.5, where the numbers of energy contributions covered by a particular CC or QCI method at nth (n = 5, 6, 7 and 8) order perturbation theory are given as functions of n. These curves clearly reveal that the discrepancy between the QCI and CC descriptions is gradually reduced from CCSD/QCISD to CCSD(T)/QCISD(T) and CCSD(TQ)/QCISD(TQ).

A noniterative improvement of a SD method by T excitations is more important for QCISD than for CCSD, since $\Delta E_T(QCISD)$ adds more terms to the QCISD correlation energy than $\Delta E_T(CCSD)$ adds to the CCSD correlation energy. As for the total number of energy contributions, QCISD(T) falls back behind CCSD at higher orders of perturbation theory as shown in Figure 5.5. Of course, this does not necessarily imply that CCSD is a better method than QCISD(T).

CCSD(T) should lead to a much better description of T effects than QCISD(T) since it contains more T contributions (including important TT coupling terms) than QCISD(T). Therefore, CCSD(T) is probably the method with the better cost-performance ratio. The difference between QCI and CC is considerably decreased at the CCSD(TQ) and QCISD(TQ) level of theory when considering in particular T correlation effects. QCISD(TQ) should lead to a performance comparable to that of CCSD(TQ).

In molecular investigations that require the inclusion of T effects, the various CC and QCI methods should lead to improved results in the following order:

$$\text{MP4(SDTQ)} < \text{QCISD(T)} < \text{CCSD(T)} < \text{QCISD(TQ)}, \text{CCSD(TQ)} < \text{CCSDT}.$$

MP4 that does not cover any TT coupling effects will always exaggerate T effects and some of this exaggeration will be carried over to QCISD(T), which includes the TT coupling effects at a relatively late stage. CCSD(T) should be the method that leads to a relatively balanced description of T effects while CCSDT is certainly a method, which comes close to FCI performance. This discussion clearly shows that, at the presence, applied work should be done with CCSD(T) while future work should concentrate on CCSDT or equivalent T methods within the CC approach. This is further discussed in chapter 6.

6. Coupled Cluster Methods with Triple Excitations

Triple (T) excitations resulting from the cluster operator $\hat{T}_3$ describe three-electron correlation effects. These effects are generally rather small, however due to the large number of these effects in an electronic system, their sum leads to a significant contribution to the total correlation energy (see the discussion in section

2.3). It has been shown that T correlation effects are particularly important in molecules with multiple bonds, nonclassical bonding, hypervalent bonding, and many other electronic situations. [11,15] In addition, one has put some hope into the expectation that CC methods with T excitations help to describe electron systems with significant multireference effects even within a single determinant approach. There are, however, at the moment two obstacles that hinder the general use of CC methods with T excitations such as CCSDT. First, development and programming of CCSDT is a rather tedious procedure which has been solved only by few experts. [20,47, see also 21] Second, the calculation of CCSDT energies involves $O(M^8)$ computational steps and, therefore, is too costly for routine calculations of larger molecules. Because of the complexity of the CCSDT equations and the associated cost factor, the development of the last years has gone in the direction of replacing CCSDT by CC methods that contain the T correlation effects in an approximated way. [35,36,51] To be mentioned in this connection are the CCSDT-n methods [51] and CCSD or QCISD with a perturbative inclusion of T effects such as CCSD(T) [36] and QCISD(T) [35]. For example, CCSD(T) and QCISD(T) are nowadays the most often used CC methods for high-accuracy calculations on nontrivial chemical problems. This has to do with the fact that the perturbative inclusion of T effects into CCSD or QCISD leads to $O(M^7)$ procedures, which can be applied to problems with 200 basis functions and more. [52]

Although CCSD(T) and QCISD(T) are the most often used CC methods for describing T effects, it is also clear from the discussion given in chapter 5 that the perturbative T methods, but in particular QCISD(T) can lead to an unbalanced description of T effects. Figure 5.5 reveals how much CCSD(T) and QCISD(T) differ from CCSDT for higher levels of perturbation theory. CCSDT, on the other hand, comes close to full CI or infinite order MPn results and, therefore, it has to be a major goal in CC theory to extend the existing methods for general use in Quantum Chemistry also to CC methods with a full account of T effects. In the following, the main features of CCSDT and approximate CC methods, that cover $\hat{T}_3$ effects fully, is described.

6.1 IMPLEMENTATION OF A COUPLED CLUSTER SINGLES, DOUBLES, AND TRIPLES METHOD: CCSDT

Truncation of the cluster operator $\hat{T}$ (introduced in chapter 4, Eq. 4.2) at $\hat{T}_3$ leads to the CCSDT method [20,47] that is defined by the projection Eq.s (6.1) - (6.3):

$$\langle \Phi_i^a | \bar{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{3!}\hat{T}_1^3) | \Phi_0 \rangle = a_i^a \Delta E_{CCSDT} \qquad (6.1)$$

$$\begin{aligned}\langle\Phi_{ij}^{ab}|\bar{H}(1+\hat{T}_1+\hat{T}_2+\hat{T}_3+\frac{1}{2}\hat{T}_2^2+\hat{T}_1\hat{T}_2+\frac{1}{2}\hat{T}_1^2+\hat{T}_1\hat{T}_3 \\ +\frac{1}{3!}\hat{T}_1^3+\frac{1}{2}\hat{T}_1^2\hat{T}_2+\frac{1}{4!}\hat{T}_1^4)|\Phi_0\rangle \\ =\langle\Phi_{ij}^{ab}|\hat{T}_2+\frac{1}{2}\hat{T}_1^2|\Phi_0\rangle\Delta E_{CCSDT}\end{aligned} \tag{6.2}$$

$$\begin{aligned}\langle\Phi_{ijk}^{abc}|\bar{H}(\hat{T}_1+\hat{T}_2+\hat{T}_3+\frac{1}{2}\hat{T}_2^2+\hat{T}_1\hat{T}_2+\frac{1}{2}\hat{T}_1^2+\hat{T}_1\hat{T}_3 \\ +\hat{T}_2\hat{T}_3+\frac{1}{3!}\hat{T}_1^3+\frac{1}{2}\hat{T}_1^2\hat{T}_2+\frac{1}{2}\hat{T}_1^2\hat{T}_3+\frac{1}{4!}\hat{T}_1^4)|\Phi_0\rangle \\ =\langle\Phi_{ijk}^{abc}|\hat{T}_3+\hat{T}_1\hat{T}_2+\frac{1}{3!}\hat{T}_1^3|\Phi_0\rangle\Delta E_{CCSDT}\end{aligned} \tag{6.3}$$

In the same way as described for CCSD in chapter 4, one can show that unlinked diagram terms cancel each other so that the S, D, and T equations (6.1) - (6.3) are obtained in connected form:

$$\langle\Phi_i^a|\bar{H}(\hat{T}_1+\hat{T}_2+\hat{T}_3+\hat{T}_1\hat{T}_2+\frac{1}{2}\hat{T}_1^2+\frac{1}{3!}\hat{T}_1^3)|\Phi_0\rangle_C=0 \tag{6.4}$$

$$\begin{aligned}\langle\Phi_{ij}^{ab}|\bar{H}(1+\hat{T}_1+\hat{T}_2+\hat{T}_3+\frac{1}{2}\hat{T}_2^2+\hat{T}_1\hat{T}_2+\frac{1}{2}\hat{T}_1^2+\hat{T}_1\hat{T}_3 \\ +\frac{1}{3!}\hat{T}_1^3+\frac{1}{2}\hat{T}_1^2\hat{T}_2+\frac{1}{4!}\hat{T}_1^4)|\Phi_0\rangle_C=0\end{aligned} \tag{6.5}$$

and

$$\begin{aligned}\langle\Phi_{ijk}^{abc}|\bar{H}(\hat{T}_2+\hat{T}_3+\frac{1}{2}\hat{T}_2^2+\hat{T}_1\hat{T}_2+\frac{1}{2}\hat{T}_1^2+\hat{T}_1\hat{T}_3+\hat{T}_2\hat{T}_3+\frac{1}{3!}\hat{T}_1^3+\frac{1}{2}\hat{T}_1^2\hat{T}_2 \\ +\frac{1}{2}\hat{T}_1^2\hat{T}_3+\frac{1}{4!}\hat{T}_1^4)|\Phi_0\rangle_C=0\end{aligned} \tag{6.6}$$

The expression for the correlation energy ΔE_{CCSDT}

$$\Delta E_{CCSDT}=\langle\Phi_0|\bar{H}(\hat{T}_2+\frac{1}{2}\hat{T}_1^2)|\Phi_0\rangle \tag{6.7}$$

keeps the same form as in the CCSD case since higher excitation cluster operators $\hat{T}_n$ $(n\geq 3)$ can not directly affect the total energy.

The equation for the CCSDT correlation energy in form of two-electron integrals is given by (6.8)

$$\Delta E_{CCSDT}=\frac{1}{4}\sum_{ij,ab}\langle ij||ab\rangle\tau_{ij}^{ab} \tag{6.8}$$

where τ_{ij}^{ab} is determined via S and D amplitudes

$$\tau_{ij}^{ab} = a_{ij}^{ab} + a_i^a a_j^b - a_i^b a_j^a \tag{6.9}$$

The S and D amplitudes are calculated by iterative solution of Eq.s (6.10) and (6.11):

$$(\epsilon_i - \epsilon_a) a_i^a = \tilde{u}_i^a + \tilde{v}_i^a + \sum_{l<m} \sum_{d<e} \langle lm||de\rangle a_{ilm}^{ade} \tag{6.10}$$

$$(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) a_{ij}^{ab} = \langle ab||ij\rangle + \tilde{u}_{ij}^{ab} + \tilde{v}_{ij}^{ab} +$$

$$\sum_{l,d<e} (\langle bl||de\rangle a_{ijl}^{ade} + \langle al||de\rangle a_{ijl}^{dbe}) + \sum_{l<m,d} (\langle lm||dj\rangle a_{ilm}^{abd} + \langle lm||di\rangle a_{ljm}^{abd})$$

$$+\frac{1}{2} \sum_{mn} \sum_{ef} \langle mn||ef\rangle \left(2a_m^e a_{ijn}^{abf} + \sum_P (-1)^P P(i/j) a_i^e a_{jmn}^{abf} \right.$$

$$\left. + \sum_P (-1)^P P(a/b) a_m^a a_{ijn}^{bef} \right) \tag{6.11}$$

which via the T amplitudes a_{ijk}^{abc} depend on the T equation (6.12):

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

$$- \sum_P (-1)^P P(i/jk|a/bc) \left[\sum_d X_1^{CCSDT}(i,d,b,c) a_{jk}^{ad} + \sum_l X_2^{CCSDT}(j,k,l,a) a_{il}^{bc} \right]$$

$$+ \sum_P (-1)^P P(a/bc) \left[\frac{1}{2} \sum_{ef} X_3^{CCSDT}(b,c,e,f) a_{ijk}^{aef} + \sum_f Y_1^{CCSDT}(f,a) a_{ijk}^{fbc} \right]$$

$$+ \sum_P (-1)^P P(i/jk) \left[\frac{1}{2} \sum_{mn} X_4^{CCSDT}(m,n,j,k) a_{imn}^{abc} + \sum_n Y_2^{CCSDT}(n,i) a_{njk}^{abc} \right]$$

$$- \sum_P (-1)^P P(i/jk|a/bc) \sum_{me} X_5^{CCSDT}(m,a,i,e) a_{jkm}^{bce} \tag{6.12}$$

For setting up S, D, and T equations, arrays $\tilde{u}_i^a$, $\tilde{v}_i^a$, $\tilde{u}_{ij}^{ab}$ and $\tilde{v}_{ij}^{ab}$, which contain the terms of the CCSD equations, have to be calculated according to Eq.s (6.13) - (6.16):

$$\tilde{u}_i^a = - \sum_{ld} \langle la||id\rangle a_l^d - \frac{1}{2} \sum_{lde} \langle la||de\rangle \tau_{il}^{de} - \frac{1}{2} \sum_{lmd} \langle lm||id\rangle \tau_{lm}^{ad} \tag{6.13}$$

$$\tilde{u}_{ij}^{ab} = \sum_{d}(\langle ab||dj\rangle a_i^d - \langle ab||di\rangle a_j^d) + \sum_{l}(\langle la||ij\rangle a_l^b - \langle lb||ij\rangle a_l^a)$$
$$+ \frac{1}{2}\sum_{de}\langle ab||de\rangle \tau_{ij}^{de} + \frac{1}{2}\sum_{lm}\langle lm||ij\rangle \tau_{lm}^{ab}$$
$$- \sum_{ld}\sum_{p}(-1)^p P(i/j|a/b)\langle lb||jd\rangle(a_{il}^{ad} - a_i^d a_l^a) \tag{6.14}$$

$$\tilde{v}_i^a = \frac{1}{2}\sum_{lm}\sum_{de}\langle lm||de\rangle \left(a_i^d a_{lm}^{ea} + a_l^a a_{im}^{ed} + 2a_l^d(a_{im}^{ae} - a_i^e a_m^a)\right) \tag{6.15}$$

$$\tilde{v}_{ij}^{ab} = \frac{1}{4}\sum_{lm}\sum_{de}\langle lm||de\rangle \left[\tau_{ij}^{de}\tau_{lm}^{ab} - 2(a_{ij}^{ad}\tau_{lm}^{be} + a_{ij}^{be}\tau_{lm}^{ad} + a_{il}^{ab}\tau_{jm}^{de} + \tau_{il}^{de}a_{jm}^{ab})\right.$$
$$\left. +4\left(a_{il}^{ad}(a_{jm}^{be} - a_j^e a_m^b) + a_{il}^{be}(a_{jm}^{ad} - a_j^d a_m^a) - a_i^d a_l^a a_{jm}^{be} - a_i^e a_l^b a_{jm}^{ad}\right)\right]$$
$$+ \sum_{P}(-1)^P P(i/j)\sum_{mn,d}\langle mn||jd\rangle(a_m^d a_{in}^{ab} - \frac{1}{2}a_i^d \tau_{mn}^{ab})$$
$$+ \sum_{P}(-1)^P P(a/b)\sum_{m,ef}\langle am||ef\rangle(a_m^e a_{ij}^{bf} - \frac{1}{2}a_m^b \tau_{ij}^{ef})$$
$$+ \sum_{P}(-1)^P P(i/j|a/b)\left(\sum_{mn,d}\langle mn||jd\rangle a_m^a(a_{in}^{bd} - a_i^d a_n^b)\right.$$
$$\left. + \sum_{m,ef}\langle am||ef\rangle a_i^e(a_{jm}^{bf} - a_j^f a_m^b)\right) \tag{6.16}$$

In addition, the intermediate arrays X_n^{CCSDT} and Y_m^{CCSDT} listed in Table 6.1 have to be evaluated. They reduce the computational cost of the CCSDT method to $O(M^8)$. The most costly terms in the T equations result from the cluster operators $\hat{T}_3$ and $\hat{T}_2\hat{T}_3$.

6.2 DEVELOPMENT OF A QCI METHOD WITH SINGLE, DOUBLE, AND TRIPLE EXCITATIONS: QCISDT

Pople, Head-Gordon, and Raghavachari (PHR) have suggested a QCISDT method in their original QCI publication [35], which turned out to be not size-extensive although the method was developed to overcome the size-extensivity error of the normal CI approach. [49] This deficiency of the QCISDT method of PHR does not mean that a size-extensive QCISDT method with just quadratic corrections added

TABLE 6.1. Intermediate arrays used in the triple amplitude equations of QCISDT and CCSDT. [a]

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

[a] The arrays τ_{ij}^{ab}, Z1(mb,id) and Z2(al,ej) are defined by:

$$\tau_{ij}^{ab} = a_{ij}^{ab} + a_i^a a_j^b - a_i^b a_j^a$$

$$Z1(mb,id) = \langle mb\|\|id\rangle + \sum_e \langle mb\|\|ed\rangle a_i^e + \sum_{ne}\langle mn\|\|ed\rangle a_{in}^{be}$$

$$Z2(al,ej) = \langle al\|\|ej\rangle - \sum_m \langle ml\|\|ej\rangle a_m^a + \sum_{mf}\langle ml\|\|ef\rangle a_{jm}^{af}$$

to the linear CISDT terms is impossible. Therefore, the question arises whether and how a size-extensive QCISDT method can be constructed. This problem automatically leads to the more general question whether there exists a hierarchy of size-extensive QCI methods that is in line with the original idea of PHR, namely a simple improvement of CI by just including quadratic correction terms. [30]

One can approach this problem in the following way [30]:

The physically not meaningful terms in the projection equations of truncated CI show up in the diagrammatic description in form of unlinked diagrams. The unlinked diagrams result from disconnected terms in the CI equations of a given truncation level. One has to eliminate all disconnected terms from the CI projection equations in order to obtain a size-extensive CI energy. Based on these considerations, a general procedure for restoring size-extensivity in a CI approach has been developed. [30] This procedure comprises three steps:

1) Analysis of disconnected terms in the CI projection equations. 2) Cancellation of disconnected terms by the addition of appropriate new terms. 3) Final test whether the addition of new terms to the CI equations does not lead to new disconnected terms.

If new disconnected terms appear, one will have to add further terms until all disconnected terms disappear. In the most general case one has to loop several times through the sequence 1) - 3) until a size-extensive method is obtained. Since the methods obtained in this way are size-extensive extended CI approaches that do not necessarily comply with the quadratic CI method of PHR, we have called them extended CI (ECI) methods. [30] Hence, *an ECI method can be considered as a CI method, to which a minimum number of terms have been added to restore size-extensivity,* or alternatively *as an approximated CC method that differs from the corresponding CI method by a minimal number of terms.*

If the CI space is restricted to S and D excitations, the new terms to be added are quadratic as has been shown by PHR.[35] However, if higher excitations are included, e.g. T excitations at the CISDT level, size-extensivity will require the inclusion of both quadratic and cubic terms as will be shown in the following. Accordingly, one would have to speak of cubic CI, quartic CI, etc. However, it is better to speak of ECI methods and to refrain from introducing a new terminology. [30]

The CISDT projection equations are given by

$$\langle \Phi_i^a | \bar{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = a_i^a \Delta E_{CISDT} \tag{6.17}$$

$$\langle \Phi_{ij}^{ab} | \bar{H} (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = a_{ij}^{ab} \Delta E_{CISDT} \tag{6.18}$$

$$\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = a_{ijk}^{abc} \Delta E_{CISDT} \tag{6.19}$$

$$\Delta E_{CISDT} = \langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle \tag{6.20}$$

There are three unlinked diagram terms ($a_i^a \Delta E_{CISDT}$, $a_{ij}^{ab} \Delta E_{CISDT}$ and $a_{ijk}^{abc} \times \Delta E_{CISDT}$) in these equations and one disconnected term associated with $\hat{T}_1$ in Eq.(6.19), which also gives an unlinked diagram contribution to the energy ΔE_{CISDT}. In order to cancel those unlinked diagram contributions one has to add quadratic terms $\hat{T}_1 \hat{T}_2$, $\frac{1}{2}\hat{T}_2^2$ and $\hat{T}_2 \hat{T}_3$ in Eq.s (6.17), (6.18) and (6.19), respectively. In this way, the three unlinked diagram terms are cancelled, however those unlinked diagram contributions resulting from $\hat{T}_1$ are not cancelled. Also, the addition of $\hat{T}_2 \hat{T}_3$ in Eq.(6.19) leads to some new unlinked diagram contributions. This can be seen if the term associated with $\hat{T}_2 \hat{T}_3$ is written as

$$\langle \Phi_{ijk}^{abc} | \bar{H} \hat{T}_2 \hat{T}_3 | \Phi_0 \rangle = \langle \Phi_{ijk}^{abc} | (\bar{H} \hat{T}_2 \hat{T}_3)_C | \Phi_0 \rangle + \langle \Phi_{ijk}^{abc} | (\bar{H} \hat{T}_2 \hat{T}_3)_D | \Phi_0 \rangle \tag{6.21}$$

where the disconnected part can further be partitioned according to

$$\langle \Phi_{ijk}^{abc} | (\bar{H} \hat{T}_2 \hat{T}_3)_D | \Phi_0 \rangle = \langle \Phi_{ijk}^{abc} | \hat{T}_3 (\bar{H} \hat{T}_2)_C | \Phi_0 + \langle \Phi_{ijk}^{abc} | \hat{T}_2 (\bar{H} \hat{T}_3)_C | \Phi_0 \rangle \tag{6.22}$$

The first term of Eq. (6.22) cancels the unlinked diagram term of the right-hand side of Eq. (6.19) while the second term of Eq. (6.22) adds both linked and unlinked diagram contributions to the correlation energy. This demonstrates clearly that the original QCI concept of PHR [35] that is based on the addition of just quadratic cluster terms does no longer work for CISDT.

Size-extensivity can only be obtained in the case of CISDT by adding further quadratic and even cubic cluster operator terms to the T equation (6.19). [30] Finally, the projection equations (6.23) - (6.26) of size-extensive ECISDT are obtained, which differ considerably from the (non-size-extensive) QCISDT equations of PHR. [30]

$$\langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle = \Delta E_{ECISDT} \tag{6.23}$$

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle = a_i^a \Delta E_{ECISDT} \tag{6.24}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \frac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle = a_{ij}^{ab} \Delta E_{ECISDT} \tag{6.25}$$

$$\begin{aligned} &\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_3 + \frac{1}{2}\hat{T}_2^2 + \hat{T}_2 \hat{T}_3 + \frac{1}{2}\hat{T}_1 \hat{T}_2^2) | \Phi_0 \rangle \\ &= (a_{ijk}^{abc} + \sum_P (-1)^P P(i/jk|a/bc) a_i^a a_{jk}^{bc}) \Delta E_{ECISDT} \end{aligned} \tag{6.26}$$

Eq.s (6.24) - (6.26) can be rewritten in connected form:

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_2)|\Phi_0\rangle_C = 0 \tag{6.27}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \frac{1}{2}\hat{T}_2^2)|\Phi_0\rangle_C = 0 \tag{6.28}$$

$$\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_2 + \hat{T}_3 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_2^2 + \hat{T}_2\hat{T}_3 + \frac{1}{2}\hat{T}_1\hat{T}_2^2)|\Phi_0\rangle_C = 0 \tag{6.29}$$

Clearly, ECISDT is not identical with CCSDT since it differs with regard to one cubic term and some quadratic terms. There is not much reason to further investigate a method such ECISDT since it offers little advantage compared to the more complete CCSDT method.

ECI methods in general are not very attractive, which becomes obvious when extending CISDTQ to size-extensive ECISDTQ as described in Ref. 30. It turns out that ECISDTQ is identical with CCSDTQ, i.e. the ECI methods do not represent a hierarchy of independent methods. ECID is identical with CCD, ECISD with QCISD, and ECISDTQ, ECISDTQP, etc. identical with the corresponding CC methods. Hence, the PHR concept of size-extensive QCI methods is not attractive, no matter whether one uses the original recipe [35] or the correct procedure worked out in Ref. 30.

Although the ECI equations may not be useful for any practical purpose, they can be used for deriving a new QCI concept. For this purpose, one starts from the ECI projection equations in their connected form and, in the same spirit as the CCSDT-n methods were developed [51], deletes all terms but the connected linear and certain quadratic terms. In the case of ECISDT (see Eq.s (6.27) - (6.29)), one keeps $\hat{T}_2\hat{T}_n$ with n = 1, 2, and 3 for S, D, and T equations, respectively. In this way, the projection equations of a size-extensive QCISDT method are defined, which we have coined $QCISDT_c$ to emphasize that we start from connected form of the projection equations and to distinguish $QCISDT_c$ from the non-size-extensive QCISDT approach of PHR.

$$\Delta E_{QCISDT_c} = \langle \Phi_0 | \bar{H}\hat{T}_2 | \Phi_0 \rangle \tag{6.30}$$

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_2)|\Phi_0\rangle_C = 0 \tag{6.31}$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \frac{1}{2}\hat{T}_2^2)|\Phi_0\rangle_C = 0 \tag{6.32}$$

$$\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_2 + \hat{T}_3 + \hat{T}_2\hat{T}_3)|\Phi_0\rangle_C = 0 \tag{6.33}$$

The $QCISDT_c$ equations differ from the original QCISDT equations (Eq.s 3.36 - 3.39) in three ways. First, only the connected part of the quadratic correction terms is included. Secondly, quadratic corrections $(\bar{H}\hat{T}_2\hat{T}_n)_C$ are added to all

CISDT equations but the energy expression. Finally, the linear term $\langle \Phi_{ijk}^{abc} | \bar{H} \hat{T}_1 | \Phi_0 \rangle$ disappears since it leads to unlinked diagram contributions that do not add to the correlation energy.

In the same way, one can derive $QCISDTQ_c$ from ECISDTQ = CCSDTQ. [30] Formally, the QCI_c equations can also be obtained by starting at the corresponding CI equations. This can be shown for the projection equations of a truncated CI method that includes up to n-fold excitations:

$$\Delta E_{CI} = \langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle \tag{6.34}$$

$$\langle \Phi_x | \bar{H} (1 + \hat{T}_1 + \hat{T}_2 + ... + \hat{T}_n) | \Phi_0 \rangle = c_x \Delta E_{CI} \qquad (x = 1, 2, ..., n) \tag{6.35}$$

or, alternatively, as

$$\langle \Phi_s | \bar{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = c_s \Delta E_{CI} \tag{6.36}$$

$$\langle \Phi_d | \bar{H} (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4) | \Phi_0 \rangle = c_d \Delta E_{CI} \tag{6.37}$$

$$\langle \Phi_x | \bar{H} (\sum_{i=x-2}^{min[x+2,n]} \hat{T}_i) | \Phi_0 \rangle = c_x \Delta E_{CI} \qquad (n \geq x \geq 3) \tag{6.38}$$

where x is a general excitation indices. For any excitation index x higher than d, there appear just two disconnected terms, namely $\langle \Phi_x | \bar{H} \hat{T}_{x-2} | \Phi_0 \rangle (= \langle ab||ij \rangle c_{x-2})$ and $c_x E_{CI}$ in the corresponding projection equation. Introducing $-\bar{H} \hat{T}_{p-2}$ and parts of the term $\bar{H} \hat{T}_2 \hat{T}_x$, namely $(\bar{H} \hat{T}_2 \hat{T} x)_C$ and $\hat{T}_x (\bar{H} \hat{T}_2)_C$, on the left side of Eq. (6.38), all disconnected terms are cancelled and the QCIc equations are obtained in their general form:

$$\Delta E_{QCI_c} = \langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle \tag{6.39}$$

$$\langle \Phi_s | \bar{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle_C = 0 \tag{6.40}$$

$$\langle \Phi_d | \bar{H} (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \frac{1}{2} \hat{T}_2^2) | \Phi_0 \rangle_C = 0 \tag{6.41}$$

$$\langle \Phi_x | (\sum_{i=x-1}^{min[x+2,n]} \hat{T}_i + \hat{T}_2 \hat{T}_x) | \Phi_0 \rangle_C = 0 \qquad (n \geq x \geq 3) \tag{6.42}$$

Eq.s (6.39) - (6.42) establish a hierarchy of size-extensive QCI methods that covers the original QCISD method of Pople and co-workers, but can easily be extended to T, Q, and higher excitations.

Since the $QCISDT_c$ projection equations possess a rather simple form compared to the corresponding CCSDT equations, it was attractive to develop $QCISDT_c$ as a new CC method including T effects. Such development is a rather tedious task and, therefore, work has to be based on more than just the assumption that a new method such as $QCISDT_c$ may approximate a more complete method such as CCSDT rather well. Therefore, $QCISDT_c$ and CCSDT are compared in the next section with the help of perturbation theory.

6.3 ANALYSIS OF CCSDT AND QCISDT

Results of the comparison of the CCSDT and $QCISDT_c$ correlation energy in terms of nth ($n \leq 6$) order MBPT as described in chapter 5 are summarized in Figures 6.1 and 6.2. [30] CCSDT covers all contributions directly made up by S, D , and T excitations as is nicely shown by the energy diagram of Figure 6.1. The body of the CCSDT diagram is made up by a ladder of SDT contributions, which reaches to infinite order. Many Q effects are also covered either fully or at least partially where the latter is also true for many higher excitation effects. Figure 6.1 reveals that CCSDT, which is correct up to fourth order, lacks just the QT contribution at fifth order and contains the QQ contribution just partially. At sixth order, CCSDT is also a rather complete method. Out of the 55 sixth order terms, it does not contain five terms, namely QTD, DQT, QQT, QTT, and TQT. Apart from this, CCSDT covers nine other terms just partially.

$QCISDT_c$ is also exact up to fourth order. At higher orders, it lacks TS, TSA, TQ, and TQA energy contributions as is shown by Eq. (6.43), which gives energy differences between CCSDT and $QCISDT_c$ up to 6th order.

$$\begin{aligned}\Delta E_{CCSDT} - \Delta E_{QCISDT_c} &= \lambda^{(5)}(E^{(5)}_{TS} + E^{(5)}_{TQ}) + \lambda^{(6)}[E^{(6)}_{DTS} + E^{(6)}_{STQ}(II) + E^{(6)}_{QTS}(II) \\ &+ E^{(6)}_{DTQ} + E^{(6)}_{TSS} + E^{(6)}_{TTS} + E^{(6)}_{TSD} + E^{(6)}_{TQD} + E^{(6)}_{TST} \\ &+ E^{(6)}_{TQQ}(I) + E^{(6)}_{TTQ} + E^{(6)}_{TPT}(II)] + O(\lambda^{(7)}) \end{aligned} \tag{6.43}$$

In most cases, contributions such as TS, TQ, TSA or TSQ have positive sign and, therefore, make the correlation energy more positive. This means that $QCISDT_c$ energies will be often lower than CCSDT energies.

According to Figure (6.2) and Eq. (6.44), which gives the difference between $QCISDT_c$ and QCISD(T) up to sixth order, $QCISDT_c$ should be superior to

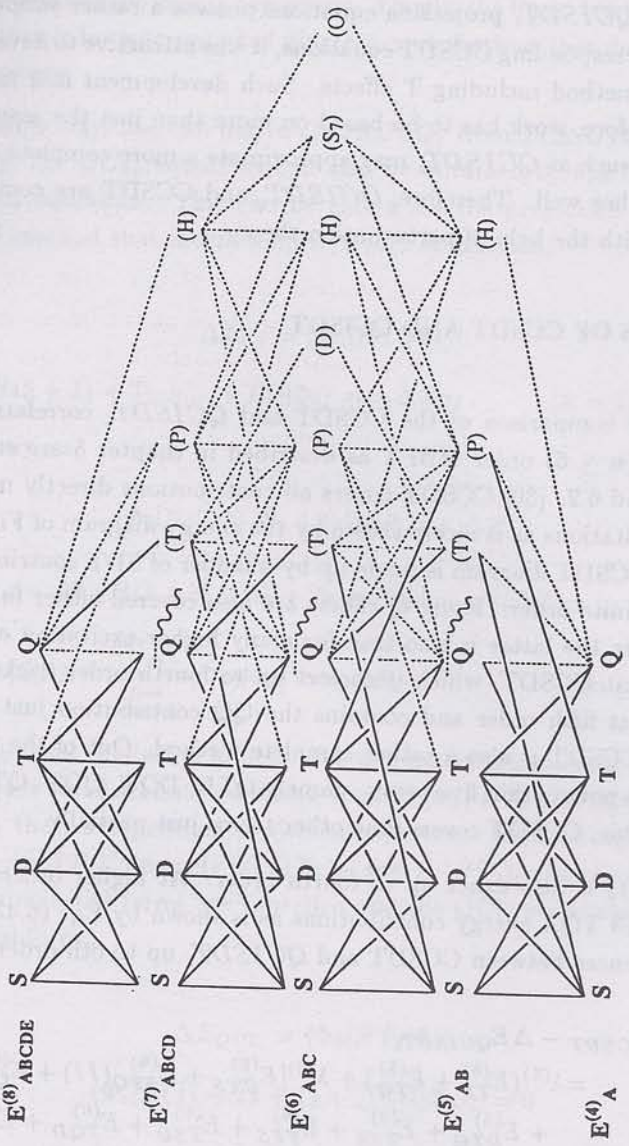


Figure 6.1. Graphical analysis of energy contributions at nth order MP perturbation theory (n= 4, 5, 6, 7, 8) covered by the CCSDT correlation energy. See explanations given for Figure 5.1. Note that solid (dashed) lines denote energy terms fully (partially) contained in the CCSDT correlation energy. *Reprinted with permission from Z. He and D. Cremer, Int. J. Quant. Chem. Symp. (1991) 25, 43. Copyright (1991) John Wiley, Inc.*

Analysis of Various Methods in Terms of MP6

	QCISD(T)	QCISDTc	ECISDT	CCSDT
SSS	yes	yes	yes	yes
SSD,DSS	y,y	y,y	y,y	y,y
SDS	yes	yes	yes	yes
SDD,DDS	y,y	y,y	y,y	y,y
SDQ,QDS	y,y	y,y	y,y	y,y
DSD	yes	yes	yes	yes
DDD	yes	yes	yes	yes
DQD	yes	yes	yes	yes
DDQ,QDD	y,y	y,y	y,y	y,y
DQQ,QQD	(y),(y)	(y),(y)	(y),(y)	(y),(y)
QDQ	yes	yes	yes	yes
QQQ	(yes)	(yes)	(yes)	(yes)
STS	yes	yes	yes	yes
STD,DTS	y,y	y,-	y,-	y,y
STQ,QTS	(y),(y)	(y),(y)	y,(y)	y,y
DTD	yes	yes	yes	yes
DTQ,QTD			(y),-	y,-
QTQ	(yes)	(yes)	(yes)	(yes)
SST,TSS	y,y	y,-	y,-	y,y
SDT,TDS	y,y	y,y	y,y	y,y
STT,TTS		y,-	y,(y)	y,y
DST,TSD	y,y	y,-	y,-	y,y
DDT,TDD	y,y	y,y	y,y	y,y
DQT,TQD			-,(y)	-,y
DTT,TTD		y,y	y,y	y,y
TDQ,QDT	y,y	y,y	y,y	y,y
TQQ,QQT			(y),-	(y),-
TTQ,QTT			(y),-	y,-
TST				yes
TDT		yes	yes	yes
TQT				
TTT		yes	yes	yes
QPQ		(yes)	(yes)	(yes)
QHQ	(yes)	(yes)	(yes)	(yes)
TPQ,QPT		(y),(y)	(y),(y)	(y),(y)
TPT		(yes)	(yes)	yes

Analysis of Various Methods in Terms of MP5

	QCISD(T)	QCISDTc	ECISDT	CCSDT
SS	yes	yes	yes	yes
DD	yes	yes	yes	yes
TT		yes	yes	yes
QQ	(yes)	(yes)	(yes)	(yes)
SD,DS	y,y	y,y	y,y	y,y
DQ,QD	y,y	y,y	y,y	y,y
ST,TS	y,y	y,-	y,-	y,y
DT,TD	y,y	y,y	y,y	y,y
TQ,QT			(y),-	y,-

Figure 6.2. Analysis of energy contributions at 5th (top) and 6th order MP perturbation theory (bottom) covered by QCISD(T), QCISDTc, ECISDT, and CCSDT correlation energies. Yes or y denote that the particular term is fully contained in the correlation energy while yes or y in parentheses indicates that the term is only partially covered. *Reprinted with permission from D. Cremer and Z. He, Theor. Chim. Acta, (1994) 88, 47. Copyright (1994) Springer Verlag.*

QCISD(T):

$$\begin{aligned}\Delta E_{QCISDT_c} - \Delta E_{QCISD(T)} &= \lambda^{(5)}(E^{(5)}_{TT} - E^{(5)}_{TS}) + \lambda^{(6)}[E^{(6)}_{STT} + 2E^{(6)}_{DTT} + E^{(6)}_{TDT} + E^{(6)}_{TTT} \\ &\quad + E^{(6)}_{QPQ}(I) + E^{(6)}_{TPQ}(I) + E^{(6)}_{QPT}(I) + E^{(6)}_{TPT}(I) \\ &\quad - E^{(6)}_{DTS} - E^{(6)}_{TSS} - E^{(6)}_{TSD}] + O(\lambda^{(7)}) \end{aligned} \tag{6.44}$$

QCISD(T) suffers from an exaggeration of T effects in molecular calculations due to the fact that TT couplings are totally missing in QCISD(T) at 5th and 6th order. [23] $QCISDT_c$, however, covers 6 of the 11 possible sixth order TAT and TTA coupling terms (partially or totally) and, hence, compares well with CCSDT that covers 9 of these terms. In summary, $QCISDT_c$ should come close to the performance of CCSDT in those cases where TS and TQ contributions are not important. Of course, this improvement is obtained at the cost of going from an $O(M^7)$ method, namely QCISD(T), to an $O(M^8)$ method. However, in view of the simplicity of $QCISDT_c$ it is worthwhile to use this approach as an alternative CC method with full inclusion of T effects.

6.4 IMPLEMENTATION AND APPLICATION OF QCISDT

The $QCISDT_c$ projection equations derived in section 6.2 have to be transformed into two-electron integral expressions in order to set up a $QCISDT_c$ computer program. [31] The $QCISDT_c$ energy expression as well as the S, D, and T equations take a similar form as the corresponding CCSDT equations if expressed in terms of two-electron integrals (in the following $QCISDT_c$ is abbreviated by $QCISDT$): [31]

$$\Delta E_{QCISDT} = \frac{1}{4}\sum_{ij,ab}\langle ij||ab\rangle a^{ab}_{ij} \tag{6.45}$$

$$(\epsilon_i - \epsilon_a)a^a_i = u^a_i + v^a_i + \sum_{l<m}\sum_{d<e}\langle lm||de\rangle a^{ade}_{ilm} \tag{6.46}$$

$$\begin{aligned}(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)a^{ab}_{ij} &= \langle ab||ij\rangle + u^{ab}_{ij} + v^{ab}_{ij} + \\ \sum_{l,d<e}(\langle bl||de\rangle a^{ade}_{ijl} + \langle al||de\rangle a^{dbe}_{ijl}) &+ \sum_{l<m,d}(\langle lm||dj\rangle a^{abd}_{ilm} + \langle lm||di\rangle a^{abd}_{ljm})\end{aligned} \tag{6.47}$$

$$\begin{aligned}(\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c)a^{abc}_{ijk} &= \\ -\sum_P(-1)^P P(i/jk|a/bc)\left[\sum_d X_1(i,d,b,c)a^{ad}_{jk} + \sum_l X_2(j,k,l,a)a^{bc}_{il}\right]\end{aligned}$$

$$+\sum_P (-1)^P P(a/bc)\left[\frac{1}{2}\sum_{ef} X_3(b,c,e,f)a_{ijk}^{aef} + \sum_f Y_1(f,a)a_{ijk}^{fbc}\right]$$

$$+\sum_P (-1)^P P(i/jk)\left[\frac{1}{2}\sum_{mn} X_4(m,n,j,k)a_{imn}^{abc} + \sum_n Y_2(n,i)a_{njk}^{abc}\right]$$

$$-\sum_P (-1)^P P(i/jk|a/bc)\sum_{me} X_5(m,a,i,e)a_{jkm}^{bce} \tag{6.48}$$

where u_i^a, v_i^a, u_{ij}^{ab}, and v_{ij}^{ab} contain the terms of the corresponding QCISD equations, namely:

$$u_i^a = -\sum_{ld}\langle la||id\rangle a_l^d - \frac{1}{2}\sum_{lde}\langle la||de\rangle a_{il}^{de} - \frac{1}{2}\sum_{lmd}\langle lm||id\rangle a_{lm}^{ad} \tag{6.49}$$

$$\begin{aligned} u_{ij}^{ab} = &\sum_d(\langle ab||dj\rangle a_i^d - \langle ab||di\rangle a_j^d) + \sum_l(\langle la||ij\rangle a_l^b - \langle lb||ij\rangle a_l^a) \\ &+ \frac{1}{2}\sum_{de}\langle ab||de\rangle a_{ij}^{de} + \frac{1}{2}\sum_{lm}\langle lm||ij\rangle a_{lm}^{ab} \\ &- \sum_{ld}\sum_P (-1)^P P(ij|ab)\langle lb||jd\rangle a_{il}^{ad} \end{aligned} \tag{6.50}$$

$$v_i^a = \frac{1}{2}\sum_{lm}\sum_{de}\langle lm||de\rangle(a_i^d a_{lm}^{ea} + a_l^a a_{im}^{ed} + 2a_l^d a_{im}^{ae}) \tag{6.51}$$

$$\begin{aligned} v_{ij}^{ab} = &\frac{1}{4}\sum_{lm}\sum_{de}\langle lm||de\rangle[a_{ij}^{de}a_{lm}^{ab} - 2(a_{ij}^{ad}a_{lm}^{be} + a_{ij}^{be}a_{lm}^{ad} \\ &+ a_{il}^{ab}a_{jm}^{de} + a_{il}^{de}a_{jm}^{ab}) + 4(a_{il}^{ad}a_{jm}^{be} + a_{il}^{be}a_{jm}^{ad})] \end{aligned} \tag{6.52}$$

The intermediate arrays X_n and Y_n are defined in Table 6.1 and compared with the corresponding CCSDT arrays. It becomes clear from Table 6.1 that the working effort for setting up a CCSDT program is considerably higher than that for setting up a QCISDT program although both CC methods have an $O(M^8)$ dependence. [31]

In the case of an existing CCSDT program, it is rather simple to install the QCISDT projection equations and to check them for possible errors. However in a situation, in which a CCSDT program is not available, it is much easier to set up QCISDT on a computer than to set up CCSDT. In any case, it is advisable

to start the programming work from an existing QCISD or CCSD program rather than to program everything from scratch.

To test the accuracy of *QCISDT* energies, we have carried out QCISDT and CCSDT test calculations for 33 different electron systems, for which FCI results are available. [31,32] It turns out that in nearly all cases, QCISDT energies are slightly more negative than the corresponding CCSDT energies. This simply reflects the fact that certain coupling terms, which lead to positive energy contributions, are neglected in QCISDT as has been discussed in section 5.3. As far as the accuracy of QCISDT results is concerned, we determined for the 33 benchmark calculations a mean absolute deviation of 0.568 mhartree from FCI values in the case of QCISDT and 0.436 mhartree in the case of CCSDT, i.e. the two methods hardly differ from each other with slight advantages for the more complete CCSDT method. Apart from this, QCISDT results can be characterized in the following way: [31,32]

(1) *QCISDT* is superior to both QCISD and QCISD(T) with regard to the reproduction of FCI energies.

(2) Compared to QCISD and QCISD(T), QCISDT is more stable in calculations of systems with multireference character.

(3) QCISDT reproduces absolute and relative CCSDT energies for the examples we have studied within 1 mhartree and 0.1 kcal/mol, respectively. Its relative energies are actually slightly better than the corresponding CCSDT energies.

An important observation could be made with regard to the timings of the QCISDT calculations. While one QCISDT iteration step requires about the same time than the corresponding CCSDT iteration step, considerable time savings are obtained in the case of QCISDT calculations because of the faster convergence of this method. In general, time savings because of faster convergence become the larger the more multireference character an electron system possesses. This property of QCISDT becomes understandable if one considers the expansion of the method in terms of perturbation theory. Because of its simpler structure, QCISDT covers considerably less energy terms at higher order of perturbation theory than CCSDT. For example, QCISDT contains 59% of all 915 MP8 terms while CCSDT covers 87% of the MP8 terms. Although most of these terms represent rather small energy contributions, their large number leads to significant additions to the correlation energy at higher orders.

Since during the CC iterations higher and higher perturbation contributions are added to the correlation energy, the method that is more complete (covers more higher order terms) will need more iteration steps to reach convergence. It seems that the number of iteration steps reflects in a way the number of correlation effects covered by a given CC method. Therefore, one can expect that

QCISDT will converge faster than CCSDT in particular in those cases where due to multireference character correlation effects of higher order play an important role.

Of course, one could argue that fast convergence reflects the unphysical nature of an approximate CC method. However, as pointed out in chapter 5 it will hardly be possible to keep track of the multitude of correlation effects and their physical nature if one reaches higher orders. Therefore, one has to make a compromise between economy and performance of a given method, which leads to useful results in the case of QCISDT.

7. Conclusions and Outlook

The most important aspects of this review can be summarized in the following way:

(1) The two traditional methods of deriving MPn perturbation theory methods, namely the algebraic and the diagrammatic approach, can be combined in a new procedure that can handle the development of higher order MP methods. This has been tested for MP4 and MP5, for which final formulas are available in the literature. [6-9] Then, the new approach has been used to derive the first full MP6 method for routine calculations. [24-26] In addition, a dissection of the MP6 correlation energy has been carried out that leads to the development of two approximated MP6 methods with an $O(M^7)$ and an $O(M^8)$ dependence. The former method promises to be used as frequent as MP4 to calculate sixth order correlation effects.

(2) A new way of analyzing and comparing Coupled Cluster methods has been developed that provides an useful basis for predicting the performance of these methods. [22,23] The analysis is based on a graphical representation of energy contributions at various orders of perturbation theory. The compact form of the graphical representations makes a quick comparison of different CC methods possible. It has been used to derive the major differences between CC and QCI methods and to suggest improvements of these methods. [30]

(3) Motivated by the unsuccessful attempts to derive a size-extensive QCISDT method [35], a procedure has been worked out to systematically extend CI methods to size-extensive methods. This investigation revealed that the original QCI concept leads just to one unique QCI method, namely QCISD [35], while all other methods either coincide with the corresponding CC methods or represent ECI

methods with other than just quadratic cluster terms. [30] Based on this result, a new QCI concept was developed that leads to the first size-extensive QCISDT method, which was programmed and tested. [30-32] Size-extensive QCISDT leads to correlation energies that differ on the average from CCSDT correlation energies by just 0.07 mhartree. QCISDT possesses significant advantages with regard to both its implementation on a computer and to its cost requirements (faster convergence in the CC iterations). [31,32]

If one speaks of perturbation theory methods as the ab initio methods of the eighties, one can definitely speak of the Coupled Cluster methods as the methods of the nineties. It is easy to foresee that more and more CC calculations will be carried out to solve pending chemical problems. Already today, CCSD(T) is considered as the method to be used in cases where high accuracy is needed. Certainly, with the next generation of computers, CCSDT will replace CCSD(T). Then, QCISDT will offer an attractive alternative to CCSDT.

MP6 in its MP6(M7) approximation will offer new possibilities of assessing higher order correlation effects at the cost of essentially a MP4 calculation. Systematic application of MP6(M7) will show to which extend this method will complement the frequently used MP2 and MP4 method.

Another important aspect in connection with the use of MPn methods is the analysis of the convergence of the MPn series, which we have not discussed in this review, although important work has been done on this topic recently. [27-29] The MPn series shows for different electronic systems different convergence behaviour. Two cases can be considered, namely one with a monotonic convergence of MPn correlation energies to the FCI value and one with erratic convergence behaviour. Based on a dissection of MP5 and MP6 correlation energies, it is possible to explain the differences in the convergence behaviour and to predict which electronic systems possess monotonous or oscillatory convergence behaviour in the MPn series. [27-29] Utilizing this knowledge, it is possible to predict rather precise values of FCI correlation energies once the MP6 correlation energy is known. [28,29]

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