

## Error analysis and improvements of coupled-cluster theory

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**Summary.** The error in the energy of the traditional coupled-cluster (TCC) approach and of several variants is analyzed in terms of the error  $\delta$  of the cluster operator  $S$ . A key feature of this analysis is that TCC can be based on an energy functional (asymmetric in  $S$  and  $S^\dagger$ ) that is made stationary with respect to variation of  $S^\dagger$ . The error of TCC scales with the particle number  $n$ , but it is not quadratic in  $\delta$ . An improved coupled-cluster method (ICC) is presented that is the next step in a hierarchy from TCC to an exact variational theory. An alternative hierarchy is possible that leads to the extended coupled-cluster (ECC) method of Arponen. Variational (VCC) and unitary (UCC) coupled cluster theories and their stationary conditions and errors are analyzed along similar lines and practicable VCC or UCC approaches are presented. An infinite summation of certain terms in the VCC expectation value is shown to lead to a coupled-pair functional of the type proposed by Ahlrichs. The various CC schemes discussed here are compared on the CC-D, CC-SD and CC-SDT levels and beyond this. Special aspects referring to properties are also discussed.

**Key words:** Coupled-cluster (CC) theory – Variational CC-Unitary CC – Coupled-pair functional (CPF) – Quadratic CI (QCI)

### 1. Introduction

Coupled-cluster (CC) theory is an established method for the calculation of correlation effects in nuclear [1] atomic [2, 3] and molecular theory [2, 4–8]. For recent reviews see [9]; as to the closely related coupled electron pair approximation (CEPA) methods see [10]. CC theory is based on the concept that the wave operator which transforms an independent-particle reference wave function  $\Phi$  to the exact wave function  $\Psi$  must be multiplicatively separable [10c, 11] and hence is conveniently written in the exponential form [1, 2, 12]

$$\Psi = \exp(S)\Phi, \quad \langle \Phi | \Phi \rangle = 1 \quad (1.1)$$

with  $S$  an additively separable operator. This ansatz guarantees that the wave function of a system of non-interacting subsystems is the product of the wave functions of these subsystems and that the energy is the sum of the subsystem energies. In a diagrammatic representation of the wave function or the energy no

unlinked diagrams (in the sense of Goldstone [13]) arise. Additively separable quantities like the energy consist of connected diagrams only. It is tacitly assumed that the reference wave function  $\Phi$  is separable. A closed-shell Slater determinant is for example separable into electron pairs. In this paper we shall always make this choice.

Much less attention has been paid to the way an approximate solution of the Schrödinger equation in the form (1.1) is constructed than to the form of the wave function itself. Minimization of the energy expectation value for the ansatz (1.1) leads to equations that are too complicated. Instead, traditional coupled-cluster theory (henceforth abbreviated as TCC) is characterized by an approach based on the method of moments (or of projected Schrödinger equations). One chooses a set of excitation operators  $X_k$ , into which one expands  $S$

$$S = \sum_k c_k X_k, \quad \langle \Phi | X_k | \Phi \rangle = 0 \quad (1.2)$$

and one then forms the scalar products of the Schrödinger equation  $H\Psi = E\Psi$  with  $\Psi$  in the form (1.1) from the left by  $\langle \Phi |$  and the  $\langle \Phi X_k^\dagger |$ . From the first scalar product one gets the energy expression

$$E = \langle \Phi | H e^S | \Phi \rangle \quad (1.3a)$$

while the other scalar products are used as conditions for determining the coefficients  $c_k$

$$\langle \Phi | X_k^\dagger (H - E) e^S | \Phi \rangle = 0 \quad (1.3b)$$

Alternatively one first multiplies the Schrödinger equation from the left by  $e^{-S}$  before one projects. Instead of (1.3) one then gets

$$E = \langle \Phi | e^{-S} H e^S | \Phi \rangle \quad (1.4a)$$

$$\langle \Phi | X_k^\dagger e^{-S} H e^S | \Phi \rangle = 0 \quad (1.4b)$$

These expressions make the connectedness obvious, but they are essentially equivalent to (1.3). In fact (1.3a) and (1.4a) are identical because the action of  $S$  on  $\Phi$  to the left vanishes. In (1.4b) we note that the action of  $e^{-S}$  on the  $\Phi$  at the left can only consist in reducing the excitation rank of  $X_k^\dagger$ . So the set of operators  $X_k^\dagger$  truncated at some particle rank together with the identity have the same effect to the left as the set  $X_k^\dagger e^{-S}$ .

There are as many (non-linear) equations (1.3) or (1.4) as there are unknowns  $c_k$  and in cases of practical interest one usually gets a consistent set of solutions. The conditions under which solutions of (1.3b) or (1.4b) exist have, to the author's knowledge, never been studied. For the linearized LCC or CEPA-0 system (see Sect. 3) it is necessary and sufficient that the  $X_k | \Phi \rangle$  are linearly independent.

If the ansatz (1.1, 2) is exact, i.e. if there is an  $S$  of the form (1.2) such that for a given  $\Phi$

$$(H - E)e^S \Phi = 0 \quad (1.5)$$

then (1.3) or (1.4) are necessary conditions for (1.5) to hold. However (1.5) will almost never hold exactly. Generally we will study a Hamiltonian expanded in a finite one-electron basis and the eigenfunctions of this algebraic Hamiltonian are obtained by the 'full-CI' approach. The full-CI wave functions will be exactly of the form (1.1) only if the operator basis is complete in the chosen one-electron space, i.e. if it contains all excitations within this space up to  $n$ -particle excitations for an  $n$ -particle system.

The motivation for the CC ansatz is in fact to get decent approximations to full CI even in a truncated operator basis  $\{X_k\}$ , e.g. for only two-particle excitation operators. With a truncated ansatz for  $S$  (1.5) cannot be satisfied exactly and necessary conditions for an unrealistic assumption to hold may be rather meaningless.

One can, of course, justify the method based on (1.3) or (1.4) for a truncated ansatz by various arguments. One of them is that a truncated ansatz may be exact in special cases. For example, it is sufficient to limit  $S$  to one- and two-particle excitation operators for a supersystem of non-interacting pairs. One can argue further that Eq. (1.3) or (1.4) implies a nonunitary similarity transformation of the exact Hamiltonian to a model Hamiltonian [14] (for the model space consisting only of  $\Phi$ ) and that many-body perturbation theory can be derived from (1.3) or (1.4) [14]. The argument that a method based on a truncated  $S_k$  is a member of a hierarchy of methods that become exact in the limit  $k \rightarrow n$  is less convincing, since this also applies to truncated CI. On the other hand there is sufficient numerical evidence [5–8] that the hierarchy of truncated CC converges faster to full CI than does the corresponding truncated CI hierarchy.

Here we shall study the traditional CC method based on (1.3) or (1.4) in terms of an error analysis (concentrating on the relation between the errors of the wave function and the energy) and compare this method with possible alternatives.

A standard argument against traditional CC theory has been that it is not variational, i.e. it does not furnish an upper bound to the exact energy. This is correct, but it is usually refuted by the argument that separability (extensivity) is more important than an upper-bound property. To get an upper bound and separability simultaneously for a truncated ansatz that is not exact appears to be at least very hard, if not impossible.

Of course, the importance of the variation principle has often been exaggerated. However, one should not forget that the variation principle has two implications, one is the upper-bound property, the other is the fact the error of the energy is quadratic in the error of the wave function. This latter property is the more important one and it is worthwhile investigating how the error of a TCC calculation depends on the error of the wave function and whether it is possible to achieve an error in the energy that is quadratic in the error of the wave function. Since one of the main aims of CC theory is to guarantee separability and hence extensivity, one should also ask how the error of the energy scales with the number of particles. It is desirable that it scales linearly. This is guaranteed if the approximate energy expression is separable i.e. consists of connected diagrams only.

The present purely formal analysis is complementary to various numerical studies [5, 8, 15, 16] in which several variants of CC were compared with full CI [17] results, and also to previous analyses in terms of perturbation theory [5, 7]. Since it is uncertain whether perturbation theory converges at all, arguments based on perturbation theory may not be too relevant. One of the main merits of CC theory is obviously that it is non-perturbative. Therefore it is recommended to analyze it as well in a non-perturbative way, at least to the extent to which this is possible. An interesting alternative to perturbation theory, much more in the spirit of the coupled-cluster approach, is a Newton–Raphson-type iterative procedure which, starting from a reference function  $\Phi$ , eventually leads to the exact wave function  $\Psi$  [18].

What we call traditional CC (TCC) has also been referred to as 'standard CC' [5] (however, we want to use the acronym SCC for simplified CC) or 'normal CC' (this name may, however, create undesired associations to the 'normal order CC theory' for open-shell states [3a]); the author's first suggestion CCC (for conventional CC) has not been accepted by the audience of the coupled-cluster workshop.

## 2. Error of the wave function

Before we study the error of the energy we must find out how the error of the wave function scales with the number of particles. Let us first take a wave function that is multiplicatively separable (i.e. for a supersystem of non-interacting subsystems). Let  $\Psi$  be the exact and  $\tilde{\Psi}$  be the approximate wave function and let  $s$  and  $t$  denote subsets of the particles.

$$\Psi = \psi_1(s)\psi_2(t) \quad (2.1a)$$

$$\tilde{\Psi} = \tilde{\psi}_1(s)\tilde{\psi}_2(t) \quad (2.1b)$$

A measure  $\Delta$  of the error of an approximate wave function  $\tilde{\Psi}$  is its distance in Hilbert space to the exact wave function  $\Psi$ . For (2.1), taking all individual wave functions  $\psi_1$ ,  $\psi_2$ ,  $\tilde{\psi}_1$ ,  $\tilde{\psi}_2$ ,  $\Psi$ , and  $\tilde{\Psi}$  real and normalized to unity we get

$$\Delta^2 = \|\Psi - \tilde{\Psi}\|^2 = 2\{1 - \langle\Psi|\tilde{\Psi}\rangle\} = \Delta_1^2 + \Delta_2^2 - \frac{\Delta_1^2\Delta_2^2}{2} \quad (2.2)$$

The square of the error is hence dominated by a term linear in the number of subsystems:  $\Delta$  scales essentially with  $\sqrt{n}$ . A measure of the error that scales exactly with the number of particles in the case of separability for a multiplicatively separable approximative real wave function is the logarithm of the real part of the overlap integral. In our example

$$\ln\langle\Psi|\tilde{\Psi}\rangle = \ln\langle\psi_1|\tilde{\psi}_1\rangle + \ln\langle\psi_2|\tilde{\psi}_2\rangle \quad (2.3)$$

In the limit of  $\Delta \rightarrow 0$  the error measure (2.3) is equal to  $\frac{1}{2}\Delta^2$ .

If the approximate wave function is not strictly separable, e.g. is of CI type, one still gets that  $\Delta^2$  is dominated by a term linear in  $n$ , but of course a relation of the type (2.3) will no longer hold. Take for example (for  $S_1$  and  $S_2$  acting on different subsystems)

$$\Psi = (1 + S_1 + S_2)\Phi; \quad \tilde{\Psi} = (1 + \tilde{S}_1 + \tilde{S}_2)\Phi \quad (2.4)$$

$$\|\Psi - \tilde{\Psi}\|^2 = \|(S_1 - \tilde{S}_1 + S_2 - \tilde{S}_2)\Phi\|^2 = \|(S_1 - \tilde{S}_1)\Phi\|^2 + \|(S_2 - \tilde{S}_2)\Phi\|^2 \quad (2.5)$$

In the following sections it is convenient not to require that  $\tilde{\Psi}$  is normalized to unity, but to assume that  $\tilde{\Psi}$  is normalized such that the error of  $\tilde{\Psi}$  is orthogonal to  $\Psi$

$$\delta = \tilde{\Psi} - \Psi; \quad \langle\delta|\Psi\rangle = 0 \quad (2.6)$$

The relation to the  $\Delta^2$  defined by (2.2) for normalized  $\tilde{\Psi}$  is then

$$\Delta^2 = \|\delta\|^2 + O(\|\delta\|^4) \quad (2.7)$$

Hence  $\|\delta\|^2$  is a measure of the error of the wave function and is dominated by a term linear in the particle number.

### 3. Asymmetric expectation values for separable and non-separable wave functions

We shall have to consider energy expressions of the type

$$\tilde{E} = \frac{\langle \Psi_1 | H | \Psi_2 \rangle}{\langle \Psi_1 | \Psi_2 \rangle} \tag{3.1}$$

where  $\Psi_1$  and  $\Psi_2$  are two different approximations to the exact wave function  $\Psi$ . Let us define the respective errors as in (2.6)

$$\delta_k = \Psi_k - \Psi; \quad \langle \delta_k | \Psi \rangle = 0, \quad \langle \Psi | \Psi \rangle = 1 \tag{3.2}$$

Noting that  $H\Psi = E\Psi$  one sees easily that

$$\tilde{E} - E = \frac{\langle \delta_1 | H - E | \delta_2 \rangle}{\langle \Psi_1 | \Psi_2 \rangle} = O(\delta_1) \cdot O(\delta_2) \tag{3.3}$$

i.e. that the error of the asymmetric expectation value (3.1) is bilinear in the relative errors of  $\Psi_1$  and of  $\Psi_2$ . In the case that  $\Psi_1 = \Psi_2$  and that  $E$  is the ground state energy of  $H$ , the error (3.3) is positive, i.e.  $\tilde{E}$  is an upper bound to  $E$ . When writing  $O(\delta)$  or  $O(S^n)$  we mean orders of the norm  $\|\delta\|$  of  $\delta$  or  $O(\|S\|^n)$  respectively.

Since expectation value energy expressions (3.1) have an error bilinear in the relative errors of the wave functions, and the relative error of the wave function is dominated by a term  $\sim \sqrt{n}$ , we conclude that the error (3.3) is dominated by a term  $O(n)$ . This is, of course, not unexpected. What one should like is that the error for a separable system is strictly linear in  $n$ , i.e. that there are no terms  $O(n^2)$  etc. This is achieved if one takes care that both  $\Psi_1$  and  $\Psi_2$  are separable. Take again a supersystem of two non-interacting subsystems

$$E = \frac{\langle \psi_{1a} \psi_{1b} | H_a + H_b | \psi_{2a} \psi_{2b} \rangle}{\langle \psi_{1a} \psi_{1b} | \psi_{2a} \psi_{2b} \rangle} = \frac{\langle \psi_{1a} | H_a | \psi_{2a} \rangle}{\langle \psi_{1a} | \psi_{2a} \rangle} + \frac{\langle \psi_{1b} | H_b | \psi_{2b} \rangle}{\langle \psi_{1b} | \psi_{2b} \rangle} \tag{3.4a}$$

$$\tilde{E} - E = \frac{\langle \delta_{1a} | H_a - E_a | \delta_{2a} \rangle}{\langle \psi_{1a} | \psi_{2a} \rangle} + \frac{\langle \delta_{1b} | H_b - E_b | \delta_{2b} \rangle}{\langle \psi_{1b} | \psi_{2b} \rangle} \tag{3.4b}$$

The expectation value of a coupled-cluster wave function is

$$E = \frac{\langle \Phi | e^{S^\dagger} H e^S | \Phi \rangle}{\langle \Phi | e^{S^\dagger} e^S | \Phi \rangle} \tag{3.5}$$

For a separable system we have  $S = S_a + S_b$  and we get

$$\begin{aligned} E &= \frac{\langle \Phi | e^{S_a^\dagger + S_b^\dagger} (H_a + H_b) e^{S_a + S_b} | \Phi \rangle}{\langle \Phi | e^{S_a^\dagger + S_b^\dagger} e^{S_a + S_b} | \Phi \rangle} \\ &= \frac{\langle \Phi | e^{S_a^\dagger} H_a e^{S_a} | \Phi \rangle}{\langle \Phi | e^{S_a^\dagger} e^{S_a} | \Phi \rangle} + \frac{\langle \Phi | e^{S_b^\dagger} H_b e^{S_b} | \Phi \rangle}{\langle \Phi | e^{S_b^\dagger} e^{S_b} | \Phi \rangle} \end{aligned} \tag{3.6}$$

and a similar expression for the approximative energy  $\tilde{E}$  in terms of the approximate  $\tilde{S}_a$  and  $\tilde{S}_b$ .

We shall henceforth use the symbol  $\delta$  for the error of the wave operator  $S$

$$\delta = \tilde{S} - S \tag{3.7}$$

The error of the coupled-cluster expectation value (3.6) is of  $O(\delta^2)$  and for a separable system it scales strictly linearly with the particle number  $n$

$$\tilde{E} - E = O(\delta^2) \tag{3.8}$$

To study the error of the energy of a (truncated) CI calculation we write the CI wave function  $\Psi$  in the form

$$\Psi = (1 + U)\Phi; \quad U = \sum_k d_k X_k \quad (3.9)$$

If  $S$  in the sense of (1.1, 2) and  $U$  in the sense of (3.9) are expanded in the same basis  $\{X_k\}$ , the energy expectation values (3.5) and

$$E = \frac{\langle \Phi | (1 + U^\dagger) H (1 + U) | \Phi \rangle}{\langle \Phi | (1 + U^\dagger) (1 + U) | \Phi \rangle} \quad (3.10)$$

will, of course, differ and so will the  $c_k$  from the  $d_k$ ; however the error of the energy in both cases is quadratic in the error of  $S$  or  $U$  respectively. We shall use the symbol  $\theta$  for the error of  $U$ . Hence for (3.10) we get

$$E - \tilde{E} = O(\theta^2) \quad (3.11)$$

The main difference between the errors  $\delta$  (of  $S$ ) and  $\theta$  (of  $U$ ) is that  $\delta$  is the error of the actual  $S$  with respect to the exact  $S$ , both of which are connected, while the actual  $U$  and the exact  $U$ , which differ by  $\theta$ , contain disconnected terms as well. If we evaluate the expectation value (3.10) with  $U$  replaced by the  $S$  which minimizes (3.5), this  $U = S$  will have a slightly larger error  $\theta$  than the optimum  $U$  (in the same operator basis), but (3.11) will still hold. Now the error of  $S = U$  as compared with the exact  $U = \exp(S) - 1$  consists of two parts, namely  $\delta$ , the error of  $S$ , and  $\frac{1}{2}S^2 + \dots$ , the error of the exact  $1 + S$  with respect to the exact  $\exp(S)$ . In this sense the CI error can be rewritten as

$$E - \tilde{E} = [O(\delta) + O(S^2)]^2 \quad (3.12)$$

It should be noted that since this error estimate is not based on the optimum choice for  $U$ , it may be too pessimistic. If the operator basis contains up to quadruple excitations one will not identify  $U$  with  $S_1 + S_2 + S_3 + S_4$  (subscripts indicate the excitation rank), but rather include  $S_1^2, S_2^2, S_1 S_2, S_1 S_3$  of which  $S_2^2$  is the most important. Then (3.12) holds with  $S^2$  replaced by  $S^3$ .

Let us now look at the energy expression (1.3a) of TCC theory. This is an asymmetric expectation value of the type (3.1) (note that  $\langle \Phi | e^S | \Phi \rangle = 1$ ) and the error is of the form (3.3). Obviously the error of  $\Phi$  is dominated by  $S\Phi$  and that of  $e^S\Phi$  by  $\delta\Phi$ , so that the error is

$$\tilde{E} - E = O(S)O(\delta) \quad (3.13)$$

This is a very poor error estimate, since it is only linear in the error of the wave function (unlike the CC expectation value, where it is quadratic). The fact that the error scales with the number of particles is only a minor consolation. In fact, if the error estimate (3.13) were the last word for CC theory, this would not even be competitive with CI. We shall see that we get a better error estimate if we also account for the condition (1.3b) used for the construction of  $S$ . More precisely, in Sect. 4 we shall reformulate (1.3b) as a stationarity condition and we shall consider alternative stationarity conditions as well; the error is sensitive to the kind of stationarity condition that one chooses.

The CI energy (3.10) can be rewritten as

$$E = \langle \Phi | H | \Phi \rangle + 2\text{Re} \langle \Phi | HU | \Phi \rangle + \langle \Phi | U^\dagger (H - E) U | \Phi \rangle \quad (3.14)$$

and this may, for example, be evaluated iteratively. By the simple change from  $E$  to  $E_0$  on the right hand side, and writing  $S$  for  $U$

$$\tilde{E} = \langle \Phi | H | \Phi \rangle + 2Re \langle \Phi | HS | \Phi \rangle + \langle \Phi | S^\dagger (H - E_0) S | \Phi \rangle; \quad E_0 = \langle \Phi | H | \Phi \rangle \quad (3.15)$$

we get an energy that is no longer an upper bound to the lowest eigenvalue of the Hamiltonian, but which is separable (at least for  $S = S_2$ ), i.e. which scales linearly with the number of particles. This is seen if one rewrites the CEPA-0 functional (3.15) in Lie-algebraic form as

$$\tilde{E} = \langle \Phi | H + [H, S - S^\dagger] + \frac{1}{2} [[H, S - S^\dagger], S - S^\dagger] | \Phi \rangle; \quad S = S_2 \quad (3.16)$$

Hence the error is also separable and it scales with  $n$ . We get

$$\tilde{E} - E = O(\delta^2) + O(S^3) \quad (3.17)$$

The second term in (3.17) represents the difference between (3.15) and a coupled-cluster expectation value, while the first term in (3.17) is the error of the expectation value due to the error of  $S$ .

Stationarity of (3.15) with respect to variation of  $S$  and  $S^\dagger$  leads to an approximation that has been derived in many different ways and has been given various names. It is the linear version of coupled-cluster theory, hence LCC [5] formerly called LCPMET [2] or CPA<sub>0</sub> [20]. It is the first non-trivial step in unitary coupled-cluster theory [10c], and can be defined as the optimum lowest order perturbation theory [21] or as perturbation theory with partial summation of certain diagrams to infinite order: DMBPT( $\infty$ ) [22]. A rather popular name is CEPA-0 [10d, 15] to indicate that it is the simplest of all CEPA variants [10]. The switch from (3.14) to (3.15) chosen here as derivation of CEPA-0 has some similarities with the change from Brillouin–Wigner (BW) to Rayleigh–Schrödinger (RS) perturbation theory. Note that RS scales with  $n$ , while BW does not, and that in some special cases BW may provide an upper bound, which RS never does.

#### 4. The method of projected Schrödinger equations and the related stationary conditions

To appreciate the meaning of the method of projected Schrödinger equations, on which traditional CC theory is based, it is useful to derive the CI method in an analogous way where this derivation turns out equivalent to that from the variation principle. Let us start from the Schrödinger equation in the form (see the comments prior to Eq. (3.10))

$$H(1 + U)\Phi = E(1 + U)\Phi; \quad U = \sum_k d_k X_k \quad (4.1)$$

(i.e. for a truncated  $U$  – again from an incorrect assumption) from which by analogy with (1.3) one gets the energy expression

$$E = \langle \Phi | H(1 + U) | \Phi \rangle \quad (4.2)$$

and the conditions

$$\langle \Phi | X_k^\dagger (H - E)(1 + U) | \Phi \rangle = 0 \quad (4.3)$$

The *a posteriori* justification of this procedure is now obvious. One multiplies (4.3) by  $d_k^*$  and sums over  $k$  with the result

$$\langle \Phi | U^\dagger (H - E)(1 + U) | \Phi \rangle = 0 \quad (4.4)$$

Adding this to (4.2) gives (3.14) and hence (3.10), i.e. the energy obtained by the method of projected Schrödinger equations is an expectation value and the 'projected Schrödinger equations' (4.3) are conditions for  $\tilde{E}$  as given by (3.10) to be stationary with respect to variation of  $U^\dagger$ .

What do we get by the same argument from (1.3b)? Multiplication of  $X_k^\dagger$  in (1.3b) by the amplitudes  $c_k^*$  (1.2) and summation over  $k$  yields the counterpart of (4.4)

$$\langle \Phi | S^\dagger (H - E) e^S | \Phi \rangle = 0 \quad (4.5)$$

and analogously to (3.10) we get

$$\tilde{E} = \frac{\langle \Phi | (1 + S^\dagger) H e^S | \Phi \rangle}{\langle \Phi | (1 + S^\dagger) e^S | \Phi \rangle} \quad (4.6)$$

This is precisely the energy expression that we make stationary in traditional CC theory, namely with respect to variation of  $S^\dagger$ .

Equation (4.6) is a typical asymmetric expectation value – on the left side it looks like CI, while on the right side like coupled-cluster. The error estimate (3.3) involves the error on the left side and that on the right side. The latter is dominated by  $\delta$ , i.e. the error of  $S$ , just as for a coupled-cluster expectation value (3.5). The former consists of two parts, the error  $\delta$  of  $S$  and the truncation error  $O(S^2)$ . We hence obtain

$$\tilde{E} - E = [O(\delta) + O(S^2)]O(\delta) \quad (4.7)$$

The same reservation as with respect to the CI error (3.12) must also be made here. In fact (4.6) remains valid if we replace  $S^\dagger$  by  $U^\dagger$ , i.e. the operator for CI in the same basis. This means the error estimate (4.7) may again be too pessimistic. A closer estimate would be

$$\tilde{E} - E = O(\theta)O(\delta) \quad (4.8)$$

i.e. the error of the energy is bilinear in the respective errors of a CC and a CI wave function in the same operator basis.

To make it clear that the  $S^\dagger$  in (4.5) and (4.6) should not necessarily be identified with the hermitean conjugate of  $S$  on the right hand side, but rather with the operator  $U^\dagger$  of the CI approach, it is better to replace  $S^\dagger$  in (4.5) and (4.6) by  $U^\dagger$ . While stationarity with respect to variation of  $U^\dagger$  leads to conditions on  $S$ , stationarity with respect to variation of  $S$ , leads to conditions on  $U^\dagger$ , to the extent that  $(1 + U^\dagger)\Phi$  will essentially become a CI wave function. We have not considered this variation, since  $U^\dagger$  is not needed for the evaluation of the energy from (1.3a).

We can now compare the energy errors in the expectation value for CC (3.8), CI (3.11) or (3.12), and traditional CC theory (4.7) or (4.8). TCC appears to lie between expectation value CC and CI. The following observation is noteworthy. If  $\delta = 0$ , i.e. if  $e^S\Phi$  is exact (e.g. for the case of a supersystem of non-interacting two-electron systems with  $S$  including  $S_1$  and truncated at the two-electron excitation rank  $S_2$ ) then both (3.8) and (4.8) vanish, while (3.11) or (3.12) do not. For this special case traditional CC is as good as expectation value CC.

The question arises how the error (4.8) scales with the number of particles for a separable system. From the asymmetric expectation value (4.6) it is not obvious that the error should scale strictly with the particle number. Fortunately an alternative formulation of (4.6) is possible. Noting that the conditions (1.4) are equivalent to (1.3), we get from (1.4b) the counterpart (4.9) of (4.5). Writing  $U^\dagger$  instead of  $S^\dagger$  (see the comments between Eqs. (4.7) and (4.8) and after (4.8))

$$\langle \Phi | U^\dagger e^{-S} H e^S | \Phi \rangle = 0 \quad (4.9)$$

and instead of the energy expression (4.6) which is stationary with respect to variation of  $S^\dagger$  we now have

$$\tilde{E} = \langle \Phi | (1 + U^\dagger) e^{-S} H e^S | \Phi \rangle \quad (4.10)$$

which must be equivalent to (4.6). This is also an asymmetric expectation value with

$$\langle \Psi_1 | = \langle \Phi | (1 + U^\dagger) e^{-S}; \quad | \Psi_2 \rangle = e^S | \Phi \rangle \quad (4.11)$$

and the error estimate (4.8) is reproduced. However, (4.10) contains only connected diagrams and the extensivity of this energy expression and hence also of its error is guaranteed. This is in agreement with what is usually claimed for TCC. The functional (4.10) has previously been studied by Arponen [19a], who has derived TCC theory from the condition that this functional should be stationary.

The error of the TCC energy is 'almost quadratic' in the error  $\delta$  of the wave operator, if the CC and CI wave functions don't differ much, i.e. for  $\|S\|$  sufficiently small such that  $\exp(S) = 1 + U \sim 1 + S$ , e.g. for the situation of typical dynamic correlation. Deviations from a  $\delta^2$  dependence of  $\tilde{E} - E$  towards a linear  $\delta$  dependence become stronger the larger  $\|S\|$  is, especially in cases of near degeneracy.

## 5. Improved coupled-cluster theory

In situations where the error  $\tilde{E} - E$  of TCC is closer to linear than quadratic in  $\delta$  (see the end of the last section), TCC is not as accurate for a given effort as one might wish. Possible improvements are rather obvious from the analysis given so far. Let us replace Eqs. (1.3b) and (4.6) characteristic of traditional coupled-cluster theory by

$$\langle \Phi | X_k^\dagger (1 + S^\dagger) (H - E) e^S | \Phi \rangle = 0 \quad (5.1a)$$

$$\tilde{E} = \frac{\langle \Phi | (1 + S^\dagger + \frac{1}{2} S^{\dagger 2}) H e^S | \Phi \rangle}{\langle \Phi | (1 + S^\dagger + \frac{1}{2} S^{\dagger 2}) e^S | \Phi \rangle} \quad (5.1b)$$

i.e. make (5.1b) rather than (4.6) stationary with respect to variation of  $S^\dagger$ .

One might use a different letter for  $S^\dagger$ , say  $\Sigma^\dagger$ , to indicate that  $\Sigma^\dagger$  is not necessarily equal to the hermitean conjugate of  $S$ . However we shall here make the restriction  $S = \Sigma$ . This makes it clear that in (5.1b) we use a truncated expansion of  $\exp S^\dagger$  on the left hand side. This also tells us how to choose the  $S^\dagger$  that (unlike in TCC theory) is needed to evaluate the energy. Otherwise one needs to formulate independent stationarity conditions for  $\Sigma^\dagger$  based on the variation of  $S$ , which would make things rather complicated.

The error estimate (4.7) is now replaced by

$$\tilde{E} - E = O(\delta) \cdot [O(\delta) + O(S^3)] \quad (5.2)$$

Inserting the stationarity condition (5.1a) into the energy expression (5.1b) leads to a simplified stationary energy expansion as the counterpart of (1.3a)

$$\tilde{E} = \frac{\langle \Phi | (1 + \frac{1}{2}S^\dagger) H e^S | \Phi \rangle}{\langle \Phi | (1 + \frac{1}{2}S^\dagger) e^S | \Phi \rangle} \quad (5.3)$$

Generalizations with  $S^\dagger$  truncated at higher powers of  $S^\dagger$  are straightforward and obvious: correspondingly, the power of  $S^\dagger$  in (5.3) and of  $S$  in (5.2) is increased. In this way we can generate a hierarchy of approximations that start with traditional CC and reach variational CC in the limit of no truncation on the left side. We call the scheme characterized by (5.1–3) ICC(2) to indicate that the highest power of  $S^\dagger$  on the left side is  $S^{\dagger 2}$ ; in this notation TCC is identical with ICC(1). The next member in the ICC hierarchy is, of course, ICC(3), for which the error formula is

$$\tilde{E} - E = O(\delta) \cdot [O(\delta) + O(S^4)] \quad (5.4)$$

These ‘improved’ coupled-cluster ansatz share some important aspects with the traditional one:

- (a) if  $e^S \Phi$  is exact, the error vanishes,
- (b) although  $e^S \Phi$  on the right hand side is formally written untruncated, the expansion in powers of  $S$  will end at a finite order as long as the left side is truncated,
- (c) the energy expressions to be made stationary are asymmetric and one is concerned about stationarity only with respect to  $S^\dagger$ , not also  $S$ , as one would in a genuinely variational approach.

Unlike for TCC, we have now no guarantee that the error scales with  $n$ . In the case of TCC the separability of the energy (and hence connectedness) was established via the equivalence of (4.6) with (4.10). The generalization of (4.10) in the spirit of ICC would be

$$\langle \Phi | X_k^\dagger (1 + S^\dagger) e^{-S} H e^S | \Phi \rangle = 0 \quad (5.5a)$$

$$\tilde{E} = \langle \Phi | (1 + S^\dagger + \frac{1}{2}S^{\dagger 2}) e^{-S} H e^S | \Phi \rangle \quad (5.5b)$$

However (5.5) is not equivalent to (5.1) since the set of bras  $\langle \Phi | X_k^\dagger (1 + S^\dagger)$  is no longer equivalent to the set  $\langle \Phi | X_k^\dagger (1 + S^\dagger) e^{-S}$ . One sees especially that the generalization of the energy expressions (5.5b) to infinite order

$$\tilde{E} = \langle \Phi | e^{S^\dagger} e^{-S} H e^S | \Phi \rangle = \langle \Phi | e^{S^\dagger} e^{-S} H e^S e^{-S^\dagger} | \Phi \rangle \quad (5.6)$$

is not an expectation value, at variance with the generalization of (5.1b) to infinite order.

Nevertheless, we may regard (5.5) as a member of another hierarchy of approximations, that eventually lead to the system

$$\langle \Phi | X_k^\dagger e^{S^\dagger} e^{-S} H e^S | \Phi \rangle = 0 \quad (5.7a)$$

$$\tilde{E} = \langle \Phi | e^{S^\dagger} e^{-S} H e^S | \Phi \rangle \quad (5.7b)$$

Equations (5.7) are just the defining equations of the ‘extended coupled cluster’ method (ECC) of Arponen et al. [19] and (5.7a) is the condition for stationarity with respect to variation of  $S^\dagger$ . The corresponding condition for stationarity with respect to variation of  $S$  (that also should be satisfied) is

$$\langle \Phi | e^{S^\dagger} e^{-S} [H, X_k] e^S | \Phi \rangle = 0 \quad (5.7c)$$

Of course (5.5) can be regarded as an approximation to (5.7) and be called ECC(2), with ECC(1) identical with TCC.

One merit of the ECC method characterized by (5.7) is that for fixed excitation rank the expansion is finite in powers of  $S$  and  $\Sigma^\dagger$ ; however this also results in greater complexity with respect to other CC variants, e.g. there is no simple relation between  $S$  and  $\Sigma^\dagger$ . The error of the ECC energy is likely to be bilinear in the errors of  $S$  and  $\Sigma^\dagger$ . Both  $S$  and  $\Sigma^\dagger$  are connected and the error of  $\Sigma^\dagger$  should be of the same order than that of  $S$ . So although the  $\tilde{E}$  given by (5.7b) is not an expectation value, its error is close to quadratic in the error of  $S$ . For the truncated ECC( $k$ ) methods, similar error estimates as for the corresponding ICC( $k$ ) scheme should hold.

We shall see that it pays to go beyond TCC only if one approaches a high-performance level. However, then the variational approaches to be discussed in Sect. 7 turn out to be preferable to both ICC or ECC.

The hierarchies of 'improved' and 'extended' coupled-cluster methods presented so far in this section are based on asymmetric expectation values. It is interesting to compare these with a hierarchy of 'improved CI' methods based on symmetric expectation values. The first member is, of course, CI or CI(1) (with a truncated  $S$ ) for which we have derived the error estimates (3.11) or (3.12). The next member would be based on the expectation value

$$\tilde{E} = \frac{\langle \Phi | (1 + S^\dagger + \frac{1}{2} S^{\dagger 2}) H (1 + S + \frac{1}{2} S^2) | \Phi \rangle}{\langle \Phi | (1 + S^\dagger + \frac{1}{2} S^{\dagger 2}) (1 + S + \frac{1}{2} S^2) | \Phi \rangle} \quad (5.8)$$

which might be called CI(2) or 'quadratic CI' (if the latter name had not already been used in a different and somewhat misleading context [23]). The members of this symmetric hierarchy are all variational, i.e. provide upper bounds, but they imply non-separable wave functions and non-extensive energies, although with increasing order the separability defects should become smaller. The error of (5.8) is analogous to (5.2)

$$\tilde{E} - E = [O(\delta) + O(S^3)]^2 = O(\delta^2) + O(\delta)O(S^3) + O(S^6) \quad (5.9)$$

It differs by the term  $O(S^6)$  from the error (5.2) of (5.1b), i.e. (5.9) does not vanish if  $\delta = 0$ .

While the TCC energy expression has only powers of  $S$  on the right hand side of  $H$  and no  $S^\dagger$ , in the methods discussed in this section powers of  $S^\dagger$  to the left of  $H$  appear as well. This reduces the error of the energy for a given accuracy of  $S$ . It can also be used to get the same accuracy of  $\tilde{E}$  with less computational effort. A detailed discussion of what one gains by having  $S^\dagger$  left of  $H$  has to be postponed until after a discussion of variational coupled-cluster theory.

## 6. Relative importance of basis operators of different excitation rank

If one decomposes the Hamiltonian  $H$  as  $H_0 + V$  such that the Hartree–Fock wave function  $\Phi$  is an eigenfunction of  $H_0$  with eigenvalue  $E_0 = \langle \Phi | H | \Phi \rangle$  and defines

$$H_\lambda = H_0 + \lambda V \quad (6.1)$$

then one can expand both  $S$  and  $E$  in powers of  $\lambda$ ; this leads immediately to the Møller–Plesset (MP) version of many-body perturbation theory (MBPT). One of the merits of CC theory is that one avoids the expansion in powers of  $\lambda$ , but

rather tries to keep implicit sums of the perturbation expansion to infinite order. Arguments in terms of MBPT in the context of CC theory are mainly used in order to analyse the quality of a CC ansatz truncated at a given excitation rank. The standard argument is that (starting from closed-shell restricted Hartree–Fock) to first order in MBPT only double excitations  $S_2$  contribute to  $S$ , to second order single to triple excitations and finally to  $k$ th up to  $(k + 1)$  fold excitations contribute. From this one concludes that if in TCC one limits  $S$  to  $S_2$  one has  $S$  correct to at least first order in MBPT, with  $S = S_1 + S_2 + S_3$  one has  $S$  correct to at least second order, and for  $S$  including up to the  $k$ -fold excitations  $S_k$  one has  $S$  correct to at least  $(k - 1)$ st order in MBPT.

A drawback of this argument is that there is no guarantee that MBPT converges [24]. If MBPT does converge the convergence is probably very slow. On the other hand the convergence of the sequence of CC calculations with increasing excitation rank included is more or less guaranteed. If the  $k$  in  $S_k$  reaches the particle number  $n$  then the calculation becomes exact (i.e. equal to that of full CI). There is also no doubt that  $S$  is usually dominated by  $S_2$ , and that the norm of higher  $S_k$  decreases (though not necessarily always monotonically). Of course,  $S_2$  dominates because the matrix element  $\langle \Phi | [V, S] | \Phi \rangle$  is non-vanishing only for  $S_2$ . Higher order  $S_k$  only contribute indirectly via  $S_k$  of lower rank. So one can justify

$$S = O(S_2); \quad S_2 = O(S); \quad S_1 = O(S^2); \quad S_k = O(S^{k-1}) \quad \text{for } k \geq 3 \quad (6.2)$$

by an argument very similar to that from perturbation theory (but not relying on its convergence). One can also arrive at these results in terms of a Newton–Raphson [18] approach to the coupled-cluster equations. Starting with  $S = 0$  one arrives in the first iteration cycle at  $S = S_2$  with an error  $O(S^2)$ . In the next cycle one obtains  $S_1$  and  $S_3$  and one also updates  $S_2$  etc. The order in powers of  $\|S\|$  in (6.2) corresponds exactly to those in powers of  $\lambda$ .

Combining (6.2) with the error formula (3.8) for a coupled-cluster expectation value for  $S = S_1 + \dots + S_k$ , i.e.  $\delta = O(S^k)$  we get

$$\tilde{E} - E = O(S^{2k}) = O(\lambda^{2k}) \quad (6.3)$$

That an energy expectation value is correct to  $O(\lambda^{2k-1})$ , i.e. has an error  $O(\lambda^{2k})$  if the wave function is correct to  $O(\lambda^{k-1})$ , is known as Wigner’s  $(2N + 1)$ -rule of perturbation theory. For the TCC energy one gets from the error formula (4.7)

$$\tilde{E} - E = O(S^{k+2}) = O(\lambda^{k+2}) \quad (6.4)$$

This would correspond to a  $(N + 2)$ -rule instead of the  $(2N + 1)$ -rule valid for an expectation value; however, as stated after Eq. (4.7) this estimate is usually too pessimistic, and a better estimate is (4.8). To evaluate this we need the error of a CI expansion up to  $k$ -fold excitations.

Truncating  $U$  at  $U_2$  gives an error of  $O(S^2)$ ; this is because both  $S_3$  and  $S_2^2$  are missing, and these are of  $O(S^2)$ . Truncating  $U$  at  $U_3$  one misses  $S_4 = O(S^3)$  and  $S_2^2 = O(S^2)$  as well as all other terms of third or higher order; the leading error is hence  $O(S^2)$ . For  $U = U_1 + \dots + U_4$  one misses  $S_5 = O(S^4)$  and  $S_2S_3 = O(S^3)$  and higher order terms, so that  $O(S^3)$  dominates. Truncation at  $U_5$  implies neglect of  $S_6 = O(S^5)$  and  $S_2^3 = O(S^3)$ , giving an error of  $O(S^3)$ . By induction one gets for truncation of CI expansion at  $U_k$  an error in  $U$

$$\theta = O(S^{[(k/2) + 1]}) \quad (6.5)$$

where  $[m]$  is the largest integer smaller than or equal to  $m$ . From (6.5) and (4.8) we then get the error formula for the TCC energy with  $S$  truncated at  $S_k$

$$\tilde{E} - E = O(S^{[(3k/2)+1]}) = O(\lambda^{[(3k/2)+1]}) \quad (6.6)$$

So for large  $k$  the error of the energy does not go as  $\lambda^{2k}$  like an expectation value would, nor as  $\lambda^k$  as one would expect from Eq. (4.7), but as  $\lambda^{(3/2)k}$ .

The result (6.6) has been known for the lowest orders [5], but the explicit formula (6.6) is probably new. Note that (6.4) and (6.6) agree for  $k = 2$  (CCSD) and  $k = 3$  (CCSDT), which are the only cases that are standard in practice.

Let us now study what one gains in going from TCC to ICC. For ICC(2) characterized by (5.1) the error formula (6.4) is replaced by

$$\tilde{E} - E = O(S^{k+3}) = O(\lambda^{k+3}) \quad (6.7)$$

There is an obvious gain for  $k = 3$  (CCSDT), because from (6.7) the ICC(2) energy is now correct to  $O(S^5)$ , but only to  $O(S^4)$  for TCC. In order to be correct to  $O(S^5)$  in TCC one has to include  $S_4$ . If one truncates at  $S_4$  the ICC(2) equations characterized by (5.1) don't present an advantage over TCC, since the error is now  $O(S^7)$  in both cases. To get an error  $O(S^8)$  one has to go to the next member ICC(3) of the ICC hierarchy. We shall see in the following sections that for highly accurate coupled-cluster calculations the variational and the unitary ansatz do present advantages.

Let us finally discuss the error of CI truncated at some excitation rank  $U_k$ . In view of (3.11) and (6.5) we get

$$\tilde{E} - E = O(S^{2[(k/2)+1]}) \quad (6.8)$$

The interesting result is that truncation at  $k = 2$  or  $k = 3$  leads to a result correct to  $O(\lambda^3)$ . In fact inclusion of connected triple excitations does not really pay as long as one omits disconnected quadruples.

The errors of various approaches for truncation of the operator basis  $S_k$  are collected in Table 1. The error of CI(2) as defined by (5.8) is of  $O(S^4)$  for  $S = S_2$  i.e. CI(2)SD and  $O(S^6)$  for  $S = S_1 + S_2 + S_3$  i.e. CI(2)SDT.

**Table 1.** Energy errors for truncation at  $S_k$  for various schemes

$k$	$\theta$	VCC UCC	TCC	ICC(2)	CI
2	2	4	4	4	4
3	2	6	5	6	4
4	3	8	7	7	6
5	3	10	8	8	6
6	4	12	10	10	8
7	4	14	11	11	8
8	5	16	13	13	10

$k$  is the excitation rank after which one truncates. The error of the wave operator  $S$  is  $O(S^k) = O(\lambda^k)$

The entries in the table indicate the exponent of  $S$  or  $\lambda$  in the error estimate for  $\theta$  (the error of the CI operator  $U$ ) and for the energies in schemes VCC etc.

## 7. Variational and unitary coupled-cluster theory

From the point of view of the error analysis, coupled-cluster theory based on stationarity of an expectation value is the best that one can do. There are essentially two possibilities to formulate a coupled-cluster expectation value, either for a wave function in intermediate normalization (7.1) or in terms of a unitary operator (7.2). We shall refer to coupled-cluster methods based on (7.1) or (7.2) [11, 14, 18, 25–33] as variational (VCC) or unitary (UCC) coupled cluster respectively. The expectation value of variational coupled-cluster theory can also be written in the form (7.3) where disconnected terms in the numerator have been cancelled with the denominator [2b, 31]. The subscript  $L$  indicates that only linked (connected) terms must be taken, taking care, however, of all EPV (exclusion principle violating) diagrams, which makes the expansion infinite.

$$\tilde{E} = \frac{\langle \Phi | e^{S^\dagger} H e^S | \Phi \rangle}{\langle \Phi | e^{S^\dagger} e^S | \Phi \rangle} \quad (7.1)$$

$$\tilde{E} = \langle \Phi | e^{-\sigma} H e^\sigma | \Phi \rangle; \quad \sigma = T - T^\dagger \quad (7.2)$$

$$\tilde{E} = \langle \Phi | e^{S^\dagger} H e^S | \Phi \rangle_L \quad (7.3)$$

There is a fourth possible energy expression, namely that obtained from (7.1) on Taylor-expanding the denominator

$$\tilde{E} = \langle \Phi | e^{S^\dagger} H e^S | \Phi \rangle \{1 + [\langle \Phi | e^{S^\dagger} e^S | \Phi \rangle - 1]\}^{-1} \quad (7.4)$$

Order by order, this is essentially identical with (7.3) – just written differently. The connectedness of (7.4) is less obvious than that of (7.3).

We are particularly concerned with closed-shell reference wave functions  $\Phi$ , but the generalization to open-shell states is usually easier than for TCC.

A closed evaluation of  $\tilde{E}$  is possible for (7.1) but this is so complicated that it has little chance of being realized. We therefore accept that  $\tilde{E}$  will be given as an infinite expansion that has to be truncated somewhere. It is important that in (7.1) one must not expand and truncate numerator and denominator separately, since then extensivity is lost (approaches of this kind where discussed in Sect. 5).

If one truncates an energy expansion given by an infinite series, one makes two errors: one due to truncation of the operator basis i.e. the error  $\delta$  of  $S$  (or  $T$ ), and one error due to truncation of the expansion in powers of  $S$ . If one truncates at  $O(S^k)$  the error of the energy is usually

$$\tilde{E} - E = O(\delta^2) + O(S^{k+1}) \quad (7.5)$$

Extensivity is guaranteed and we need not worry about it. The error formula (7.5) differs from those of TCC or ICC, which contain a factor  $O(\delta)$ , such that the error vanishes if  $\delta = 0$ , i.e. if  $e^S \Phi$  is exact. This is now no longer the case. One may regard this as a drawback, but it is less serious than one might think, especially since in view of the discussion in Sect. 6  $\delta$  can usually be expressed in orders of  $\|S\|$ . We must accept that unlike in TCC or ICC theory the special case of a supersystem of non-interacting two-electron systems is not treated exactly (unless one uses closed summations of infinite series as in Sect. 8).

Let us denote the  $k$ th order contribution (in powers of  $S$  or  $T$ ) to the energy as  $E^{(k)}$ . Note the conceptual difference between the  $k$ th order in powers of  $S$  (where actually  $k$ -fold products of  $S$  operators appear) and the shorthand notation  $O(S^k)$  which means  $O(\|S\|^k)$ , and which is dominated by the largest contribution to  $S$ , which will usually be contained in the two-electron part  $S_2$ .

The lowest  $E^{(k)}$  of the unitary expansion (UCC) (7.2) (see also [25b]) are (we have omitted terms like  $\langle \Phi | HT^3 | \Phi \rangle$  which necessarily vanish)

$$\begin{aligned}
E^{(0)} &= \langle \Phi | H | \Phi \rangle \\
E^{(1)} &= \langle \Phi | [H, \sigma] | \Phi \rangle = 2 \operatorname{Re} \langle \Phi | HT | \Phi \rangle \\
E^{(2)} &= \frac{1}{2} \langle \Phi | [[H, \sigma], \sigma] | \Phi \rangle = \operatorname{Re} \langle \Phi | HT^2 + T^\dagger HT - T^\dagger TH | \Phi \rangle \\
E^{(3)} &= \frac{1}{6} \langle \Phi | [[[H, \sigma], \sigma], \sigma] | \Phi \rangle = \frac{1}{3} \operatorname{Re} \langle \Phi | -HT^\dagger T^2 - HTT^\dagger T + HT^{\dagger 2} T | \Phi \rangle \\
&\quad + \operatorname{Re} \langle \Phi | T^\dagger HT^2 - T^\dagger HT^\dagger T | \Phi \rangle \\
E^{(4)} &= \frac{1}{24} \langle \Phi | [[[[H, \sigma], \sigma], \sigma], \sigma] | \Phi \rangle \\
&= \frac{1}{12} \operatorname{Re} \langle \Phi | -HT^\dagger T^3 - HTT^\dagger T^2 - HT^2 T^\dagger T + HT^{\dagger 2} T^2 \\
&\quad + HT^\dagger T T^\dagger T + HTT^{\dagger 2} T | \Phi \rangle \\
&\quad + \frac{1}{3} \operatorname{Re} \langle \Phi | T^\dagger HT^3 - T^\dagger HT^\dagger T^2 - T^\dagger HTT^\dagger T + T^\dagger HT^{\dagger 2} T | \Phi \rangle \\
&\quad + \frac{1}{4} \operatorname{Re} \langle \Phi | T^\dagger THT^\dagger T - T^\dagger T^\dagger HT^\dagger T - T^\dagger THT^2 + T^{\dagger 2} HT^2 | \Phi \rangle \quad (7.6)
\end{aligned}$$

while the corresponding contributions to the nonunitary variational energy VCC (7.3, 4) are

$$\begin{aligned}
E^{(0)} &= \langle \Phi | H | \Phi \rangle \\
E^{(1)} &= 2 \operatorname{Re} \langle \Phi | HS | \Phi \rangle \\
E^{(2)} &= \operatorname{Re} \langle \Phi | HS^2 + S^\dagger HS | \Phi \rangle_L \\
&= \operatorname{Re} \langle \Phi | HS^2 + S^\dagger HS | \Phi \rangle - \langle \Phi | H | \Phi \rangle \langle \Phi | S^\dagger S | \Phi \rangle \\
E^{(3)} &= \operatorname{Re} \langle \Phi | S^\dagger HS^2 | \Phi \rangle_L \\
&= \operatorname{Re} \langle \Phi | S^\dagger HS^2 | \Phi \rangle - 2 \operatorname{Re} \langle \Phi | HS | \Phi \rangle \langle \Phi | S^\dagger S | \Phi \rangle \\
&\quad - \langle \Phi | H | \Phi \rangle \operatorname{Re} \langle \Phi | S^\dagger S^2 | \Phi \rangle \\
E^{(4)} &= \frac{1}{4} \langle \Phi | S^{\dagger 2} HS^2 | \Phi \rangle_L + \frac{1}{3} \langle \Phi | S^\dagger HS^3 | \Phi \rangle_L \\
&= \frac{1}{4} \langle \Phi | S^{\dagger 2} HS^2 | \Phi \rangle + \frac{1}{3} \langle \Phi | S^\dagger HS^3 | \Phi \rangle \\
&\quad - \{ \langle \Phi | S^\dagger HS | \Phi \rangle + \operatorname{Re} \langle \Phi | HS^2 | \Phi \rangle \} \langle \Phi | S^\dagger S | \Phi \rangle \\
&\quad - 2 \operatorname{Re} \langle \Phi | HS | \Phi \rangle \operatorname{Re} \langle \Phi | S^\dagger S^2 | \Phi \rangle \\
&\quad - \langle \Phi | H | \Phi \rangle \{ \frac{1}{4} \langle \Phi | S^{\dagger 2} S^2 | \Phi \rangle + \frac{1}{3} \langle \Phi | S^\dagger S^3 | \Phi \rangle - \langle \Phi | S^\dagger S | \Phi \rangle^2 \} \quad (7.7)
\end{aligned}$$

In (7.6) and (7.7) all commutators have been resolved into simple products. So the connected nature is no longer obvious, and various terms in the sums taken apart may well contain disconnected diagrams which only cancel when everything is taken together. Of course, one can ignore all these disconnected contributions. Then all terms which are products of matrix elements can be ignored from the outset. It may, however, turn out convenient not to cancel all disconnected terms, but only those where the two factors have no common indices, which we refer to as disjoint [32]. After cancellation both joint disconnected diagrams and connected diagrams (which are *a fortiori* joint) survive. We use the subscript  $J$  for joint diagrams. So all diagrams in (7.6) or (7.7) could be given the subscript  $J$  (if they do not already carry the subscript  $L$  for linked = connected). The difference between linked ( $L$ ) and joint ( $J$ ) is that for a classification into joint and disjoint, EPV diagrams must be omitted (otherwise

these diagrams would be counted twice). While linkedness is determined by the topology of the diagrams only, the discrimination between joint and disjoint requires diagrams with spin-orbital labels.

The zeroth, first and second order terms in (7.6) and (7.7) agree (with  $T$  replaced by  $S$ ), while there are differences to third and higher orders. This is best seen if we consider the special case when  $S$  or  $T$  consists of two-particle excitation operators only, i.e.  $S = S_2$ ,  $T = T_2$ . In this case (7.6) and (7.7) simplify to

$$\begin{aligned} E^{(2)} &= \text{Re} \langle \Phi | T^\dagger H T - T^\dagger T H | \Phi \rangle \\ E^{(3)} &= \frac{2}{3} \text{Re} \langle \Phi | T^\dagger H T^2 | \Phi \rangle - \frac{4}{3} \langle \Phi | T^\dagger T | \Phi \rangle \text{Re} \langle \Phi | H T | \Phi \rangle \\ E^{(4)} &= \frac{1}{4} \langle \Phi | T^{\dagger 2} H T^2 | \Phi \rangle - \frac{1}{3} \text{Re} \langle \Phi | T^\dagger H T^\dagger T | \Phi \rangle \\ &\quad - \frac{1}{3} \langle \Phi | T^\dagger H T | \Phi \rangle \langle \Phi | T^\dagger T | \Phi \rangle \\ &\quad + \langle \Phi | H | \Phi \rangle \left\{ \frac{1}{3} \langle \Phi | T^\dagger T | \Phi \rangle^2 + \frac{1}{12} \langle \Phi | T^{\dagger 2} T^2 | \Phi \rangle \right\} \end{aligned} \quad (7.8)$$

$$\begin{aligned} E^{(2)} &= \langle \Phi | S^\dagger H S | \Phi \rangle_L = \langle \Phi | S^\dagger H S | \Phi \rangle - \langle \Phi | H | \Phi \rangle \langle \Phi | S^\dagger S | \Phi \rangle \\ E^{(3)} &= \text{Re} \langle \Phi | S^\dagger H S^2 | \Phi \rangle_L \\ &= \text{Re} \langle \Phi | S^\dagger H S^2 | \Phi \rangle - 2 \text{Re} \langle \Phi | H S | \Phi \rangle \langle \Phi | S^\dagger S | \Phi \rangle \\ E^{(4)} &= \frac{1}{4} \langle \Phi | S^{\dagger 2} H S^2 | \Phi \rangle_L \\ &= \frac{1}{4} \langle \Phi | S^{\dagger 2} H S^2 | \Phi \rangle - \langle \Phi | S^\dagger H S | \Phi \rangle \langle \Phi | S^\dagger S | \Phi \rangle \\ &\quad + \langle \Phi | H | \Phi \rangle \left\{ \langle \Phi | S^\dagger S | \Phi \rangle^2 - \frac{1}{4} \langle \Phi | S^{\dagger 2} S^2 | \Phi \rangle \right\} \end{aligned} \quad (7.9)$$

One sees that  $E^{(3)}$  in (7.8) is formally  $2/3$  of  $E^{(3)}$  in (7.9); while the relation between  $E^{(4)}$  in (7.8) and (7.9) is somewhat more complicated, there is roughly a factor 3 between the two expressions.

The fact that the UCC expressions are somewhat more complicated is compensated by an obviously faster convergence. This becomes manifest if, for a moment, we consider a two-particle state. For this, the expressions (7.8) and (7.9) simplify even more, namely to

$$\begin{aligned} E^{(3)} &= -\frac{4}{3} t^2 \text{Re} \langle \Phi | H T | \Phi \rangle \\ E^{(4)} &= -\frac{1}{3} t^2 \langle \Phi | T^\dagger H T | \Phi \rangle + \frac{1}{3} t^4 \langle \Phi | H | \Phi \rangle \\ E^{(5)} &= \frac{4}{15} t^4 \text{Re} \langle \Phi | H T | \Phi \rangle \end{aligned} \quad (7.10)$$

$$\begin{aligned} E^{(3)} &= -2s^2 \text{Re} \langle \Phi | H S | \Phi \rangle \\ E^{(4)} &= -s^2 \langle \Phi | S^\dagger H S | \Phi \rangle + s^4 \langle \Phi | H | \Phi \rangle \\ E^{(5)} &= 2s^4 \text{Re} \langle \Phi | H S | \Phi \rangle \end{aligned} \quad (7.11)$$

with

$$t^2 = \langle \Phi | T^\dagger T | \Phi \rangle; \quad s^2 = \langle \Phi | S^\dagger S | \Phi \rangle \quad (7.12)$$

In this case a summation to infinite order is possible, with the respective results [10c]

$$E = \cos^2 t \langle \Phi | H | \Phi \rangle + \frac{2 \sin t \cos t}{t} \text{Re} \langle \Phi | H T | \Phi \rangle + \frac{\sin^2 t}{t^2} \langle \Phi | T^\dagger H T | \Phi \rangle \quad (7.13)$$

$$E = (1 + s^2)^{-1} \left\{ \langle \Phi | H | \Phi \rangle + \text{Re} \langle \Phi | H S | \Phi \rangle + \langle \Phi | S^\dagger H S | \Phi \rangle \right\} \quad (7.14)$$

In this special case there is a simple relation between  $S$  and  $T$ , namely

$$S = \frac{\tan t}{t} T = \{1 + O(t^2)\} T \quad (7.15)$$

Some contributions of higher orders in VCC arise in lower orders in UCC. The  $k$ th order of UCC should generally be a better approximation than the  $k$ th order of VCC. Although the same error estimate (7.5) applies to both schemes, they have a different factor for the  $O(S^{k+1})$  term.

Let us now return to the general case. We truncate the expansion of  $\tilde{E}$  at some  $k$ th order in  $S$  or  $T$  and make this expansion stationary with respect to variation of the coefficients  $c_k$  or  $d_k$  in which  $T$  or  $S$  are expanded in the operator basis  $\{X_k\}$

$$S = \sum_k c_k X_k; \quad T = \sum_k d_k X_k \quad (7.16)$$

For  $E$  according to (7.7) truncated at  $E^{(2)}$  we get the stationary condition

$$Re\{\langle \Phi | HX_k | \Phi \rangle + \langle \Phi | HSX_k + S^\dagger HX_k | \Phi \rangle\}_L = 0 \quad (7.17)$$

Multiplication of (7.17) by  $c_k$  and summation over  $k$  yields

$$Re\{\langle \Phi | HS | \Phi \rangle + \langle \Phi | HS^2 + S^\dagger HS | \Phi \rangle\}_L = 0 \quad (7.18)$$

If we combine the consequence (7.18) of the energy being stationary with the second order energy expression we get

$$E = E^{(0)} + E^{(1)} + E^{(2)} = \langle \Phi | H | \Phi \rangle + Re\langle \Phi | HS | \Phi \rangle = E^{(0)} + \frac{1}{2}E^{(1)} \quad (7.19)$$

In a completely analogous way one can show that for  $E$  truncated at  $k$ th order and made stationary one gets as a generalization of (7.18) and (7.19)

$$E^{(1)} + 2E^{(2)} + 3E^{(3)} + \dots + kE^{(k)} = 0 \quad (7.20)$$

$$E = E^{(0)} + E^{(1)} + \dots + E^{(k)} = E^{(0)} + \frac{k-1}{k} E^{(1)} + \frac{k-2}{k} E^{(2)} + \dots + \frac{1}{k} E^{(k-1)} \quad (7.21)$$

For  $k = 3$  or  $4$  (7.21) reads

$$E = E^{(0)} + E^{(1)} + E^{(2)} + E^{(3)} = E^{(0)} + \frac{2}{3}E^{(1)} + \frac{1}{3}E^{(2)} \quad (7.22a)$$

$$E = E^{(0)} + \dots + E^{(4)} = E^{(0)} + \frac{3}{4}E^{(1)} + \frac{1}{2}E^{(2)} + \frac{1}{4}E^{(3)} \quad (7.22b)$$

Of course, one can use (7.21) to eliminate other than just the highest order terms in (7.20), e.g.

$$E = E^{(0)} + \frac{1}{2}E^{(1)} - \frac{1}{2}E^{(3)} - E^{(4)} - \frac{3}{2}E^{(5)} - \dots \quad (7.23)$$

It should be noted that the well-known energy expression in intermediate normalization (1.3a) does not follow from stationarity of the energy expectation value (7.1) with respect to variation of  $S^\dagger$  and  $S$ , it only follows from variation with respect to  $e^S$  as a whole, i.e. in a CI type approach. The expression (1.3a) is hence compatible with stationarity of (7.1) only if the ansatz (1.1) is exact. This is, for example, the case for a two electron system, as described by (7.14), where one easily sees that

$$\frac{1}{2}E^{(3)} + E^{(4)} + \frac{3}{2}E^{(5)} + \dots = 0 \quad (7.24)$$

and (7.23) immediately implies (7.3a). It does, of course, not hold in the unitary normalization as given by (7.13).

In such a truncated VCC or UCC approach one is sure to get the error of the energy linear in the number of particles and otherwise of  $O(S^{k+1})$  and there is an obvious hierarchy, namely that of approximations defined in powers of  $S$  or  $T$ . There is also a second hierarchy, already known from TCC, namely in terms of the maximum excitation rank included in the basis. We must combine the two hierarchies to a single consistent one.

We are further faced with the observation that the stationarity condition mixes orders in powers of  $S$ . In CEPA-0, that may also be called VCC(3) – the 3 indicates that this is correct to third order in  $S$  or  $\lambda$  (see later) – there is the simple relation  $E^{(2)} = -\frac{1}{2}E^{(1)}$ ; hence  $E^{(1)}$  and  $E^{(2)}$  are of the same order of magnitude.

One should realize that the approach in this section is somewhat converse to that used in the derivation of TCC. In TCC we have started from the stationarity conditions and a simplified energy expression that only holds if the stationarity conditions are satisfied, and we have then constructed the functionals that we actually make stationary. The error analysis was then based on these functionals. Now we start from the functionals to be made stationary, get then the stationarity conditions and finally the simplified energy expressions that hold in the case of stationarity. The error analysis has to be based on the truncated energy expressions to be made stationary. The stationarity conditions are used to determine  $S$  and hence tell something about  $S$ .

We know that usually  $S$  is dominated by the double excitation part  $S_2$ . Let us therefore first consider the case that  $S = S_2$ . For  $k$  even, products of an even number of  $S_2$  or  $S_2^\dagger$  operators contribute to  $E^{(k)}$ , while for  $k$  odd it is products with an odd number. For  $k$  odd, only that part of  $H$  contributes that takes care of a double excitation or de-excitation, i.e. matrix elements like  $V_{ab}^{ij}$  (for  $i, j$  occupied,  $a, b$  virtual). These are exchange-type matrix elements. For  $k$  even the  $S$  and  $S^\dagger$  factors must cancel each other and the matrix elements of  $H$  are of the form  $f_{is}^i, f_a^a, V_{ij}^{ij}, V_{ia}^{ia}$ , where  $f_q^p$  are matrix elements of the Fock operator. Such matrix elements are usually much larger (in the language of perturbation theory matrix elements involving  $V$  carry a factor  $\lambda$  and are hence smaller by a factor  $\lambda$  than matrix elements involving  $f$ ; but even the Coulomb-like matrix elements like  $V_{ia}^{ia}$  are usually significantly larger than  $V_{ab}^{ij}$ ). This means that the  $E^{(k)}$  with  $k$  odd are relatively much smaller than  $E^{(k)}$  with  $k$  even, to the extent that for the  $S_2$  which makes the energy functional stationary,  $E^{(3)}$  is of the same order of magnitude as  $E^{(4)}$  and  $E^{(5)}$  as  $E^{(6)}$ . The  $E^{(k)}$  with  $k$  odd are always smaller by one order of  $\|S\|$  than indicated by the formal appearance of  $S$ . So  $E^{(1)} = O(S^2)$ ;  $E^{(2)} = O(S^2)$ ;  $E^{(3)} = O(S^4)$ ;  $E^{(4)} = O(S^4)$  etc. The same conclusions can also be obtained in terms of perturbation theory, i.e. by treating  $H_0$  and  $\lambda V$  differently, but we don't wish to formalize this decomposition of  $H$ .

In view of this we must revise our error formula for CEPA-0 (i.e. for truncation of VCC or UCC at  $k = 2$ ) from (3.17) to

$$\tilde{E} - E = O(\delta^2) + O(S^4) \quad (7.25)$$

i.e. as with CCSD, CEPA-0 is correct to  $O(S^3)$ ; the two schemes differ by some terms  $O(S^4)$ , but none contains all terms  $O(S^4)$ .

In principle one may truncate VCC or UCC at any  $k$ . However truncation at even orders is usually preferable. For truncation at  $k$  odd, one includes one term and omits another one of the same order of magnitude, while for truncation at  $k$  even, the next term ignored is smaller by  $O(S^2)$  than the last one considered. So the next recommended VCC or UCC truncation after CEPA-0 is that after

$k = 4$ . To be consistent with the nomenclature of Bartlett et al. [25], who defined truncated VCC and UCC schemes somewhat differently (see later), we refer to a scheme truncated at  $E^{(k)}$  as VCC( $k + 1$ ) or VUCC( $k + 1$ ). In this convention CEPA-0 is identical with VCC(3) or VUCC(3) and the next recommended improvement would be VCC(5) or VUCC(5). For these latter schemes we have the error formula

$$\tilde{E} - E = O(\delta^2) + O(S^6) \quad (7.26)$$

We write VUCC( $k$ ) rather than UCC( $k$ ), because UCC( $k$ ) schemes have already been defined somewhat differently by Bartlett and Noga [25]. To have an approximation scheme consistently correct to  $(S^5)$ , i.e. to have  $\delta = O(S^3)$ , we have to take  $S = S_1 + S_2 + S_3$ , i.e. explicitly the VCC(5)SDT or VUCC(5)SDT approach. The hierarchy continues with VCC(7)SDTQ or VUCC(7)SDTQ, which are accurate to  $O(S^7)$ .

Being aware of the accuracy  $O(S^m)$  achievable at a given level, it usually does not make much sense to include terms of higher order than is generally achievable. Consider for example VUCC(5) with  $\sigma = \sigma_1 + \sigma_2 + \sigma_3$ . It is sufficient to include  $\sigma_2$  up to 4-fold commutators,  $\sigma_1$  and  $\sigma_3$  only up to double commutators, and treat mixed commutators analogously. Explicitly this means that we take in VUCC(5)

$$\begin{aligned} E = & \langle \Phi | H + [H, \sigma_1] + [H, \sigma_2] + \frac{1}{2}[[H, \sigma_1], \sigma_1] + \frac{1}{2}[[H, \sigma_1], \sigma_2] \\ & + \frac{1}{2}[[H, \sigma_2], \sigma_1] + \frac{1}{2}[[H, \sigma_2], \sigma_2] + \frac{1}{2}[[H, \sigma_1], \sigma_3] \\ & + \frac{1}{2}[[H, \sigma_3], \sigma_1] + \frac{1}{2}[[H, \sigma_3], \sigma_3] + \frac{1}{2}[[H, \sigma_3], \sigma_2] \\ & + \frac{1}{2}[[H, \sigma_2], \sigma_3] + \frac{1}{6}[[[H, \sigma_2], \sigma_2], \sigma_2] \\ & + \frac{1}{6}[[[H, \sigma_1], \sigma_2], \sigma_2] + \frac{1}{6}[[[H, \sigma_2], \sigma_1], \sigma_2] + \frac{1}{6}[[[H, \sigma_2], \sigma_2], \sigma_1] \\ & + \frac{1}{6}[[[H, \sigma_3], \sigma_2], \sigma_2] + \frac{1}{6}[[[H, \sigma_2], \sigma_3], \sigma_2] + \frac{1}{6}[[[H, \sigma_2], \sigma_2], \sigma_3] \\ & + \frac{1}{24}[[[[H, \sigma_2], \sigma_2], \sigma_2], \sigma_2] + \frac{1}{24}[[[[H, \sigma_1], \sigma_2], \sigma_2], \sigma_2] \\ & + \dots + \frac{1}{24}[[[[[H, \sigma_2], \sigma_2], \sigma_2], \sigma_3]] | \Phi \rangle \end{aligned} \quad (7.27)$$

As to the question whether VCC or UCC is preferable, we can make the following remark. The UCC expressions are usually somewhat more complicated (e.g. compare Eqs. (7.6) and (7.7)), but UCC should converge faster. In the two-electron case the  $E^{(k)}$  of UCC converge essentially as  $\cos^2 t$ , while those of VCC converge as  $(1 + s^2)^{-1}$ . If one truncates either function at  $O(x^{2n})$ , the error is, of course,  $O(x^{2n+2})$ , but for  $\cos^2 t$  it is dominated by  $[(2n + 2)!]^{-1} t^{2n+2}$  while for  $[1 + s^2]^{-1}$  it is  $s^{2n+2}$ . While  $\cos^2 t$  converges for all  $t$ ,  $[1 - s^2]^{-1}$  converges only for  $|s| < 1$ .

Both variational and unitary coupled-cluster expansions have been studied in detail by Bartlett et al. [25a,b]. For a recent application see [25c]. The variational coupled-cluster method of Bartlett and Noga, called XCC (for expectation-value coupled-cluster), differs from the present VCC mainly in the following aspect. These authors decompose  $H$  into  $H_0$  and  $V$  such that for example

$$E^{(2)} = \langle \Phi | H_0 S^2 + S^\dagger H_0 S | \Phi \rangle + \langle \Phi | V S^2 + S^\dagger V S | \Phi \rangle = E_0^{(2)} + E_1^{(2)} \quad (7.28)$$

Then the energy contributions are regrouped, the contributions  $\tilde{E}^{(k)}$  of the XCC expansions are defined as

$$\bar{E}^{(k)} = \bar{E}_0^{(k)} + \bar{E}_1^{(k-1)} \quad (7.29)$$

$H_0$  and  $V$  are hence treated separately very much in the tradition of perturbation theory where  $V$  appears with an extra factor  $\lambda$ . It is more in the spirit of the variational approach not to separate  $H_0$  and  $V$ . The choice of Bartlett et al. also allows one to define XCC( $k$ ) or UCC ( $k$ ) for  $k$  even.

For  $k$  odd Bartlett's XCC( $k$ ) and our VCC( $k$ ) should not differ too much, similarly our VUCC( $k$ ) should be similar to but not identical with their UCC( $k$ ). A numerical comparison of the two kinds of hierarchies has not yet been made.

## 8. Infinite summation of joint renormalization terms

For the special case of a supersystem consisting of  $n$  non-interacting two-electron systems both the Hamiltonian  $H$  and the cluster operator  $S = S_2$  can be divided into parts acting on different exclusive subspaces

$$H = \sum_{\mu=1}^n H_{\mu}; \quad S = \sum_{\mu=1}^n S_{\mu} \quad (8.1)$$

The subscript on  $S$  now counts subsystems and does *not* mean the excitation rank. The VCC energy expectation value can then be summed as shown in (7.14) for a two-electron system with the result

$$\tilde{E} = \langle \Phi | H | \Phi \rangle + \sum_{\mu} \frac{2 \operatorname{Re} \langle \Phi | H_{\mu} S_{\mu} | \Phi \rangle + \langle \Phi | S_{\mu}^{\dagger} [H_{\mu}, S_{\mu}] | \Phi \rangle}{1 + \langle \Phi | S_{\mu}^{\dagger} S_{\mu} | \Phi \rangle} \quad (8.2)$$

This is of the form of the coupled pair functional (CPF) proposed by Ahrlich [34] and looks very much like the CEPA-0 functional, but with each pair correlation part divided by an individual denominator. The expression (8.2) is exact for this special supersystem in the sense that if the operator basis consists of all two-particle excitation operators constructable from the one-electron basis, then (8.2) is equal to the 'full-CI' expectation value.

One may object that (8.2) is only valid if one chooses the  $S$  operators such that they perform excitations within the subspaces, and not if one chooses an arbitrary basis in the full orbital space and takes excitations in terms of these. In other words, the expression (8.2) is not unitary-invariant. This is a minor drawback for such supersystems since one usually knows the subspaces, but for a generalization to systems that are not strictly separable one would prefer a unitary-invariant formulation.

For the discussion in this section it is important to note that we must distinguish orbital labels. This implies that we should include only those diagrams that obey the Pauli principle. Diagrams corresponding to

$$\langle \Phi | S_{\mu}^{\dagger} H S_{\mu} S_{\mu} | \Phi \rangle \quad (8.3)$$

are necessarily of EPV type and should not be present. This means that we must not start from expressions where all disconnected diagrams have been cancelled. Rather, we should let only disconnected diagrams with distinct orbital labels cancel (i.e. disjoint diagrams), while joint disconnected diagrams should be kept. These diagrams will then be summed as far as they form geometrical series to yield an energy denominator. The book-keeping of spin-orbital indices makes things rather tedious.

Let us start with a discussion of  $E^{(3)}$  of VCC (7.9) without making special assumptions on the state

$$E^{(3)} = \operatorname{Re} \langle \Phi | S^{\dagger} H S^2 - 2 S^{\dagger} S H S | \Phi \rangle \quad (8.4)$$

We write (using the tensor notation for normal product operators [27])

$$S = \sum_{i < j} S_{ij} = \frac{1}{2} \sum'_{i,j} S_{ij}; \quad S^\dagger = \frac{1}{2} \sum'_{i,j} S^{ij} \quad (8.5a)$$

$$S_{ij} = \sum'_{a,b} c_{ab}^{ij} a_{ij}^{ab}; \quad S^{ij} = \sum'_{a,b} c_{ij}^{ab} a_{ab}^{ij}, \quad c_{ab}^{ij} = -c_{ab}^{ji} = \dots \quad (8.5b)$$

$$g_{ij} = \sum'_{a,b} \bar{g}_{ab}^{ij} a_{ij}^{ab}; \quad g^{ij} = \sum'_{a,b} \bar{g}_{ij}^{ab} a_{ab}^{ij} \quad (8.5c)$$

$$a_{ij}^{ab} = a_a^\dagger a_b^\dagger a_j a_i; \quad g_{ab}^{ij} = \langle ab | r_{12}^{-1} | ij \rangle; \quad \bar{g}_{ab}^{ij} = g_{ab}^{ij} - g_{ab}^{ji} \quad (8.5d)$$

The labels refer to spin-orbitals and so the summations over  $i$  and  $j$  go from 1 to  $2n$ . Then (8.4) becomes

$$\begin{aligned} E^{(3)} &= \frac{1}{2} \text{Re} \sum'_{i,j} \sum'_{k,l} \langle \Phi | S^{ij} g^{kl} S_{ij} S_{kl} + S^{ij} g^{kl} S_{il} S_{kj} + S^{ij} g^{kl} S_{ik} S_{jl} - S^{ij} S_{ij} g^{kl} S_{kl} | \Phi \rangle \\ &= \frac{1}{2} \text{Re} \sum'_{i,j \neq k,l} \langle \Phi | S^{ij} g^{kl} (S_{il} S_{kj} + S_{ik} S_{jl}) | \Phi \rangle \\ &\quad - \sum'_{i,j} \langle \Phi | S^{ij} S_{ij} g^{ij} S_{ij} | \Phi \rangle - \sum'_{i,j,k} \langle \Phi | S^{ij} S_{ij} (g^{ki} S_{ki} + g^{kj} S_{kj}) | \Phi \rangle \end{aligned} \quad (8.6)$$

In the special case that a decomposition (8.1) is possible, this reduces to

$$\begin{aligned} E^{(3)} &= -2 \sum'_{\mu} \langle \Phi | S^{\mu} S_{\mu} H^{\mu} S_{\mu} | \Phi \rangle = -2 \sum'_{\mu} \langle \Phi | S^{\mu} S_{\mu} | \Phi \rangle \langle \Phi | H^{\mu} S_{\mu} | \Phi \rangle \\ S_{\mu} &= S_{\mu, n+\mu}; \quad H_{\mu} = g_{\mu, n+\mu} \end{aligned} \quad (8.7)$$

and a factorization is possible in which the first term in the geometric series leads to (8.2). In the general case given by (8.6) the second and third terms can be factorized together to yield

$$\sum'_{i,j} \langle \Phi | g^{ij} S_{ij} | \Phi \rangle D_{ij} \quad (8.8a)$$

$$D_{ij} = \langle \Phi | S^{ij} S_{ij} | \Phi \rangle + \sum_k \{ \langle \Phi | S^{ik} S_{ik} | \Phi \rangle + \langle \Phi | S^{kj} S_{kj} | \Phi \rangle \} \quad (8.8b)$$

However, the first term in (8.6) cannot be factorized. For a generalization of (8.2) one has three choices:

1. One ignores the first term in (8.6) and uses the factorization (8.8b), i.e. one sums up a geometric series in this  $D_{ij}$ . In a different context this choice has been suggested by Kelly and Sessler [35].

2. One argues that the fully-joint terms dominate, where the two factors in (8.6) agree in the two indices, i.e. one keeps only the second term in (8.6) and replaces  $D_{ij}$  of (8.8b) by  $\langle \Phi | S^{ij} S_{ij} | \Phi \rangle$ .

3. One finds a compromise between these two choices, neither of which is unitary-invariant, by requiring unitary invariance in cases of special interest. This concept goes back to W. Meyer [10a] and has recently been taken up by R. Ahlrichs et al. [34]. The main idea is that the requirement of unitary invariance is relevant when localized non-interacting (or slightly interacting) pairs are identical, such that canonical orbitals differ significantly from localized ones; this is not the case for sufficiently different pairs. Hence, one should require unitary invariance for a supersystem consisting of identical localized pairs. It can be

made plausible (see Appendix A) that in this special case the first term in (8.6) is just half of the last one, such that a factorization of the type (8.8) is possible, but with

$$D_{ij} = \langle \Phi | S^{ij} S_{ij} | \Phi \rangle + \frac{1}{2} \sum_k \{ \langle \Phi | S^{ik} S_{ik} | \Phi \rangle + \langle \Phi | S^{kj} S_{kj} | \Phi \rangle \} \quad (8.9)$$

It is then rather straightforward to find all terms in the infinite order VCC expression that factorize (at least approximately) and to recognize geometrical series that can be summed. Assuming further that the arithmetic mean of  $1 + D_{ij}$  and  $1 + D_{kl}$  differs only a little from the geometric mean, one can arrive at the expression

$$\begin{aligned} \tilde{E} \approx & \langle \Phi | H | \Phi \rangle + \sum_{i < j} \frac{2 \operatorname{Re} \langle \Phi | H S_{ij} | \Phi \rangle + \langle \Phi | S_{ij}^\dagger (H - E_0) S_{ij} | \Phi \rangle}{1 + D_{ij}} \\ & + \sum_{(i < j) \neq (k < l)} \frac{\langle \Phi | S_{ij}^\dagger H S_{kl} | \Phi \rangle}{\sqrt{(1 + D_{ij})(1 + D_{kl})}} \end{aligned} \quad (8.10)$$

which has been proposed by R. Ahlrichs et al. [34] on more heuristic grounds and has been called coupled-pair functional (CPF). (As to a precursor of CPF see [36].)

We mention that one of the main contributions of Sinanoğlu [37] to many-electron theory has been to recognize that the cluster structure of the wave function implies a substantial cancellation between terms in the numerator and the denominator in the energy expectation value, with the result that in a good approximation each pair gets its individual denominator.

As shown by Gdanitz and Ahlrichs [38] it is often a very good approximation to take all energy denominators equal, i.e. to choose

$$D_{ij} = n^{-1} \langle \Phi | S^\dagger S | \Phi \rangle; \quad \forall i, j \quad (8.11)$$

This approximation (which can be based on Eq. (A.2) of Appendix A), referred to as ‘averaged coupled-pair’ functional (ACPF), has actually been proposed for multiference states; we consider here only the special case of a single Slater determinant reference function. It should be mentioned that Pulay [39] has also proposed a functional which is made stationary in the CEPA approximation. It does not contain individual denominators like CPF.

Although CPF-type methods have been very successful in practice, their somewhat ad-hoc introduction [34] may have been regarded as a drawback, since CPF did not appear as a member in a hierarchy of approximations that eventually led to an exact solution. The present derivation can remedy this drawback. While summing certain contributions in VCC to infinite order one need not neglect the remaining ones as in CPF, but one can evaluate them exactly up to a given order.

The present derivation of CPF from VCC has some similarities to the older derivation [10c] of CEPA from TCC. In both cases one uses the fact that the most important diagrams going beyond CEPA-0 factorize. Nevertheless, although the working equations of CEPA and CPF are very similar, there is a significant conceptual difference. While in the derivation of CEPA the TCC-D equations were taken for granted, we have here started from the VCC expectation value, i.e. the problem of the validity of the TCC equations is circumvented. By the partial summation of geometrical series we have managed to get exact

results for the special case of a supersystem of non-interacting pairs while keeping all the other advantages of VCC.

In this context one should mention that an alternative to CEPA-type methods, now called ACC (for approximate coupled-cluster [40]), have been proposed by Jankowski and Paldus [7]. These start from the TCC equations and neglect certain classes of diagrams in such a way that all the factorizable diagrams are kept. Since this procedure is only based on the topology of the diagrams and not on labels, it is automatically unitary-invariant, although numerically there is little difference from the corresponding CEPA methods. Since not all diagrams which are kept factorize in the form (8.8a), an ACC generalization of CPF does not appear to be possible. It is somewhat astonishing that ACC has hardly been applied [40]. A short account of the application of the ACC philosophy to the  $E^{(3)}$  of VCC (8.4) is given in Appendix B.

### 9. Comparison of various coupled-cluster methods for an ansatz limited to double substitutions (CCD)

The simplest approach is CEPA-0 or LCC-D with the functional (in this section  $S$  or  $T$  is always equal to  $S_2$  or  $T_2$ )

$$\text{CEPA-0: } F_0(S) = \langle \Phi | H + HS + S^\dagger H + S^\dagger [H, S] | \Phi \rangle \quad (9.1)$$

The TCC functional (4.13) has an extra term in addition to (9.1)

$$\text{TCC-D: } F(S^\dagger) = F_0(S^\dagger) + \langle \Phi | \frac{1}{2} S^\dagger H S^2 - S^\dagger S H S | \Phi \rangle \quad (9.2)$$

We have written this as  $F(S^\dagger)$  to indicate that it is only made stationary with respect to variation of  $S^\dagger$ .

We do not consider ICC because for  $S = S_2$  the error is of  $O(S^4)$  as for TCC, but ICC is much more complicated. For variational coupled cluster up to third order in  $S$  we get

$$\text{VCC(4)D: } F_4(S) = F_0(S) + \text{Re} \langle \Phi | S^\dagger H S^2 - 2S^\dagger S H S | \Phi \rangle \quad (9.3)$$

The corresponding expression of VUCC(4)D is

$$\text{VUCC(4)D: } F_4(T) = F_0(T) + \frac{2}{3} \text{Re} \langle \Phi | T H T^2 - 2T^\dagger T H T | \Phi \rangle \quad (9.4)$$

If we go to the next order in VCC or VUCC (remember our remark in Sect. 7 that one should not truncate at an odd order in  $S$  or  $T$ ) we get respectively

$$\begin{aligned} \text{VCC(5)D: } F_5(S) = F_4(S) + \frac{1}{4} \langle \Phi | S^{\dagger 2} (H - E_0) S^2 | \Phi \rangle \\ - \langle \Phi | S^\dagger (H - E_0) S | \Phi \rangle \langle \Phi | S^\dagger S | \Phi \rangle \end{aligned} \quad (9.5)$$

$$\begin{aligned} \text{UCC(5)D: } F_5(T) = F_4(T) + \frac{1}{4} \langle \Phi | T^{\dagger 2} (H_0 - E_0) T^2 | \Phi \rangle \\ - \frac{1}{3} \text{Re} \langle \Phi | T^\dagger (H_0 - E_0) T^\dagger T^2 | \Phi \rangle \\ - \frac{1}{3} \langle \Phi | T^\dagger (H_0 - E_0) T | \Phi \rangle \langle \Phi | T^\dagger T | \Phi \rangle \end{aligned} \quad (9.6)$$

Finally, we also consider the CPF functional (8.10).

Let us assume that the additional terms to  $F_0(S)$  are so small that it is sufficient to make  $F_0(S)$  stationary with respect to variation of  $S$  and to evaluate the corrections in terms of this  $S$ . Then we can use the fact that

$$\langle \Phi | HS + S^\dagger H | \Phi \rangle + 2 \langle \Phi | S^\dagger HS | \Phi \rangle - 2 \langle \Phi | S^\dagger S | \Phi \rangle \langle \Phi | H | \Phi \rangle = 0 \quad (9.7)$$

to simplify the VCC(5) and VUCC(5) expressions.

$$\begin{aligned} \text{VCC(5)D: } E_5 = & F_0(S) + \text{Re} \langle \Phi | S^\dagger H S^2 - S^\dagger S H S | \Phi \rangle \\ & + \frac{1}{4} \langle \Phi | S^{\dagger 2} (H - E_0) S^{\dagger 2} | \Phi \rangle \end{aligned} \quad (9.8)$$

$$\begin{aligned} \text{VUCC(5)D: } E_5 = & F_0(T) + \text{Re} \langle \Phi | \frac{2}{3} T^\dagger H T^2 - T^\dagger T H T | \Phi \rangle \\ & + \frac{1}{4} \langle \Phi | T^{\dagger 2} (H - E_0) T^2 | \Phi \rangle \\ & - \frac{1}{3} \text{Re} \langle \Phi | T^\dagger (H - E_0) T^\dagger T^2 | \Phi \rangle \end{aligned} \quad (9.9)$$

We see that in (9.2), (9.8) and (9.9) the contribution

$$- \text{Re} \langle \Phi | S^\dagger S H S | \Phi \rangle = \langle \Phi | S^\dagger S | \Phi \rangle \text{Re} \langle \Phi | H S | \Phi \rangle \quad (9.10)$$

is the same (except for the fact that in TCC the ‘*Re*’ is missing), while the term  $\langle \Phi | S^\dagger H S^2 | \Phi \rangle$  appears with different factors and there are additional terms in  $S^{\dagger 2} S^2$  or  $T^{\dagger 2} T^2$  in (9.8) and (9.9). In the case where TCC is exact, the term  $\langle \Phi | S^\dagger H S^2 | \Phi \rangle$  vanishes and so the three expressions TCC, VCC(4) agree except for the terms in  $S^{\dagger 2} S^2$  or  $T^{\dagger 2} T^2$ . CPF also agrees with TCC for this case.

From the point of view the error analysis we have

$$\begin{aligned} \text{CEPA-0: } & O(S^4) + O(\delta^2) \\ \text{TCC-D, CPF-D: } & O(S^2) \cdot O(\delta) \\ \text{VCC(5)D; UCC(5)D: } & O(S^6) + O(\delta^2) \end{aligned}$$

All errors are linear in  $n$ . Which approach is the most accurate? Of course,  $\delta$  is determined by the neglect of triple substitutions which are of  $O(S^2)$ , and hence the error for all methods discussed here is of  $O(S^4)$ . In the special case that single and triple (and higher) substitutions don’t contribute at all,  $\delta = 0$  and TCC as well as CPF are best, since they become exact, while VCC(5) or VUCC(5) are not bad with an error  $O(S^6)$ ; CEPA-0 is the worst, with an error  $O(S^4)$ . Consider an intermediate case of weakly coupled pairs where  $\delta$  does not vanish but is very small, say  $\delta = O(S^3)$ ; in this case VCC(5) or VUCC(5) are best with an error of  $O(S^6)$ , while TCC has only an error  $O(S^5)$ . VUCC(5) should generally be better than VCC(5) since VUCC converges faster than VCC.

The main conclusion is that in a coupled-cluster treatment limited to  $S = S_2$  all methods discussed here – except CEPA-0 – are of comparable quality. Depending on the case one may be slightly better than the other. In spite of its asymmetry TCC is quite competitive, at least for energy calculations. For other properties the situation changes somewhat (see Sect. 12).

From the point of view of the computational effort CEPA-0 is cheaper than TCC-D, and TCC-D is cheaper than the other schemes discussed here. However all approaches scale with  $N_{it} \cdot n^6$  where  $N_{it}$  is the number of iterations and  $n$  the dimension of the basis (see Sect. 12), so the computational effort should not differ significantly.

## 10. Coupled-cluster methods with single and double substitutions (CCSD)

Since both  $S_1$  and  $S_3$  are of  $O(S^2)$  it does not appear to be very consistent to include  $S_1$  (in addition to  $S_2$ ) but to ignore  $S_3$ . There are, nevertheless, a few arguments in favour of a CCSD approach.

1.  $S_1$  is computationally much cheaper than  $S_3$ .
2. For properties  $S_1$  is (unlike  $S_3$ ) much more important than for the energy, and as important as  $S_2$ .

3. The Hartree–Fock reference function  $\Phi$  can be regarded as accounting for  $S_1$  to infinite order (in the absence of  $S_2$ ,  $S_3$  etc.), i.e. one has from the outset treated single excitations in a privileged way. This has been possible since  $e^{S_1}$  applied to a Slater determinant yields another Slater determinant (this trivial statement is often referred to as Thouless' theorem). So there is some point in treating  $S_1$  in a privileged way even in the presence of  $S_2$ .

4. If  $\Phi$  is not the Hartree–Fock function,  $S_1$  is very important and has to be included. One may want to have a theory that does not require this special choice of  $\Phi$ . However, the simplifications proposed in view of the smallness of  $S_1$  are then not valid.

5. In the open-shell case, where the Brillouin theorem holds in a limited way only, some single excitations are necessary even to lowest order.

In principle we could study the same methods as in Sect. 9, but there is not too much point in repeating everything now with  $S = S_1 + S_2$ . Since  $S_3$  is neglected, the error  $\delta$  is of  $O(S^2)$ , and hence the overall error of all methods is of  $O(S^4)$  – scaling linearly with  $n$ . By inclusion of  $S_1$  one can only hope to get a part of the contribution  $O(S^4)$ . As will be pointed out in Sect. 11, the error of TCC-SDT is of  $O(S^5)$ , while with ICC-SDT, VCC(5)-SDT, UVCC(5)-SDT one achieves an error  $O(S^6)$ . On the SD level it does not make sense to go beyond TCC-SD, except in special cases where  $S_1$  is much more important than  $S_3$ ; however, then an approach based on Brueckner orbitals may be preferable.

CEPA-0 with inclusion of single substitutions, which may also be referred to as LCC-SD, is characterized by

$$\begin{aligned} \text{LCC-SD: } F_0(S_1, S_2) = & \langle \Phi | H + HS_1 + S_1^\dagger H + HS_2 + S_2^\dagger H + S_2^\dagger [H, S_2] \\ & + S_1^\dagger [H, S_2] + S_2^\dagger [H, S_1] + S_1^\dagger [H, S_1] | \Phi \rangle \quad (10.1) \end{aligned}$$

Often one can omit those contributions that vanish by virtue of the Brillouin theorem, i.e.  $\langle \Phi | HS_1 + S_1^\dagger H | \Phi \rangle$ . The TCC-SD [5c] functional has extra contributions in addition to (10.1)

$$\begin{aligned} \text{TCC-SD: } F(S_1^\dagger, S_2^\dagger) = & F_0(S_1^\dagger, S_2^\dagger) + \langle \Phi | \frac{1}{2}(1 + S_1^\dagger + S_2^\dagger)HS_1^\dagger \\ & + (S_1^\dagger + S_2^\dagger)H(S_1 S_2 + \frac{1}{6}S_1^3) \\ & + S_2^\dagger H(\frac{1}{2}S_2^2 + \frac{1}{2}S_1^2 S_2 + \frac{1}{24}S_1^4) | \Phi \rangle \quad (10.2) \end{aligned}$$

We argued at the beginning of this section that there is no point in going beyond terms of  $O(S^4)$  as long as we neglect  $S_3$ . Neglecting terms of higher order than  $O(S^4)$  we are left with

$$\text{SCC-SD: } F(S_1^\dagger, S_2^\dagger) = F_0(S_1^\dagger, S_2^\dagger) + \langle \Phi | \frac{1}{2}HS_1^\dagger + S_2^\dagger HS_1 S_2 + \frac{1}{2}S_2^\dagger HS_2^2 | \Phi \rangle \quad (10.3)$$

where SCC stands for 'simplified coupled-cluster'.

It is interesting to compare this with other simplified CC-SD approaches proposed in the literature. The most recent and most popular one is Pople et al.'s 'quadratic CI' [23a], which corresponds to the following functional

$$\text{QCISD: } F(S_1^\dagger, S_2^\dagger) = F_0(S_1^\dagger, S_2^\dagger) + \langle \Phi | S_1^\dagger HS_1 S_2 + \frac{1}{2}S_2^\dagger HS_2^2 | \Phi \rangle \quad (10.4)$$

QCISD misses the terms  $\frac{1}{2}HS_1^\dagger$  and  $S_2^\dagger HS_1 S_2$  which are of  $O(S^4)$  while it contains the term  $S_1^\dagger HS_1 S_2$  that is of  $O(S^5)$ . As to the controversy on QCI, both concerning the name and the quality of this approximation see [23b,c].

The CPMET-C approximation which Paldus et al. [2c] proposed long ago does contain  $\frac{1}{2}HS_1^2$  and  $S_2^\dagger HS_1 S_2$  but differs from (10.3) in containing the  $O(S^5)$  contribution  $S_1^\dagger HS_1 S_2$ . Another old approximation, called CCSD-1 [5a], differs from (10.4) in the neglect of the  $S_1^\dagger HS_1 S_2$  term.

There have been numerical studies comparing QCISD with TCC-SD [16], which indicate that QCISD is often a valid approximation to TCC-SD, namely in those cases where the reference function does not suffer from near degeneracy with some other Slater determinants. It remains to be seen whether SCC-SD as defined by (10.3) is superior to QCISD. Anyhow the computational costs of TCC-SD, SCC-SD and QCISD are not significantly different. Of course, as pointed out before, QCISD is one of many simplified coupled-cluster treatments and the name 'quadratic CI' may be misleading [23].

## 11. Coupled-cluster methods including single and triple substitutions (CCSDT)

In this section we choose

$$S = S_1 + S_2 + S_3 \quad (11.1)$$

The functional (4.13) to be made stationary with respect to variation of  $S^\dagger$  in traditional coupled-cluster theory is then

$$\begin{aligned} \text{TCC-SDT: } E = \langle \Phi | & (1 + S_1^\dagger + S_2^\dagger) H (1 + S_1 + S_2 + \frac{1}{2} S_1^2) \\ & + (S_1^\dagger + S_2^\dagger + S_3^\dagger) H (S_3 + S_1 S_2 + \frac{1}{6} S_1^3) \\ & + (S_2^\dagger + S_3^\dagger) H (\frac{1}{2} S_2^2 + S_1 S_3 + \frac{1}{2} S_2 + \frac{1}{24} S_1^4) \\ & + S_3^\dagger H (S_1 + S_2 + \frac{1}{2} S_1^2 + S_2 S_3 + \frac{1}{2} S_1^2 S_3 + \frac{1}{2} S_1 S_2^2 \\ & + \frac{1}{6} S_1^3 S_2 + \frac{1}{120} S_1^5) | \Phi \rangle_L \end{aligned} \quad (11.2)$$

and as shown earlier, the error is of  $O(S^5)$ . Hence, it does not make much sense to consider contributions to (11.2) that are of higher order in  $S$ : if we keep only terms up to  $O(S^4)$ , then the error will still be  $O(S^5)$ . Noting that  $S_1 = O(S^2)$ ,  $S_3 = O(S^2)$  we get the simplified coupled cluster functional

$$\begin{aligned} \text{SCC-SDT: } E = \langle \Phi | & (1 + S_1^\dagger + S_2^\dagger) H (1 + S_1 + S_2) + \frac{1}{2} H S_1^2 \\ & + (S_1^\dagger + S_2^\dagger + S_3^\dagger) H S_3 + S_2^\dagger H (S_1 S_2 + \frac{1}{2} S_2^2) \\ & + S_3^\dagger H (S_1 + S_2 + \frac{1}{2} S_2^2) | \Phi \rangle \end{aligned} \quad (11.3)$$

Again we can compare with other simplified methods in current use, such as the CCSDT- $k$  methods ( $k = 1, 2, 3$ ) of Bartlett and coworkers [5g,i,j]. All CCSDT- $k$  variants start (implicitly) from the full TCC-SDT functional, but the contributions with  $S_3^\dagger$  on the left side are replaced by

$$\langle \Phi | S_3^\dagger (H_0 S_3 + H S_2) | \Phi \rangle \text{ in CCSDT-1} \quad (11.4a)$$

$$\langle \Phi | S_3^\dagger (H_0 S_3 + H S_2 + \frac{1}{2} H S_2^2) | \Phi \rangle \text{ in CCSDT-2} \quad (11.4b)$$

$$\langle \Phi | S_3^\dagger [H_0 S_3 + H \exp(S_1 + S_2)] | \Phi \rangle \text{ in CCSDT-3} \quad (11.4c)$$

where  $H_0$  is the one-electron part of  $H$ . In view of our analysis these approximations are somewhat unbalanced. Nevertheless they have turned out to be quite powerful and usually only slightly inferior to full TCC-SDT [5i]. The merit of

CCSDT- $k$  is that the computer time scales with  $N_{it} \cdot n^7$  rather than  $N_{it} \cdot n^8$  as in full CCSDT (see Sect. 12).

Other methods correct to  $O(S^4)$  are the XCC(4) or UCC(4) approaches by Bartlett et al. [25]. Our VCC and UCC truncation at  $k = 3$  which would define VCC(4)SDT or VUCC(4)SDT is unbalanced and nor recommended.

If we want an error  $O(S^6)$  we may use TCC-SDTQ including  $S_4$  (which would even imply an error  $O(S^7)$ , see Table 1). It is simpler to use ICC(2)SDT, ECC(2)SDT, VCC(5)SDT or VUCC(5)SDT. In these schemes one achieves an accuracy  $O(S^6)$  without the need to include  $S_4$ .

The numerator of the ICC(2)SDT functional (5.5b) becomes

$$\langle \Phi | \left( 1 + S^\dagger + \frac{1}{2} S^{\dagger 2} \right) H \left( 1 + S + \frac{1}{2} S^2 + \cdots + \frac{1}{8!} S^8 \right) | \Phi \rangle \quad (11.5)$$

with  $S$  of the form (11.1). At first glance this looks terrible. However, the term  $S^8$  on the right only involves  $S_1$  and arises for  $S_3^{\dagger 2}$  on the left. Such terms are of  $O(S^{10})$  and certainly negligible. The requirement that the error should be of  $O(S^6)$  eliminates the majority of terms in (11.5) and we get the following extra contributions due to the  $S^{\dagger 2}$  factors in (11.5)

$$\begin{aligned} & \langle \Phi | \frac{1}{2} S_1^{\dagger 2} H (1 + S_2) + S_1^\dagger S_2^\dagger H (S_1 + S_2 + S_3 + \frac{1}{2} S_2^2) + S_1^\dagger S_3^\dagger H S_2 \\ & + \frac{1}{2} S_2^{\dagger 2} H (S_2 + S_3 + S_1 S_2 + \frac{1}{2} S_2^2 + S_2 S_3 + \frac{1}{6} S_3^2) + S_2^\dagger S_3^\dagger H (S_3 + \frac{1}{2} S_2^2) | \Phi \rangle \quad (11.6) \end{aligned}$$

It is convenient to represent the overall energy numerator (with a similar denominator) in tabular form, as seen in Table 2. One may refer to this approach with the error  $O(S^6)$ , which is accurate to at least fifth order of perturbation theory, as simplified improved coupled-cluster, but we regard the simplification as part of the improvement and simply call it ICC.

Now we must compare this with VCC(5) or VUCC(5) including  $S_3$  (or  $T_3$ ). We only take the former (as to the latter see Eq. (7.27)).

$$\begin{aligned} \text{VCC(5)SDT: } E = Re \langle \Phi | & H + 2HS_1 + 2HS_2 + HS_1^\dagger + S_1^\dagger HS_1 \\ & + 2S_1^\dagger HS_2 + 2S_1^\dagger HS_3 + 2S_2^\dagger HS_1 S_2 + S_2^\dagger HS_2 + 2S_2^\dagger HS_3 \\ & + S_2^\dagger HS_1^2 + S_2^\dagger HS_2^2 + 2S_2^\dagger HS_1 S_2 + 2S_2^\dagger HS_1 S_3 \\ & + S_3^\dagger HS_3 + S_3^\dagger HS_1^2 + 2S_3^\dagger HS_1 S_2 + 2S_3^\dagger HS_2 S_3 \\ & + \frac{1}{4} S_2^\dagger HS_2^2 + S_2^{\dagger 2} HS_1 S_2 + S_2^{\dagger 2} HS_2 S_3 | \Phi \rangle_L \quad (11.7) \end{aligned}$$

The terms in (11.7) differ from the numerator of ICC(2)SDT as given in Table 2 in only two ways: (a) the index  $L$  (for linked) in (11.7), and (b) the presence of the term  $\frac{1}{12} S_2^{\dagger 2} HS_2^3$  in ICC but not in VCC. This term is, in fact of  $O(S^6)$  because  $S_2^{\dagger 2} H_0 S_2^3$  vanishes. The existence of this term in ICC but not in VCC, reminds one of the occurrence of the  $S^\dagger HS^2$  term in TCC-D but not VCC(3) (which is identical with CEPA-0). An advantage of (11.7) is that it can be minimized directly, while for ICC we have a functional with a denominator whose minimization requires the introduction of Lagrange multipliers, i.e. a pseudoeigenvalue problem.

For an error of  $O(S^6)$  we recommend to use a VCC theory based on (11.7) or a UCC theory based on the corresponding VUCC(5) expression (7.27). The latter leads to a slightly more complicated functional, but the result should be more accurate due to the faster convergence of UCC in powers of  $S$ . The only advantage of ICC is that like TCC it is exact for a supersystem of non-interacting

**Table 2.** Representation of the ICC and VCC(5) functionals with  $S = S_1 + S_2 + S_3$ 

	1	$S_1$	$S_2$	$S_3$	$\frac{1}{2}S_1^2$	$\frac{1}{2}S_2^2$	$S_1S_2$	$S_1S_3$	$S_2S_3$	$\frac{1}{6}S_2^3$
1	×	×	×		×					
$S_1^\dagger$	×	×	×	×			×			
$S_2^\dagger$	×	×	×	×	×	×	×	×		
$S_3^\dagger$		×	×	×		×	×		×	
$\frac{1}{2}S_1^{\dagger 2}$	×		×							
$\frac{1}{2}S_2^{\dagger 2}$			×	×		×	×		×	(×)
$S_1^\dagger S_2^\dagger$		×	×	×		×				
$S_1^\dagger S_3^\dagger$			×							
$S_2^\dagger S_3^\dagger$				×		×				

The left entry refers to operators on the left of  $H$  in the numerator for ICC, the upper entry to operators on the right of  $H$ , a × means that the respective term is present, e.g.  $\langle \Phi | S_1^\dagger H S_1 S_2 | \Phi \rangle$ . The same terms arise in the denominator for ICC, but with  $H$  omitted. For VCC there is no denominator and a subscript  $L$  has to be added. The term (×) is only present in ICC

two-electron systems, which VCC is not. However, the very fact that one wants to include  $S_1$  and  $S_3$  indicates that one does not deal with such a special supersystem (for which  $S_1 = S_3 = 0$ ) and the question of whether this would be described accurately is rather irrelevant. To describe such a system better than real ones may even lead to some undesired imbalance. The more that one wants to push the accuracy the more TCC loses with respect to ICC, VCC or UCC.

## 12. Comments on the computational effort

If we consider only double-excitation operators, then a matrix element  $\langle \Phi | X_\mu^\dagger V X_\nu | \Phi \rangle$  is characterized by 6 orbital labels (some of which may coincide): 4 labels for either  $X_\mu^\dagger$  or  $X_\nu$ , but they must not differ in more than two labels. Generally for  $X_\mu$  and  $X_\nu$   $p$ -particle excitation operators the corresponding matrix element has  $2p + 2$  orbital labels. In iterative CI theory (with  $N_{it}$  the number of iterations) one must sum over all labels, which means that for CI-SD the term-determining step goes as  $N_{it}n^6$ , for CI-SDT as  $N_{it}n^8$  and for CI-SDTQ as  $N_{it}n^{10}$ . The same dependence holds for an iterative approach to the solution of the coupled-cluster equations. The additional terms in the CC equations that involve products of  $S$  operators can be factorized (i.e. one need not sum over all labels simultaneously) and have a weaker  $n$ -dependence. The matrix elements of  $H_0$  require one order of  $n$  less (since  $X_\mu$  and  $X_\nu$  must at most differ in one orbital label).

If one wants to compare the computer times for different molecules with basis sets of the same quality, it is the overall  $n$ -dependence just described that matters, since the numbers  $n_{occ}$  of occupied orbitals and  $n_{virt}$  of virtual orbitals are essentially proportional. If one considers a single molecule and keeps  $n_{occ}$  fixed, but varies the size of the basis, one should discriminate between the dependence on  $n_{occ}$  and  $n_{virt}$ , with  $n_{virt} \gg n_{occ}$ . The rate-determining matrix elements are then those with  $p$  hole labels and  $p + 2$  particle labels, i.e. we have  $N_{it}n_{occ}^2 n_{virt}^4$  for CI-SDT and  $N_{it}n_{occ}^3 n_{virt}^5$  for CI-SDTQ etc.

In ICC, ECC, VCC or UCC theory the  $n$ -dependence is essentially the same as in TCC up to the same excitation level, since again the contributions with

products of  $S$  operators in the matrix elements have a lower  $n$ -dependence. This means that for TCC-SDT, which is correct to  $O(\lambda^4)$  and in, for example, VCC(5)-SDT correct to  $O(\lambda^5)$  the same  $n$ -dependence holds, namely  $N_{it} \cdot n^8$ . Analogously TCC-SDTQ, correct to  $O(\lambda^6)$  and VCC(7)-SDT correct to  $O(\lambda^7)$  require both  $n_{it} \cdot n^{10}$ .

In TCC theory one is somehow obliged to iterate the CC equations to self-consistency, because these equations, (1.3b), represent the stationary conditions and the simplified energy expression (1.3a) only holds if (1.3b) is solved exactly. If one has not done so and nevertheless uses (1.3a), one makes an error (3.13) of the energy that is only linear in the error of  $S$ . One is then better off if one evaluates the energy from (4.6) or (4.10) because these expressions are controlled by the error estimate (4.7) or (4.8) irrespective of whether these expressions have been made stationary. On this basis approaches can be justified in which one does not satisfy the stationarity condition exactly and nevertheless gets reliable results.

In this philosophy VCC and UCC approaches are the most natural frame. Let us, for example, start from VCC(3)SD and determine  $S_1$  and  $S_2$  on this level accurately. We then take the VCC(5)SDT functional, insert the formerly determined  $S_1$  and  $S_2$  and perform one single iteration for  $S_3$ . Finally we evaluate  $E$  from the VCC(5) functional. So one avoids multiplying the rate determining  $n^8$  step by the factor  $N_{it}$ . However, if one does not satisfy the stationarity conditions exactly one should not evaluate the energy from an expression which only holds when the stationarity condition is satisfied.

### 13. Properties

So-called first order properties like the dipole moment can be defined either as expectation values or as derivatives of the energy with respect to some parameter (the dipole moment is the gradient of the energy with respect to the strength of an external field) while second order properties are defined as second derivatives of the energy or first derivatives of expectation values.

In terms of exact wave functions the alternative definitions are equivalent. Let  $\Omega$  be some operator associated with a property and let

$$H_\lambda = H_0 + \lambda\Omega; \quad H_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda \quad (13.1)$$

then

$$\left(\frac{\partial E}{\partial \lambda}\right)_{\lambda=0} = \langle \Psi | \Omega | \Psi \rangle \quad (13.2)$$

which is known as Hellmann–Feynman theorem. From (13.1) it also follows that

$$\left(\frac{\partial^2 E}{\partial \lambda^2}\right)_{\lambda=0} = \text{Re} \langle \Psi | \Omega | \Psi^{(1)} \rangle \quad (13.3)$$

where  $\Psi^{(1)}$  is the solution of

$$(H_0 - E_0)\Psi^{(1)} = (\Omega - \langle \Psi | \Omega | \Psi \rangle)\Psi \quad (13.4a)$$

and satisfies the intermediate normalization condition

$$\langle \Psi | \Psi^{(1)} \rangle = 0 \quad (13.4b)$$

Neither (13.2) nor (13.3/4) hold generally for an approximate wave function and one gets different results from the alternative definitions, i.e. the left hand side or right hand side of (13.2) or (13.3).

It has been pointed out mainly by Sadlej [41] that the energy derivatives are generally preferable to expectation values. On the other hand expectation values are more easily calculated and numerically more stable. It is therefore preferable to use methods where the two expressions agree. This is not only the case for exact wave functions, but also in the framework of 'stationary perturbation theory' [42] (for its formulation in the more traditional framework see e.g. [43]). The main idea of stationary perturbation theory [42] is to require

$$\delta \langle \Phi(\lambda) | H + \lambda \Omega | \Phi(\lambda) \rangle = 0 \quad \forall \lambda, \quad \langle \Phi(\lambda) | \Phi(\lambda) \rangle = 1 \quad (13.5)$$

We describe norm-conserving variations of  $\Phi$  as

$$\Phi \rightarrow \Phi' = e^X \Phi; \quad X = -X^\dagger \quad (13.6)$$

for a set of operators  $X$  that constitute a Lie algebra, which leads to the Brillouin condition

$$\langle \Phi | [H, X] | \Phi \rangle = 0 \quad (13.7)$$

equivalent to the stationarity requirement (13.5). The dependence of  $\Phi(\lambda)$  on  $\lambda$  is formulated as

$$\Phi(\lambda) = e^{Y(\lambda)} \Phi_0; \quad Y(\lambda) = \sum_{k=0}^{\infty} \lambda^k Y_k \quad (13.8)$$

where  $Y(\lambda)$  is an element of the Lie algebra of operators for which the Brillouin theorem (13.7) holds. From (13.5) and (13.8) we easily get

$$E = \sum_{k=0}^{\infty} \lambda^k E_k \quad (13.9a)$$

$$E_1 = \langle \Phi_0 | \Omega | \Phi_0 \rangle \quad (13.9b)$$

$$E_2 = \frac{1}{2} \langle \Phi_0 | [\Omega, Y_1] | \Phi_0 \rangle \quad (13.9c)$$

where  $Y_1$  is solution of

$$\langle \Phi_0 | [\Omega, X] + [[H_0, X], Y_1] | \Phi_0 \rangle = 0 \quad (13.10)$$

or is equivalently determined by the requirement that  $Y_1$  minimizes the generalized Hylleraas functional

$$\delta \langle \Phi_0 | [\Omega, Y_1] + \frac{1}{2} [[H_0, Y_1], Y_1] | \Phi_0 \rangle = 0 \quad (13.11)$$

A well-known special case of stationary perturbation theory is coupled Hartree–Fock (CHF) where the Lie algebra  $\{X\}$  consists of the antihermitean linear combinations of the one particle excitation operators  $a_p^q = a_q^\dagger a_p$ . Not only the Hellman–Feynman theorem (13.9b) holds, but also the equivalence between the dipole-length and dipole-velocity formulas for transition matrix elements – at least in the limit of a complete one-electron basis [42].

In view of our error analysis we note that the error of an energy expectation value is quadratic in the error of the wave function; hence a first order property calculated as the derivative of an energy expectation value has an error quadratic in the error of the wave function. This is not the case for a property calculated as an expectation value unless the Hellman–Feynman theorem holds, i.e. in stationary perturbation theory.

These observations make methods based on stationary conditions for the energy preferable for the calculation of properties. Truncated VCC or UCC expressions, even CEPA-0, are in this sense nearly as good as genuine expectation values. Traditional coupled cluster on the other hand, neither fulfills a Hellman–Feynman theorem, nor provides a convenient way to expectation values. Here the standard procedure [44] is equivalent to making the TCC functional (4.13) in the presence of a perturbation  $\lambda V$

$$E[S^\dagger, \lambda] = \langle \Phi | [1 + S^\dagger(\lambda)] e^{-S(\lambda)} (H + \lambda V) e^{S(\lambda)} | \Phi \rangle \quad (13.12)$$

stationary with respect to variation of  $S^\dagger(\lambda)$ . Alternatively one may also consider  $\Phi$  as dependent on  $\lambda$ . This would imply that one first performs a coupled Hartree–Fock calculation in order to determine  $\Phi(\lambda)$  and then performs a CC calculation to include correlation effects. In this case  $S(\lambda)$  is determined by double excitations as in usual CC, since a  $\lambda$ -dependent Brillouin theorem holds. If one takes  $\Phi$  independent of  $\lambda$ , then the necessary change of  $\Phi$  appears in the  $S(\lambda)$  which then has a large proportion of single excitations.

The error or properties obtained from (13.12) is of the same kind as the error of the energy i.e. something like (4.7) holds.

We have stressed several times that due to the Brillouin theorem the correlation operator  $S$  or  $T$  is dominated by double excitations and that the influence of single excitations on the energy is small – of similar size to that of triple excitations. This is true as far as the energy is concerned, but not for properties unless one satisfies a Brillouin theorem for all  $\lambda$ , which one usually does not.

Imagine that we wish to calculate a one-electron property by double perturbation theory where  $H_{10}$  is the operator associated with this property while  $H_{01}$  accounts for correlation

$$H = H_0 + \lambda H_{10} + \mu H_{01} \quad (13.13)$$

Then as usual the property without correlation is

$$E_{10} = \langle \Phi_0 | H_{10} | \Phi_0 \rangle \quad (13.14a)$$

while the first-order correlation correction is

$$E_{11} = Re \langle \Phi_0 | H_{10} | \Phi_{01} \rangle = Re \langle \Phi_0 | H_{01} | \Phi_{10} \rangle \quad (13.14b)$$

This vanishes if  $\Phi_{01} = 0$  in view of the Brillouin condition at  $\lambda = 0$ . The second-order correlation correction to this property is

$$E_{12} = \langle \Phi_{01} | H_{10} | \Phi_{01} \rangle + Re \langle \Phi_0 | H_{10} | \Phi_{02} \rangle \quad (13.14c)$$

This is not determined by the first-order correlation correction  $\Phi_{01}$  to the wave function alone, but also by the second order one  $\Phi_{02}$ . On the other hand, since  $H_{10}$  is a one-electron operator, only the single excitations contained in  $\Phi_{02}$  contribute. Although arising first to second order, these are as important as the double excitations that already contribute to first order.

What one would like to have is a kind of ‘coupled coupled-cluster’ approach where the first ‘coupled’ is understood in the same sense as coupled Hartree–Fock, i.e. one starts from (13.5) with  $\Phi(\lambda)$  a coupled-cluster wave function, and applies stationary perturbation theory. In view of the Lie-algebraic structure of stationary perturbation theory, the UCC ansatz appears to fit best into this scheme. One must, of course, truncate the Hausdorff expansion. Let us truncate this after double commutators and let  $\sigma$  (independent of  $\lambda$ ) describe the

correlation part.  $H_0$  includes the electron interaction and we expand in powers of  $\lambda$ . One then gets

$$E_0 = \langle \Phi_0 | H_0 + [H_0, \sigma] + \frac{1}{2} [[H_0, \sigma], \sigma] | \Phi_0 \rangle \quad (13.15a)$$

which after making  $E_0$  stationary with respect to variation of  $\sigma$  leads to

$$E_0 = \langle \Phi_0 | H_0 + \frac{1}{2} [H_0, \sigma] | \Phi_0 \rangle \quad (13.15b)$$

For  $E_1$  we get

$$\begin{aligned} E_1 = & \langle \Phi_0 | \Omega + [H_0, Y_1] + \frac{1}{2} [[H_0, \sigma], Y_1] + \frac{1}{2} [H_0, Y_1], \sigma \\ & + [\Omega, \sigma] + \frac{1}{2} [[\Omega, \sigma], \sigma] | \Phi_0 \rangle \end{aligned} \quad (13.16)$$

The Brillouin theorem only removes  $[H_0, Y_1]$ . A Hellman–Feynman theorem holds if

$$\langle \Phi_0 | [H_0, X] + \frac{1}{2} [[H_0, \sigma], X] + \frac{1}{2} [[H_0, X], \sigma] | \Phi_0 \rangle = 0 \quad (13.17)$$

which is, in fact, the lowest order Brillouin–Brueckner condition. If (13.17) is satisfied, then (13.16) becomes

$$E_1 = \langle \Phi_0 | \Omega + [\Omega, \sigma] + \frac{1}{2} [[\Omega, \sigma], \sigma] | \Phi_0 \rangle \quad (13.18)$$

which is a (truncated) expectation value with a correlated wave function. Under the same condition the second-order expression becomes

$$E_2 = \langle \Phi_0 | [\Omega, Y_1] + \frac{1}{2} [[\Omega, \sigma], Y_1] + \frac{1}{2} [[\Omega, Y_1], \sigma] + \frac{1}{2} [[H_0, Y_1], Y_1] | \Phi_0 \rangle \quad (13.19)$$

which is a kind of Hylleraas functional (13.10), essentially with  $\Omega$  replaced by  $\Omega + [\Omega, \sigma]$ .

It should be mentioned that Bartlett et al. [25] have proposed their hierarchy of expectation value coupled cluster (XCC) methods mainly for the evaluation of properties, and have applied this successfully. One of the motivations of Arponen et al. [19] to replace TCC by ECC has also been to get better approximations for properties.

#### 14. Beyond single Slater determinant reference functions

Throughout this paper we have assumed that the reference wave function is a single closed-shell Slater determinant. Some results are certainly generalizable to the open-shell or multiconfiguration reference case, though this generalization is usually not trivial.

The nice property related to closed-shell reference wave functions is that we have only two types of one-particle states (occupied vs unoccupied or particles vs holes) such that the various basis excitation operators  $X_k$  (from which  $S$  or  $T$  is constructed) commute and the wave operator can easily be formulated in intermediate normalization. This property is lost for more general reference functions.

The present state of affairs appears to be that a consistent separable coupled cluster theory in the open-shell case is not possible for a single state, but only in a valence-universal way which means that a manifold of states have to be taken together [45]. This creates new problems related to intruder states. These can be avoided if one introduces incomplete model spaces, but this creates new problems of a different kind [46]. CEPA-0 type improvements of MC-SCF theory

have turned out to be successful [5e, 30] while MBPT2 based on MC-SCF [47] appears to be less satisfactory.

Under these circumstances it appears to be too difficult at the moment to apply the present analysis to the open-shell case. However, the author is convinced that this will be helpful for finding out what one should really do in the open-shell or multiconfiguration case, in order to get a minimal error for a tolerable computational effort.

On the other hand, even for closed-shell states it may not be the most economic approach to start from a Hartree–Fock reference function and apply a coupled-cluster method up to high excitation rank; rather, it may be preferable first to perform an MC-SCF calculation and then use a coupled-cluster ansatz with low excitation rank. Therefore a careful study of CC superimposed on MC-SCF is badly needed.

## 15. Conclusions

The main messages of this paper are as follows.

1. The traditional method of moments (of projected Schrödinger equations) is not necessarily the best way to construct coupled-cluster wave functions.
2. The traditional approach is equivalent to a stationarity condition for a certain functional  $F(S^\dagger)$  with respect to variation of  $S^\dagger$  (not with respect to  $S^\dagger$  and  $S$  as in variational theories). Other functionals to be made stationary can be defined. These correspond to improved CC (ICC), extended CC (ECC), variational CC (VCC) or unitary CC (UCC), truncated at various orders in powers of  $S$  (or  $T$ ).
3. The derivation of TCC and the other CC variants from stationarity conditions on energy functionals gives additional insight and has other advantages. Such a functional is, for example, a valid approximation to the energy of a state even if it is only approximately stationary. Functionals symmetric in  $S$  and  $S^\dagger$  are superior to asymmetric ones, because then stationarity with respect to variation of  $S^\dagger$  implies stationarity with respect to variation of  $S$  and vice versa.
4. The error of the energy in any of these CC approaches depends sensitively on the functional chosen. All error estimates depend on the error  $\delta$  of  $S$ , and on  $S$  itself. The ideal error estimate  $O(\delta^2)$  holds for (untruncated) variational or unitary coupled cluster. In VCC or UCC (truncated at  $k$ th order in  $S$  (or  $T$ )) there is an additional error term  $O(S^{k+1})$ . Traditional coupled cluster has an error of the form  $O(\delta)f(\delta, S)$ , i.e. the error vanishes if  $\delta = 0$ .
5. TCC is much better than one might have guessed and on the level where one includes single and double excitations (TCC-SD) it is hard to beat. The other CC schemes win if one wants to push the theory to high performance. For an accuracy beyond that of TCC-SDT it is more economic to switch to ICC(2)-SDT or VCC(5)-SDT rather than to go to TCC-SDTQ.
6. In TCC there is only a hierarchy based on the excitation rank, i.e. on whether one includes  $S_2$ ,  $S_2 + S_1 + S_3$  etc. In VCC or UCC there is a second hierarchy based on the truncation order. However, it is straightforward to combine the hierarchies in a consistent way. Truncated VCC or UCC can be improved by summing certain terms in a CPF-type way to infinite orders.

7. For properties it is very important to start from the energy functionals that are stationary in the presence of the perturbation. Single excitations become much more important than for the energy.

8. In CC methods, especially those where one does not have to rely on satisfying a stationarity condition exactly, simplifications are often possible which consist in neglecting contributions that are of higher order than the overall accuracy of the scheme. In a method correct to  $O(S^3)$  it will usually not pay to include terms of say  $O(S^5)$ . However, this argument can become dangerous in some cases. If one ignores all terms beyond some  $O(\lambda^k)$  one arrives at strict perturbation theory, which one wants to avoid since the superiority of CC over PT consists in summing certain classes of diagrams to infinite order. Also, according to the error analysis CEPA-0 and CC-SD are of the same order, but CC-SD is often much better, especially in cases of near degeneracy where  $S$  is particularly large.

We close with a general remark. Whenever one introduces a new approximate quantum chemical *ab-initio* method or promotes an old one, it is customary first to give a list of qualities that a good approximative scheme should have and then to point out that the method to be promoted has the more important ones of the desired qualities. A typical list is that of Pople et al. [23a]. In the light of the present analysis there are – as far as the energy is concerned – actually only two qualities required. For a given computational effort that one can afford it should (a) have the smallest possible error, and (b) the error should be consistent for isomers of one molecule, for a displacement along the reaction coordinate, or for different systems that one wants to compare. The consistency of the error is dependent on the computational algorithm chosen, but depends even more on the basis set – a point which is not always fully appreciated [48, 49]. The error of the energy is small if it goes quadratically with the error of the wave function and if it scales linearly with the number of particles. Either quality by itself is less important than a good compromise between the two.

In the introduction to this paper we have pointed out that one should not overestimate the importance of the variation principle. Now we must add that one should not overestimate the importance of extensivity either, i.e. of the correct scaling with the particle number. Consistency along one potential surface is often more important than consistency between two calculations for different electron numbers. A dimerisation energy can always be obtained from a calculation of the dimer at its equilibrium distance and at a very large distance.

Exactness for the special case of non-interacting pairs is also much less important than is often claimed. It has even been found that this property leads to a bias in the description of interacting electron pairs [16] (like  $\text{Be}_n$  clusters).

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## Appendix A

### On the justification of the denominator (8.9)

We give here a plausibility argument rather than a rigorous proof for the approximate unitary invariance of the denominator (8.9). We first assume that

all localized pairs  $S_\mu$  are equivalent to each other in the sense that they have the same  $\epsilon_\mu$  and  $s_\mu^2$

$$\langle \Phi | HS | \Phi \rangle = \sum_{\mu=1}^n \langle \Phi | H^\mu S_\mu | \Phi \rangle = n\epsilon_\mu \tag{A.1a}$$

$$\langle \Phi | S^\dagger S | \Phi \rangle = \sum_{\mu=1}^n \langle \Phi | S^\mu S_\mu | \Phi \rangle = ns_\mu^2 \tag{A.1b}$$

For  $E^{(3)}$  as given by (8.4) we get

$$\begin{aligned} E^{(3)} &= 2 \sum'_{\mu,\nu} \langle \Phi | S^\mu H^\nu S_\mu S_\nu | \Phi \rangle - 2 \sum_{\mu,\nu} \langle \Phi | S^\mu S_\mu H^\nu S_\nu | \Phi \rangle \\ &= 2n(n-1)s_\mu^2\epsilon_\mu - 2n^2s_\mu^2\epsilon_\mu = -2ns_\mu^2\epsilon_\mu \\ &= -\frac{2}{n} \langle \Phi | S^\dagger S | \Phi \rangle \langle \Phi | HS | \Phi \rangle \end{aligned} \tag{A.2}$$

We now assume that there is a transformation to delocalized orbitals such that all spin-orbital pairs are equivalent in the sense

$$\langle \Phi | HS | \Phi \rangle = \sum_{i<j=1}^{2n} \langle \Phi | \bar{g}^{ij} S_{ij} | \Phi \rangle = n(2n-1)\epsilon_{ij} \tag{A.3a}$$

$$\langle \Phi | S^\dagger S | \Phi \rangle = \sum_{i<j=1}^{2n} \langle \Phi | S^{ij} S_{ij} | \Phi \rangle = n(2n-1)s_{ij}^2 \tag{A.3b}$$

Then in view of (A.2), we get for  $E^{(3)}$

$$E^{(3)} = -2n(2n-1)^2s_{ij}^2\epsilon_{ij} \tag{A.4}$$

The second term in (8.6) yields

$$-\sum'_{i,j} \langle \Phi | S^{ij} S_{ij} g^{ij} S_{ij} | \Phi \rangle = -2n(2n-1)s_{ij}^2\epsilon_{ij} \tag{A.5a}$$

and the third term in (8.6)

$$-\sum'_{i,j,k} \langle \Phi | S^{ij} S_{ij} (g^{ki} S_{ki} + g^{kj} S_{kj}) | \Phi \rangle = -4n(2n-1)(2n-2)s_{ij}^2\epsilon_{ij} \tag{A.5b}$$

One easily sees that (A.5a) plus half of (A.5b) yields (A.4). It is rather tedious to see directly that in this case the first term in (8.6) just cancels one half of the third term.

### Appendix B

We apply the philosophy behind ACC to the  $E^{(3)}$  as given by (7.7). We ignore labels and take the fully linked expression. Then we get 4 types of contributions to  $\langle \Phi | S^\dagger HS^2 | \Phi \rangle$ , namely

$$-c_{ij}^{ab} \bar{g}_{kl}^{cd} c_{ab}^{jl} c_{cd}^{ik} = -(\bar{g}_{kl}^{cd} c_{cd}^{ik})(c_{ij}^{ab} c_{ab}^{jl}) \tag{B.1}$$

$$-c_{ij}^{ab} \bar{g}_{kl}^{cd} c_{ac}^{ij} c_{bd}^{kl} \tag{B.2}$$

$$+c_{ij}^{ab} \bar{g}_{kl}^{cd} c_{ac}^{ik} c_{bd}^{jl} \tag{B.3}$$

$$+c_{ij}^{ab} \bar{g}_{kl}^{cd} c_{ed}^{ij} c_{ab}^{kl} = (\bar{g}_{kl}^{cd} c_{cd}^{ij})(c_{ij}^{ab} c_{ab}^{kl}) \tag{B.4}$$

For a 2-electron system (B.2) and (B.3) cancel, and there are reasons to assume that (B.2) and (B.3) are usually small. The EPV-contributions to (B.1) and (B.4) yield exactly the contributions to (8.6) which factorize. In keeping (B.1) and (B.4) one takes care of these contributions, but one has additional ones that guarantee unitary invariance. In some sense (B.1) and (B.4) factorize as well, namely as indicated (one can sum over particle indices in each factor in parentheses) but not in the simple form that allows for a summation of a geometrical series as is needed for the construction of a CPF theory.

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