COMPARISON OF THE BRILLOUIN–WIGNER COUPLED CLUSTER THEORY WITH THE STANDARD COUPLED CLUSTER THEORY. CANCELLATION OF DISCONNECTED TERMS IN THE BRILLOUIN–WIGNER COUPLED CLUSTER THEORY

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In our article (Hubac I., Neogrady P.: Phys. Rev. A *50*, 4558 (1994)) we have developed size-extensive Brillouin–Wigner coupled cluster (BWCC) theory. We have shown that the BWCC theory is fully equivalent to the standard coupled cluster theory. However, the BWCC theory does not obey the so-called linked cluster theorem. In this article we discuss the cancellation of disconnected terms in the BWCC theory.

Key words: Brillouin–Wigner perturbation theory; Coupled clusters; Size consistency; Linked cluster theorem.

The standard coupled cluster (CC) theory in its nondegenerate version for closed-shell systems represents one of the most efficient methods for the inclusion of correlation effects in atoms and molecules[1–13]. Nevertheless, its multireference version is far from being a standard method to account for correlation effects of generally open-shell systems. One of the main problems that the multireference coupled cluster (MR CC) theory as well as relative multireference many-body perturbation theory (MR MBPT) have to face to is the problem of intruder states which may even cause divergence of both theories. In our recent articles[14,15] we have developed the Brillouin–Wigner coupled cluster (BWCC) theory. We have shown that the BWCC theory is fully equivalent to the standard CC theory, but it differs by the fact that it does not employ the linked cluster theorem. Therefore, a question arises how it is with the cancellation of disconnected diagrams in the BWCC theory since we have shown that the BWCC theory is a size-extensive method. In this article we will discuss the cancellation of disconnected terms in the BWCC method in order to make clear the relation between the BWCC and standard CC theories. This question is also important with respect to possibility of multireference formulation of the BWCC theory.

THEORETICAL

The details of the BWCC theory were presented in our articles[14,15]. Here, we mention the main points again. The electronic Hamiltonian of an atomic or molecular system can be expressed in the second-quantized form as

$$\hat{H} = \sum_{PQ} \langle P\,|\hat{h}|\,Q\rangle\, \hat{X}_P^+ \hat{X}_Q + \frac{1}{2} \sum_{PQRS} \langle PQ\,|\hat{v}|\,RS\rangle\, \hat{X}_P^+ \hat{X}_Q^+ \hat{X}_S \hat{X}_R \ , \qquad (1)$$

where $\langle P\,|h|\,Q\rangle$ is a one-electron integral, $\langle PQ\,|v|\,RS\rangle$ is a two-electron integral and $\{P,Q,R,S,\ldots\}$ represents one-electron orthonormal basis set of spinorbitals on which we define the system of creation ($\hat{X}_P^+$) and annihilation ($\hat{X}_P$) operators. Using the hole-particle formalism the electronic Hamiltonian (*1*) can be expressed in the form

$$\hat{H} = \langle \Phi_0\,|\hat{H}|\,\Phi_0\rangle + \sum_{PQ} f_{PQ}\, N[\hat{X}_P^+ \hat{X}_Q] + \frac{1}{2} \sum_{PQRS} \langle PQ\,|\hat{v}|\,RS\rangle\, N[\hat{X}_P^+ \hat{X}_Q^+ \hat{X}_S \hat{X}_R] \ , \qquad (2)$$

where N[...] denotes the normal ordered product of creation and annihilation operators with respect to the Fermi vacuum $|\Phi_0\rangle$ and f_{PQ} are matrix elements of the Fock operator

$$f_{PQ} = \langle P\,|\hat{h}|\,Q\rangle + \sum_{I \in \Phi_0} \langle PI\,|\hat{v}|\,QI\rangle - \langle PI\,|\hat{v}|\,IQ\rangle \qquad (3)$$

with the summation being over all spinorbitals occupied in $|\Phi_0\rangle$. As is usual in perturbation theory, let us split the exact Hamiltonian (*2*) into two parts, namely

$$\hat{H} = \hat{H}_0 + \hat{V} \qquad (4)$$

$$\hat{H}_0 = \langle \Phi_0\,|\hat{H}|\,\Phi_0\rangle + \sum_{P} \varepsilon_P\, N[\hat{X}_P^+ \hat{X}_P] \qquad (5)$$

$$\hat{V} = \sum_{PQ} (f_{PQ} - \varepsilon_P \delta_{PQ})\, N[\hat{X}_P^+ \hat{X}_Q] + \frac{1}{2} \sum_{PQRS} \langle PQ\,|\hat{v}|\,RS\rangle\, N[\hat{X}_P^+ \hat{X}_Q^+ \hat{X}_S \hat{X}_R] \ , \qquad (6)$$

where $\hat{H}_0$ is a zeroth-order Hamiltonian, ε_P are one-electron (spinorbital) energies and $\hat{V}$ is a perturbation. This type of partitioning is denoted as a Møller–Plesset (MP) one. In general, our perturbation $\hat{V}$ consists of two parts, namely the one-electron part and two-electron part. We recall that the one-electron part vanishes when the Hartree-Fock

spinorbitals are employed; however, in this work we will in general assume that non-Hartree–Fock spinorbitals are used. Let us further assume that we know the solution of the characteristic problem of the zeroth-order Hamiltonian

$$\hat{H}_0 \Phi_i = E_i \Phi_i \tag{7}$$

and our task is to find a solution of the Schrödinger equation for the exact Hamiltonian $\hat{H}$

$$\hat{H} \Psi_i = \mathcal{E}_i \Psi_i \ . \tag{8}$$

If we are interested in the ground state, the exact wave function Ψ_0 and the exact energy $\mathcal{E}_0$ can be expanded in the Brillouin–Wigner (BW) perturbation series as follows

$$|\Psi_0\rangle = (1 + \hat{B}\hat{V} + \hat{B}\hat{V}\hat{B}\hat{V} + \ldots)\, |\Phi_0\rangle \tag{9}$$

$$\mathcal{E}_0 = \langle \Phi_0 |\hat{H}| \Phi_0 \rangle + \langle \Phi_0 |\hat{V} + \hat{V}\hat{B}\hat{V} + \hat{V}\hat{B}\hat{V}\hat{B}\hat{V} + \ldots| \Phi_0 \rangle \ , \tag{10}$$

where $\hat{B}$ is the BW type of propagator

$$\hat{B} = \sum_{i \neq 0} \frac{|\Phi_i\rangle \langle \Phi_i|}{\mathcal{E}_0 - E_i} \ . \tag{11}$$

We recall that the BW perturbation expansion (*9*) at the same time prescribes the normalization of the exact wave functions to be

$$\langle \Phi_0 | \Psi_0 \rangle = \langle \Phi_0 | \Phi_0 \rangle = 1 \tag{12}$$

which is referred to as an intermediate normalization. If we introduce a new operator $\hat{\Omega}$ as

$$\hat{\Omega} = 1 + \hat{B}\hat{V} + \hat{B}\hat{V}\hat{B}\hat{V} + \ldots \tag{13}$$

the exact wave function (*9*) can be expressed in the form

$$|\Psi_0\rangle = \hat{\Omega}\,|\Phi_0\rangle \ . \tag{14}$$

As one can see, the operator $\hat{\Omega}$ is a wave operator (it transforms the zeroth-order wave function of the ground state into the exact wave function) and obeys the operator equation

$$\hat{\Omega} = 1 + \hat{B}\hat{V}\hat{\Omega} \tag{15}$$

that may be viewed as a Bloch equation in the Brillouin–Wigner form in contrast to the standard Bloch equation

$$\hat{H}\hat{\Omega} = \hat{\Omega}\hat{H}\hat{\Omega} \tag{16}$$

that determines the wave operator $\hat{\Omega}$ in the MR Rayleigh–Schrödinger perturbation theory as well as MR CC theories[16–20]. In order to obtain the wave operator $\hat{\Omega}$ in a form suitable for practical calculations, we project Eq. (*15*) onto the excited configurations Φ_i from the left and the ground state configuration from the right which brings us a system of equations

$$(\mathcal{E}_0 - E_i)\,\langle\Phi_i\,|\hat{\Omega}|\,\Phi_0\rangle = \langle\Phi_i\,|\hat{V}\hat{\Omega}|\,\Phi_0\rangle \tag{17}$$

that may be viewed as a matrix formulation of the Bloch equation in the Brillouin–Wigner form. Using the wave operator (*13*), the exact energy (*10*) can be written as

$$\mathcal{E}_0 = \langle\Phi_0\,|\hat{H}_0|\,\Phi_0\rangle + \langle\Phi_0\,|\hat{V}\hat{\Omega}|\,\Phi_0\rangle \ . \tag{18}$$

So far, we have specified the wave operator $\hat{\Omega}$ by means of the BW perturbation expansion (*13*) or (*15*). If we adopt an exponential ansatz for the wave operator $\hat{\Omega}$, we may speak about the Brillouin–Wigner coupled-cluster theory; *i.e.*

$$\hat{\Omega} = \mathrm{e}^{\hat{T}} \ , \tag{19}$$

where $\hat{T}$ is a cluster operator defined with respect to the ground state configuration Φ_0 and, in general, involves one-body ($\hat{T}_1$), two-body ($\hat{T}_2$) up to the N-body ($\hat{T}_N$) cluster components

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_N \tag{20}$$

with N being the total number of electrons. Substituting the exponential ansatz (*19*) into the expression for the exact energy (*18*), we get

$$\mathcal{E}_0 = \langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle + \langle \Phi_0 | \hat{V} \, \mathrm{e}^{\hat{T}} | \Phi_0 \rangle \tag{21}$$

which implies that the correlation energy $\Delta\mathcal{E}_0$

$$\Delta\mathcal{E}_0 = \mathcal{E}_0 - E_0 = \mathcal{E}_0 - \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \tag{22}$$

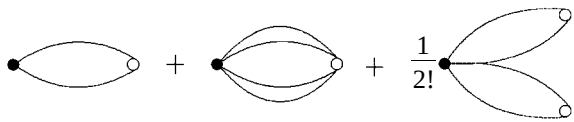
is given by the expression

$$\Delta\mathcal{E}_0 = \langle \Phi_0 | \hat{V} \, \mathrm{e}^{\hat{T}} | \Phi_0 \rangle \ . \tag{23}$$

Since at most doubly-excited clusters may contribute to the energy, the correlation energy takes the final form

$$\Delta\mathcal{E}_0 = \langle \Phi_0 | \hat{V}\hat{T}_1 | \Phi_0 \rangle + \langle \Phi_0 | \hat{V}\hat{T}_2 | \Phi_0 \rangle + \frac{1}{2!} \langle \Phi_0 | \hat{V}\hat{T}_1^2 | \Phi_0 \rangle \tag{24}$$

or by means of diagrammatic techniques (nonoriented Hugenholtz diagrams)

$\Delta\mathcal{E}_0 =$  (*25*)

where the one-electron part of the perturbation $\hat{V}$ is represented by a full circle with one pair of fermion lines, two-electron part of $\hat{V}$ by a full circle with two pairs of fermion lines, one-electron cluster operator $\hat{T}_1$ by an open circle with one pair of fermion lines and, finally, two-electron cluster operator $\hat{T}_2$ by an open circle with two pairs of fer-

mion lines. Expressions (*24*) and (*25*) are used for the calculation of the correlation energy in the BWCC theory as well as in standard CC theories.

Substituting the exponential ansatz (*19*) into the Bloch equation (*15*), we get the basic equation for the cluster operator $\hat{T}$ in the BW form[14,15]

$$e^{\hat{T}} = 1 + \hat{B}\hat{V}\, e^{\hat{T}} \ . \qquad (26)$$

The unknown cluster components $\hat{T}_n$ can be determined from the Bloch equation in the matrix form (*17*). Substituting the exponential ansatz (*19*) and taking the configurations Φ_i from the subspace spanned by *n* times excited configurations provides us with

$$(\mathfrak{E}_0 - E_i)\, \langle \Phi_i\, |\hat{T}_n|\, \Phi_0 \rangle = \langle \Phi_i\, |\hat{V}\, e^{\hat{T}}|\, \Phi_0 \rangle - (\mathfrak{E}_0 - E_i)\, \langle \Phi_i\, |e^{\hat{T}} - \hat{T}_n|\, \Phi_0 \rangle \qquad (27)$$

and this equation can be used for the calculation of cluster amplitudes in the BWCC theory. It is worthwhile to note that the first term on the right hand side can be diagrammatically represented by means of connected as well as disconnected diagrams, whereas only disconnected diagrams come into consideration in the case of the second term. For the case of monoexcited amplitudes the previous equation reduces to

$$(\mathfrak{E}_0 - E_i)\, \langle \Phi_I^A\, |\hat{T}_1|\, \Phi_0 \rangle = \langle \Phi_I^A\, |\hat{V}\, e^{\hat{T}}|\, \Phi_0 \rangle \qquad (28)$$

and, analogously, for the case of biexcited amplitudes we have

$$(\mathfrak{E}_0 - E_i)\, \langle \Phi_{IJ}^{AB}\, |\hat{T}_2|\, \Phi_0 \rangle = \langle \Phi_{IJ}^{AB}\, |\hat{V}\, e^{\hat{T}}|\, \Phi_0 \rangle - \frac{1}{2!}\, (\mathfrak{E}_0 - E_i)\, \langle \Phi_{IJ}^{AB}\, |\hat{T}_1^2|\, \Phi_0 \rangle \ , \qquad (29)$$

where $|\Phi_I^A\rangle$ and $|\Phi_{IJ}^{AB}\rangle$ represent singly and doubly excited configurations with respect to the ground state.

Cancellation of the Disconnected Terms in the Case of the BWCC with Doubles Theory

If we adopt a simple approximation in the exponential ansatz (*19*), such that

$$\hat{T} = \hat{T}_2 \ , \qquad (30)$$

we speak about the BWCC with Doubles (BWCCD) theory. The expression for the correlation energy (Eqs (*24*) and (*25*)) will simplify to the form

$$\Delta\mathfrak{E}_0 = \langle\Phi_0 |\hat{V}\hat{T}_2| \Phi_0\rangle = \quad (31)$$

and the Eq. (*29*) for the two-body cluster operator $\hat{T}_2$ will have the form

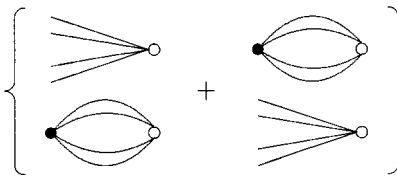
$$(\mathfrak{E}_0 - E_i)\, \langle\Phi_{IJ}^{AB} |\hat{T}_2| \Phi_0\rangle = \langle\Phi_{IJ}^{AB} |\hat{V}\, e^{\hat{T}_2}| \Phi_0\rangle = \langle\Phi_{IJ}^{AB} |\hat{V}(1 + \hat{T}_2 + \frac{1}{2!}\hat{T}_2^2)| \Phi_0\rangle \ . \quad (32)$$

Since we do not work with the linked cluster theorem, contributions originating from the matrix element $\langle\Phi_{IJ}^{AB} |\hat{V}\, e^{\hat{T}_2}| \Phi_0\rangle$ can be split into connected (C) and disconnected (DC) ones; so one can write

$$(\mathfrak{E}_0 - E_i)\, \langle\Phi_{IJ}^{AB} |\hat{T}_2| \Phi_0\rangle = \langle\Phi_{IJ}^{AB} |\hat{V}\, e^{\hat{T}_2}| \Phi_0\rangle_C + \frac{1}{2!}\langle\Phi_{IJ}^{AB} |\hat{V}\hat{T}_2^2| \Phi_0\rangle_{DC} \ . \quad (33)$$

Contribution of the disconnected part can be easily computed with the use of diagrammatic techniques

$$\frac{1}{2!}\langle\Phi_{IJ}^{AB} |\hat{V}\hat{T}_2^2| \Phi_0\rangle_{DC} = \frac{1}{2} \quad + \quad = t_{IJ}^{AB}\Delta\mathfrak{E}_0 \ , \quad (34)$$



where t_{IJ}^{AB} denotes the antisymmetrized biexcited cluster amplitudes.

If we substitute for the disconnected term into Eq. (*33*), we get

$$(\mathfrak{E}_0 - E_i)\, t_{IJ}^{AB} = \langle\Phi_{IJ}^{AB} |\hat{V}\, e^{\hat{T}_2}| \Phi_0\rangle_C + t_{IJ}^{AB}\, \Delta\mathfrak{E}_0 \quad (35)$$

which implies

$$(E_0 - E_i)\, t_{IJ}^{AB} = \langle\Phi_{IJ}^{AB} |\hat{V}\, e^{\hat{T}_2}| \Phi_0\rangle_C \ . \quad (36)$$

Here, we have to note that Eq. (*35*) reduces to Eq. (*36*) only in the case when the cluster amplitudes are fully converged. So, the cancellation of disconnected contributions in the BWCCD theory is done iteratively and the full cancellation is achieved by the full convergence of cluster amplitudes. One can thus conclude that both approaches, *i.e.* standard CCD theory with the use of the linked cluster theorem and the BWCCD theory are fully equivalent.

Cancellation of the Disconnected Terms in the Case of the BWCC with Singles and Doubles Theory

If we adopt the following approximation of the cluster operator (*20*)

$$\hat{T} = \hat{T}_1 + \hat{T}_2 \tag{37}$$

we speak about the BWCC with Singles nad Doubles (BWCCSD) theory. Now, the correlation energy $\mathfrak{E}_0$ is determined by Eqs (*24*) and (*25*), one-body cluster operator $\hat{T}_1$ by Eq. (*28*) and two-body cluster operator $\hat{T}_2$ by Eq. (*29*). In order to simplify expressions for cluster amplitudes we proceed in an analogous way as in the case of the BWCCD theory. Let us start with the monoexcited cluster amplitudes. Since higher than triply-excited clusters do not contribute, Eq. (*28*) reduces to the form

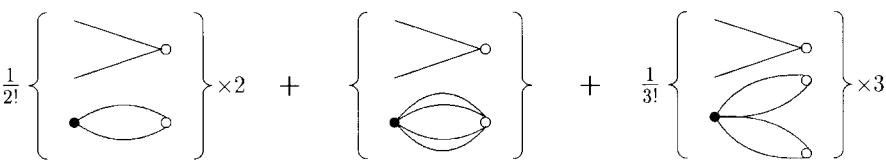
$$\begin{aligned}(\mathfrak{E}_0 - E_i)\,\langle \Phi_I^A |\hat{T}_1| \Phi_0\rangle &= \langle \Phi_I^A |\hat{V} \exp(\hat{T}_1 + \hat{T}_2)| \Phi_0\rangle \\ &= \langle \Phi_I^A |\hat{V}(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2!}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3)| \Phi_0\rangle \ . \end{aligned} \tag{38}$$

If we split contributions coming from the matrix element $\langle \Phi_I^A |\hat{V} \exp(\hat{T}_1 + \hat{T}_2)| \Phi_0\rangle$ into connected and disconnected ones, we have

$$(\mathfrak{E}_0 - E_i)\,\langle \Phi_I^A |\hat{T}_1| \Phi_0\rangle = \langle \Phi_I^A |\hat{V} \exp(\hat{T}_1 + \hat{T}_2)| \Phi_0\rangle_C + \langle \Phi_I^A |\hat{V} \exp(\hat{T}_1 + \hat{T}_2)| \Phi_0\rangle_{DC} \ . \tag{39}$$

The contribution of the disconnected part can be expressed in the form

$$\langle \Phi_I^A |\hat{V} \exp(\hat{T}_1 + \hat{T}_2)| \Phi_0\rangle_{DC} = \langle \Phi_I^A |\hat{V}(\frac{1}{2!}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3)| \Phi_0\rangle_{DC} = \tag{40}$$



which implies

$$\langle \Phi_I^A \,|\hat{V} \exp(\hat{T}_1 + \hat{T}_2)|\, \Phi_0\rangle_{DC} = t_I^A \,\Delta\mathfrak{E}_0 \ , \tag{41}$$

where t_I^A denotes the monoexcited cluster amplitudes.
Substituting for the disconnected part into Eq. (*39*) leads us to the equation

$$(\mathfrak{E}_0 - E_i)\, t_I^A = \langle \Phi_I^A \,|\hat{V} \exp(\hat{T}_1 + \hat{T}_2)|\, \Phi_0\rangle_C + t_I^A \,\Delta\mathfrak{E}_0 \tag{42}$$

that can be simplified with the use of the MP partitioning (*4*)–(*6*) to the final form

$$(\varepsilon_I - \varepsilon_A)\, t_I^A = \langle \Phi_I^A \,|\hat{V} \exp(\hat{T}_1 + \hat{T}_2)|\, \Phi_0\rangle_C \ . \tag{43}$$

Here, we should again stress that Eq. (*42*) reduces to Eq. (*43*) only in the case when the cluster amplitudes are fully converged.

The two-body cluster amplitudes are determined by Eq. (*29*). In contrast to one-body cluster amplitudes, the right hand side of Eq. (*29*) now consists of two terms. Here we recall that the first term can be expanded in the form

$$\begin{aligned}\langle \Phi_{IJ}^{AB} \,|\hat{V} \exp(\hat{T}_1 + \hat{T}_2)|\, \Phi_0\rangle = \langle \Phi_{IJ}^{AB} \,|\hat{V}(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2!}\hat{T}_1^2 + \frac{1}{2!}\hat{T}_2^2 + \hat{T}_1\hat{T}_2 + \\ + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{2!}\hat{T}_1^2\hat{T}_2 + \frac{1}{4!}\hat{T}_1^4)|\, \Phi_0\rangle\end{aligned} \tag{44}$$

since higher than quadruply-excited clusters do not contribute. The second term can be calculated easily, *i.e.*

$$\begin{aligned}-\frac{1}{2!}(\mathfrak{E}_0 - E_i)\,\langle \Phi_{IJ}^{AB} \,|\hat{T}_1^2|\, \Phi_0\rangle = -\frac{1}{2}(\mathfrak{E}_0 - E_i)\ \hat{\wp}_{AB}\,\hat{\wp}_{IJ}\,[t_I^A t_J^B] = \\ = -(\mathfrak{E}_0 - E_i)\,(t_I^A t_J^B - t_J^A t_I^B) \ ,\end{aligned} \tag{45}$$

where $\hat{\wp}_{IJ}$ and $\hat{\wp}_{AB}$ are antisymmetrizers of the form

$$\hat{\wp}_{IJ} = 1 - \hat{P}(I \leftrightarrow J) \tag{46}$$

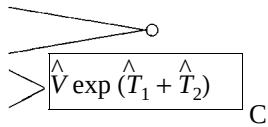
so the equation for biexcited amplitudes (*29*) will read

$$(\mathfrak{E}_0 - E_i)\, t_{IJ}^{AB} = \langle \Phi_{IJ}^{AB} | \hat{V} \exp(\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle - (\mathfrak{E}_0 - E_i)\, (t_I^A t_J^B - t_J^A t_I^B) \ . \qquad (47)$$

If we split contributions coming from the first term into connected and disconnected ones, we have

$$(\mathfrak{E}_0 - E_i)\, t_{IJ}^{AB} = \langle \Phi_{IJ}^{AB} | \hat{V} \exp(\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle_C + \langle \Phi_{IJ}^{AB} | \hat{V} \exp(\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle_{DC} -$$
$$- (\mathfrak{E}_0 - E_i)\, (t_I^A t_J^B - t_J^A t_I^B) \ . \qquad (48)$$

Disconnected contributions can be divided into three groups: the first group (I) consists of diagrams containing one $\hat{T}_1$ operator disconnected, the second group (II) consists of diagrams containing two $\hat{T}_1$ operators both disconnected and the third group (III) consists of diagrams containing the operator $\hat{T}_2$ disconnected. The first group can be diagrammatically represented by means of linked diagrams, *i.e.*



which implies (see also ref.[7])

$$\langle \Phi_{IJ}^{AB} | \hat{V} \exp(\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle_{DC}^{(I)} = \hat{\mathcal{O}}_{AB} \hat{\mathcal{O}}_{IJ} [t_I^A \langle \Phi_J^B | \hat{V} \exp(\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle_C] \ . \qquad (49)$$

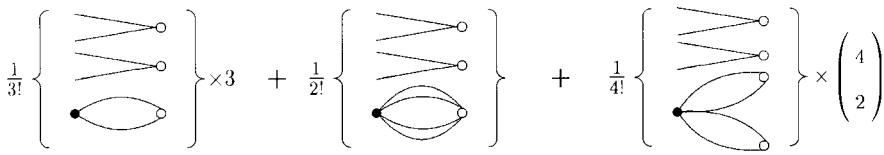
If we substitute for the connected part from Eq. (*43*), the whole contribution of the first group will equal to

$$\langle \Phi_{IJ}^{AB} | \hat{V} \exp(\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle_{DC}^{(I)} = \hat{\mathcal{O}}_{AB} \hat{\mathcal{O}}_{IJ} [t_I^A (\varepsilon_B - \varepsilon_J)\, t_J^B] =$$
$$= (\varepsilon_I + \varepsilon_J - \varepsilon_A - \varepsilon_B)\, (t_I^A t_J^B - t_J^A t_I^B) \qquad (50)$$

or with the use of the MP partitioning (*4*)–(*6*)

$$\langle \Phi_{IJ}^{AB} | \hat{V} \exp(\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle_{DC}^{(I)} = (E_0 - E_i)\, (t_I^A t_J^B - t_J^A t_I^B) \ . \qquad (51)$$

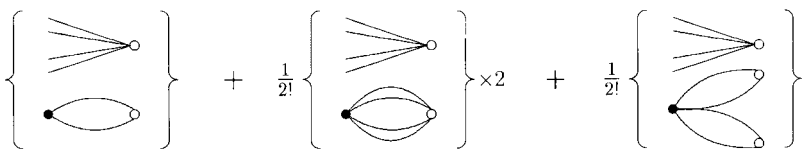
The second group can be diagrammatically represented by means of unlinked diagrams, *i.e.*



so one can write (see also ref.[7])

$$\langle \Phi_{IJ}^{AB} | \hat{V} \exp (\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle_{DC}^{(II)} = \Delta\mathfrak{E}_0 \, (t_I^A t_J^B - t_J^A t_I^B) \ . \tag{52}$$

The third group can be diagrammatically represented by means of unlinked diagrams, *i.e.*



which provides us with (see also ref.[7])

$$\langle \Phi_{IJ}^{AB} | \hat{V} \exp (\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle_{DC}^{(III)} = \Delta\mathfrak{E}_0 \, t_{IJ}^{AB} \ . \tag{53}$$

If we sum contributions (*51*), (*52*) and (*53*) together, the overall contribution of the disconnected part will be

$$\langle \Phi_{IJ}^{AB} | \hat{V} \exp (\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle_{DC} = \Delta\mathfrak{E}_0 \, t_{IJ}^{AB} + (\mathfrak{E}_0 - E_i) \, (t_I^A t_J^B - t_J^A t_I^B) \ . \tag{54}$$

Substituting for the disconnected part into Eq. (*48*) gives us the following equation for the biexcited cluster amplitudes

$$(\mathfrak{E}_0 - E_i) \, t_{IJ}^{AB} = \langle \Phi_{IJ}^{AB} | \hat{V} \exp (\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle_C + \Delta\mathfrak{E}_0 \, t_{IJ}^{AB} \tag{55}$$

and this equation can be simplified using the MP partitioning to the final form

$$(\varepsilon_I + \varepsilon_J - \varepsilon_A - \varepsilon_B)\, t_{IJ}^{AB} = \langle \Phi_{IJ}^{AB} | \hat{V} \exp(\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle_C \ . \qquad (56)$$

Equations for the monoexcited amplitudes (*43*) as well as for the biexcited amplitudes (*56*) are equivalent to those used in the standard CCSD theory; so one can conclude that both approaches, CCSD and BWCCSD are fully equivalent in the case of fully converged amplitudes.

Cancellation of the Disconnected Terms in the Case of the Linear BWCC with Doubles Theory

If we adopt simple approximation in the exponential ansatz (*19*)

$$\hat{T} = \hat{T}_2 \qquad (57)$$

and, at the same time, we neglect nonlinear terms in the exponential expansion, we can speak about the linear BWCCD (L-BWCCD) theory. Then, the correlation energy for the ground state $\Delta\mathfrak{E}_0$ is given by the same expression as in the BWCCD case, *i.e.*

$$\Delta\mathfrak{E}_0 = \langle \Phi_0 | \hat{V}\hat{T}_2 | \Phi_0 \rangle \qquad (58)$$

or using the configuration state function (CSF) formalism as

$$\Delta\mathfrak{E}_0 = \sum_i \langle \Phi_0 | \hat{V} | \Phi_i^{(2)} \rangle \langle \Phi_i^{(2)} | \hat{T}_2 | \Phi_0 \rangle \ , \qquad (59)$$

where the summation is over all biexcited configurations $| \Phi_i^{(2)} \rangle$. As concerns the determination of the biexcited cluster amplitudes, here we have two possibilities. The first possibility lies in the complete neglect of nonlinear terms, so the equation for the biexcited amplitudes (*32*) will simplify to the form

$$(\mathfrak{E}_0 - E_i) \langle \Phi_{IJ}^{AB} | \hat{T}_2 | \Phi_0 \rangle = \langle \Phi_{IJ}^{AB} | \hat{V}(1 + \hat{T}_2) | \Phi_0 \rangle \qquad (60)$$

which can be rewritten in CSF formalism as

$$(\mathfrak{E}_0 - E_i)\,\langle \Phi_i^{(2)} |\hat{T}_2| \Phi_0\rangle = \langle \Phi_i^{(2)} |\hat{V}| \Phi_0\rangle + \sum_j \langle \Phi_i^{(2)} |\hat{V}| \Phi_j^{(2)}\rangle \langle \Phi_j^{(2)} |\hat{T}_2| \Phi_0\rangle \ , \qquad (61)$$

where $|\Phi_i^{(2)}\rangle$ and $|\Phi_j^{(2)}\rangle$ are biexcited configurations. The given equation is dependent on the correlation energy and is the same as in the configuration interaction method limited to doubles (CI-D); so the complete neglect of nonlinear terms brings us equivalence with the CI-D method. The second possibility is somewhat more sophisticated. In order to destroy dependence on the exact energy, we neglect only connected quadratic terms in Eq. (*32*), whereas the disconnected quadratic terms stay present. If we realize that the contribution of the disconnected nonlinear term is determined by Eq. (*34*), we get

$$(\mathfrak{E}_0 - E_i)\,\langle \Phi_{IJ}^{AB} |\hat{T}_2| \Phi_0\rangle = \langle \Phi_{IJ}^{AB} |\hat{V}(1 + \hat{T}_2)| \Phi_0\rangle + \Delta\mathfrak{E}_0\,\langle \Phi_{IJ}^{AB} |\hat{T}_2| \Phi_0\rangle \qquad (62)$$

what can be simplified to the form

$$(\varepsilon_I + \varepsilon_J - \varepsilon_A - \varepsilon_B)\, t_{IJ}^{AB} = \langle \Phi_{IJ}^{AB} |\hat{V}(1 + \hat{T}_2)| \Phi_0\rangle \qquad (63)$$

or in the CSF formalism

$$(E_0 - E_i)\,\langle \Phi_i^{(2)} |\hat{T}_2| \Phi_0\rangle = \langle \Phi_i^{(2)} |\hat{V}| \Phi_0\rangle + \sum_j \langle \Phi_i^{(2)} |\hat{V}| \Phi_j^{(2)}\rangle \langle \Phi_j^{(2)} |\hat{T}_2| \Phi_0\rangle \ . \qquad (64)$$

Equations (*63*) and (*64*) are now independent of the correlation energy and they are equivalent with those used in the standard L-CCD theory. The advantage of this approach is that we are able to perform the L-CCD calculations in the CSF formalism; for comparison see also the article by Cizek and Paldus[3].

DISCUSSION

In our previous articles[14,15] we turned our attention to the Brillouin–Wigner based coupled cluster method. We have shown that we are able to obtain identical results as with the standard nondegenerate CC theory at practically no extra expenses. In this article we present more detail explanation of cancellation of disconnected contributions in the BWCC theory and we show how the both approaches become identical. Here we should mention that Eqs (*35*), (*36*), (*42*), (*43*), (*55*), (*56*), (*62*) and (*63*) not only directly lead to standard CC theories but they also correspond to denominator shifts in standard CC theories with the denominator shift being cancelled out when the equations are fully

converged. This way of cancellation of disconnected contributions is manifested by different shifts in different iterations and their full cancellation in the fully converged case.

As is well known, the standard nondegenerate CC theory is considered to be the best method to account for correlation energy of closed-shell systems, however, its use in the case of electron quasi-degeneracy or, in general, open-shell systems is far from being satisfactory. One of the main obstacles is the occurrence of the so-called intruder states in existing MR CC theories. The problem of intruder states is common to both MR MBPT as well as MR CC theories and has stimulated development of many new perturbative methods based on various shifting techniques. From this point of view, the multireference formulation of the BWCC method (with the presence of denominator shifts) seems to be very interesting and will be our task in the next future.

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