

CEPA

THE COUPLED ELECTRON PAIRS APPROACH.§1 Introduction

The Coupled Cluster (CC) equations are rather complicated, leading to time-consuming algorithms. Therefore various approximation methods have been worked out, which are about as demanding as a CI calculation with the same configuration set while being at least size consistent for some model systems. Here the corrections for size consistency are not added afterwards (Davidson, Pople), but they are incorporated implicitly into the energy calculation.

However, there are some pitfalls in the choice of the approximations to be made. In the first place, the resulting method will not be variational, just like the CC method itself. This is a serious drawback, unless the deviations from the CC results are small. A second criterium to be satisfied is the invariance with respect to orbital transformations. In a HF calculation only the space of the occupied orbitals is determined, since the HF determinant is invariant under transformations of the occupied orbitals. This also holds for CC and (S)DCI wave functions. However, approximations to the CC method do not automatically satisfy this condition.

There are two CEPA philosophies :

- 1) (Meijer, Ahlrichs). This is the practical approach : a simple algorithm with size consistency and orbital invariance for simple model systems.
- 2) (Hurley). This is the theoretical approach : as close as possible to the CC equations. This algorithm is more complicated, but appears not to work better in practice. Therefore the first choice is to be preferred.

Exercise 3.1

Show that the DCI energy is invariant under transformations of the orbitals which are occupied in the HF function. Show that the same is true for the virtual orbitals.

§2 The CEPAA method

The starting point for obtaining approximations to the CC method is the idea that linearisation of the equations should work, because we want a linear relationship between the correlation energy and the number of electrons (or the number of separated pairs in a model system). This is in line with the result that 2nd order RSPT is trivially size consistent (no cancellation of higher order terms is needed in the 2nd order).

We start with the CCD equations (see Eq (2.29) and (2.31)). For the first equation we have :

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$$E = E_0 + \langle 0 | \mathbf{H} \mathbf{T} | 0 \rangle \quad (3.1)$$

and for the other equations :

$$\langle D_{IJ}^{AB} | \mathbf{H} (1 + \mathbf{T} + \frac{1}{2} \mathbf{T}^2) | 0 \rangle = E d_{IJ}^{AB} \quad (3.2)$$

By substituting Eq (3.1) into (3.2) we find :

$$\langle D_{IJ}^{AB} | \mathbf{H} (1 + \mathbf{T} + \frac{1}{2} \mathbf{T}^2) | 0 \rangle = (E_0 + \langle 0 | \mathbf{H} \mathbf{T} | 0 \rangle) d_{IJ}^{AB} \quad (3.3)$$

We now neglect all terms which are quadratic in the coefficients (note that \mathbf{T} is linear in the d_{IJ}^{AB} , see Eq (2.18)). The result may be written as :

$$\langle D_{IJ}^{AB} | (\mathbf{H} - E_0) (1 + \mathbf{T}) | 0 \rangle = 0 \quad (3.4)$$

This is the linearized version of the CC equations, also known as L-CCA (Linearized Coupled Cluster Approach), LCPMET (Linear Coupled Pair Many Electron Theory) or CEPA0, (Coupled Electron Pair Approach, version 0). This is the most drastic approximation to the CCD equations which is still size consistent. Eq (3.4) amounts to an inhomogeneous linear set of equations and it is equivalent to the zeroth order solution to the DCI equations. We can see this as follows.

Eq (3.1) may be written in matrix form (as in Eq (1.21a)) :

$$E_{\text{corr}} = E - E_0 = \mathbf{H}_{\text{int}}^{\leq} \mathbf{d} \quad (3.5a)$$

where \mathbf{H}_{int} is the (column) vector with elements

$$(\mathbf{H}_{\text{int}})_{IJAB} = \langle D_{IJ}^{AB} | \mathbf{H} | 0 \rangle \quad (3.5b)$$

From Eq (3.4) we have :

$$\langle D_{IJ}^{AB} | \mathbf{H} | 0 \rangle + \langle D_{IJ}^{AB} | (\mathbf{H} - E_0) \mathbf{T} | 0 \rangle = 0 \quad (3.6)$$

or in matrix form (cf Eq (1.21b)) :

$$\mathbf{H}_{\text{int}} + \mathbf{H}_{\text{ex}} \mathbf{d} = \mathbf{0} \quad (3.7a)$$

where \mathbf{H}_{ex} is the matrix with elements

$$(\mathbf{H}_{\text{ex}})_{IJAB, KLCD} = \langle D_{IJ}^{AB} | \mathbf{H} - E_0 | D_{KL}^{CD} \rangle \quad (3.7b)$$

Solving Eq (3.7) for \mathbf{d} and substituting the result into Eq (3.5) yields :

$$E = E_0 - \mathbf{H}_{\text{int}}^{\leq} \mathbf{H}_{\text{ex}}^{-1} \mathbf{H}_{\text{int}} \quad (3.8)$$

It will be shown below that this result is size consistent for simple model systems. However, it is not very accurate.

§3 The diagonal shift

In order to enable a direct comparison to the DCI method we write Eqs (3.1) and (3.4) in the form :

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$$\langle 0 | (\mathbf{H} - E)(1 + \mathbf{T}) | 0 \rangle = 0 \quad (3.9)$$

$$\langle D_{IJ}^{AB} | (\mathbf{H} - E + E_{\text{corr}})(1 + \mathbf{T}) | 0 \rangle = 0 \quad (3.10)$$

Eq (3.9) is identical to the first DCI equation in intermediate normalisation, which may be written in our formalism as :

$$\Psi_{\text{DCI}} = (1 + \mathbf{T}) | 0 \rangle \quad (3.11)$$

Note that the first equation always has the same form. The only difference is in the values of the amplitudes or coefficients contained in \mathbf{T} (the d_{IJ}^{AB} of Eq (2.18)).

For the other DCI equations we have :

$$\langle D_{IJ}^{AB} | (\mathbf{H} - E)(1 + \mathbf{T}) | 0 \rangle = 0 \quad (3.12)$$

A set of equations describing both DCI and CEPA methods is obtained by replacing Eq (3.9-10) by :

$$\langle 0 | (\mathbf{H} - E)(1 + \mathbf{T}) | 0 \rangle = 0 \quad (3.13a)$$

$$\langle D_{IJ}^{AB} | (\mathbf{H} - E + \Delta E_{IJ}^{AB})(1 + \mathbf{T}) | 0 \rangle = 0 \quad (3.13b)$$

Eq (3.13b) is identical to the DCI equations if we choose

$$\Delta E_{IJ}^{AB} = 0 \quad (3.14)$$

whereas the CEPA0 method is obtained with

$$\Delta E_{IJ}^{AB} = E_{\text{corr}} \quad (3.15)$$

ΔE_{IJ}^{AB} is a diagonal shift, since it corresponds to a contribution $\Delta E_{IJ}^{AB} d_{IJ}^{AB}$ in Eq (3.13), that is, the effect is a change in the corresponding diagonal element of the H-matrix.

From the analogy between Eqs (3.10), (3.12) and (3.13b) it appears that CEPA-type equations like Eqs (3.13) may be solved in a way which is closely related to the usual way of solving the DCI equations. Therefore it is easy to modify a CI program in such a way that CEPA calculations may be done by just slightly modifying the code. In fact, the CEPA equations are solved in the form of a pseudo-eigenvalue problem.

An explicit expression for the shift may be derived from the CC equations by comparing Eq (3.13b) to Eq (3.2). Apparently the shift should correspond to the \mathbf{T}^2 term in Eq (3.2) :

$$\Delta E_{IJ}^{AB} d_{IJ}^{AB} = \frac{1}{2} \langle D_{IJ}^{AB} | \mathbf{H} \mathbf{T}^2 | 0 \rangle \quad (3.16)$$

Note that the first diagonal element (E_0) is not shifted, since the first secular equation, Eq (3.9) is linear in the coefficients d_{IJ}^{AB} .

Several alternatives may be generated from Eq (3.16) by approximating the right hand side in different ways. Since the diagonal elements for the double excitations are all lowered by the shift, the CEPA0 energy will be lower than the SDCI energy. It may even be lower than the FCI energy, since the variational character of the method has been lost by the introduction of the diagonal shift.

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§4 The direct term approximation

The right hand side of Eq (3.16) contains all products of all double excitations, leading to many contributions of double excitation coefficient products to the same quadruple excitation. In all CEPA variants only one contribution is used for each quadruple excitation by assuming that only the term involving D_{IJ}^{AB} contributes :

$$\frac{1}{2} \langle D_{IJ}^{AB} | \mathbf{H} \mathbf{T}^2 | 0 \rangle \approx \langle D_{IJ}^{AB} | \mathbf{H} \mathbf{T} | D_{IJ}^{AB} \rangle = d_{IJ}^{AB} \quad (3.17)$$

The factor 1/2 disappears since D_{IJ}^{AB} may appear in both \mathbf{T} factors. This is called the direct term approximation. Note that this approximation depends on the double excitation for which the shift is being calculated. In general it does not guarantee that the numerically most important contribution is selected. However, for the most important double excitations, that is, if I and J belong to the same electron pair, it does (probably) just that.

By substituting Eq (3.17) into Eq (3.16) we obtain :

$$\Delta E_{IJ}^{AB} = \langle D_{IJ}^{AB} | \mathbf{H} \mathbf{T} | D_{IJ}^{AB} \rangle \quad (3.18)$$

In the CEPA0 method it is assumed that :

$$\langle D_{IJ}^{AB} | \mathbf{H} \mathbf{T} | D_{IJ}^{AB} \rangle \approx \langle 0 | \mathbf{H} \mathbf{T} | 0 \rangle = E_{\text{corr}} \quad (3.19)$$

In this approximation the matrix element equivalence of Eq (2.37)

$$\langle D_{IJ}^{AB} | \mathbf{H} | Q_{IJKL}^{ABCD} \rangle = \langle 0 | \mathbf{H} | D_{KL}^{CD} \rangle \quad (3.20)$$

is used. Further it is assumed that each term in \mathbf{T} in the left hand side of Eq (3.19) generates a quadruple excitation, for which Eq (3.20) may be used in order to obtain the result of Eq (3.19). However, this amounts to a rather serious overestimation of the shift, since those terms in \mathbf{T} for which one or more indices coincide with I, J, A or B do not contribute because of the Pauli principle. For example :

$$\tau_{IK}^{CD} | D_{IJ}^{AB} \rangle = \tau_{IK}^{CD} \tau_{IJ}^{AB} | 0 \rangle = -\tau_{IJKI}^{ABCD} | 0 \rangle = 0 \quad (3.21)$$

These terms are called the Exclusion Principle Violating (EPV) terms (as in Many Body Perturbation Theory). They lead to energies which are too low.

The EPV terms may be avoided in several more or less exact ways. We start with rewriting Eq (3.1), as follows :

$$E = E_0 + \sum_{I < J} \epsilon_{IJ} \quad (3.22a)$$

with

$$\epsilon_{IJ} = \langle 0 | \mathbf{H} | \sum_{A < B} D_{IJ}^{AB} \rangle = d_{IJ}^{AB} \quad (3.22b)$$

ϵ_{IJ} is called the pair correlation energy for the MSOs I and J.

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A practically useful approximation is then obtained by taking :

$$\Delta E_{IJ}^{AB} = E_{\text{corr}} - \frac{1}{2} \sum_K (\varepsilon_{IK} + \varepsilon_{KJ}) \quad (3.23)$$

This defines the CEPA1 method. It has the advantage that the shifts are invariant under transformations of either the (HF) occupied MSOs or the virtual MSOs.

In the following the size consistency of the CEPA1 method for a model system of n identical non-interacting electron pairs will be shown, using localised orbitals. Because of the above-mentioned invariance of the shifts CEPA1 is also size consistent if delocalised orbitals are used. Eqs (3.13) may be solved analogously to solving the DCI equations, that is by diagonalising the \mathbf{H} -matrix. In each iteration, however, a diagonal matrix ΔE_{DD} with elements ΔE_{IJ}^{AB} is added to \mathbf{H} . Since ΔE_{IJ}^{AB} depends on the coefficients d_{IJ}^{AB} , the convergence of the process is slower than in the case of a DCI calculation. The calculation of the shifts, however, does not add much to the computer time needed.

§5 Application to systems without interaction

The wave function may be written as (cf Eqs (1.24)) :

$$\Psi = \Phi_0 + d \sum_i |D_i\rangle \quad (3.24)$$

and for the interaction between a double excitation and the HF function we have :

$$\langle D_i | \mathbf{H} | 0 \rangle = K \quad (3.25)$$

The energy is given by :

$$E = E_0 + d \langle 0 | \mathbf{H} | \sum_i D_i \rangle = E_0 + ndK \quad (3.26)$$

and for the other equations we have :

$$\begin{aligned} \langle D_i | \mathbf{H} | 0 \rangle + \langle D_i | \mathbf{H} - E + \Delta E_i | D_i \rangle d &= \\ = K + (E_0 + \Delta - E_0 - E_{\text{corr}} + \Delta E_i)d &= K + (\Delta - E_{\text{corr}} + \Delta E_i)d = 0 \end{aligned} \quad (3.27)$$

In the DCI method we take :

$$\Delta E_i = 0 \quad (3.28)$$

which yields (with $E_{\text{corr}} = ndK$ according to Eq (3.26)) :

$$d = \frac{-K}{\Delta - ndK} \quad (3.29)$$

Since d depends on n , the DCI result is not size consistent.

In the CEPA0 method we have :

$$\Delta E_i = E_{\text{corr}} \quad (3.30)$$

and we get :

$$d = \frac{-K}{\Delta} \quad (3.31)$$

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We see that the coefficient does not depend on n and from Eq (3.26) it follows that the energy varies linearly with n .

For our model system the interpair correlation contributions ε_{IJ} with $I \neq J$ vanish, since these correspond to excitations involving different electron pairs. Therefore in CEPA1 we have

$$\frac{1}{2} \sum_{\mathbf{K}} (\varepsilon_{IK} + \varepsilon_{KJ}) = \frac{1}{2} (\varepsilon_{i\bar{i}} + \varepsilon_{i\bar{i}}) = \varepsilon_{i\bar{i}} = \varepsilon_i \quad (3.32)$$

Therefore

$$\Delta E_{IJ}^{AB} = E_{\text{corr}} - \varepsilon_i \quad (3.33a)$$

with

$$\varepsilon_i = \langle 0 | \mathbf{H} | D_i \rangle d_i = dK \quad (3.33b)$$

and the coefficient is given by :

$$d = \frac{-K}{\Delta - dK} \quad (3.34)$$

Again d does not depend on n and therefore CEPA1 is also size consistent.

Exercise 3.2

Show that for our model system any method is size consistent if it satisfies the condition that d is independent of n .

Exercise 3.3

Show that the CEPA0 result for this model system is identical to the result of a 2nd order Epstein-Nesbet perturbation treatment.

From the CEPA equations it follows that the size consistency condition is also satisfied for larger (closed shell) subsystems. Again we use localised orbitals. Eq (3.13a) shows that the energy is additive if d_A and d_B are independent of each other, where d_A and d_B are the coefficients of the double excitations on A and B respectively, that is, if the other equations (3.13b) are separable All coefficients d_{IJ}^{AB} vanish, unless orbitals I,J,A and B belong to the same molecule. Eq (3.13b) then yields :

$$\begin{aligned} \langle D_A | \mathbf{H} | 0 \rangle + \sum_{A^c} \langle D_A | \mathbf{H} - E + \Delta E(D_A) | D_{A^c} \rangle d_{A^c} + \\ + \sum_B \langle D_A | \mathbf{H} - E + \Delta E(D_A) | D_B \rangle d_B = 0 \end{aligned} \quad (3.35)$$

where $\Delta E(D_A)$ is the shift for $| D_A \rangle$. The last term in Eq (3.35) vanishes since $| D_A \rangle$ and $| D_B \rangle$ do not interact. For the first term we have :

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$$\langle D_A | \mathcal{H} | 0 \rangle = \langle D_A | \mathcal{H}_A + \mathcal{H}_B | 0_A \rangle = \langle D_A | \mathcal{H}_A | 0_A \rangle$$

In the second term we have :

$$\langle D_A | \mathcal{H} - E + \Delta E(D_A) | D_{A\otimes} \rangle = \langle D_A | \mathcal{H}_A | D_{A\otimes} \rangle \quad (A \otimes A)$$

$$\langle D_A | \mathcal{H} - E_0 | D_A \rangle = \langle D_A | \mathcal{H}_A + \mathcal{H}_B - E_0 | D_A \rangle = E_A^0 + \Delta_A^D + E_B^0 - E_A^0 - E_B^0 = \Delta_A^D$$

$$\Delta E(D_A) - E + E_0 = \Delta E(D_A) - E_{\text{corr}} = \begin{cases} 0 & \text{for CEPA0} \\ -\frac{1}{2} \sum_K (\epsilon_{IK}^A + \epsilon_{KJ}^A) & \text{for CEPA1} \end{cases}$$

Therefore Eq (3.33) reduces to the monomer equation for A. In the same way the equations for d_b only depend on the double excitations on B and the dimer equations are indeed separable.

The model system of n H_2 molecules may also be used to show that CEPA0 will yield energies which are too low, whereas CEPA1 yields the Full CI result. The Full CI result follows from a variational calculation for one of the monomers (two configurations) (cf Eq (1.31):

$$\begin{vmatrix} -E & K \\ K & \Delta - E \end{vmatrix} = 0 \quad (3.36a)$$

which yields

$$E_{\text{FCI}} = \frac{\Delta}{2} [1 - \sqrt{1+C}] \quad (3.36b)$$

with (Eq (1.27b))

$$C = \frac{4K^2}{\Delta^2}$$

and

$$d_{\text{FCI}} = \frac{E_{\text{FCI}}}{K} = \frac{1 - \sqrt{1+C}}{\sqrt{C}} \quad (3.36c)$$

According to Eq (3.31) we have for CEPA0 :

$$d_{\text{CEPA0}} = -\frac{\sqrt{C}}{2} \quad (3.37)$$

These results may be compared using the power expansion for $\sqrt{1+x}$:

$$\sqrt{1+x} = 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \dots$$

which yields :

$$d_{\text{FCI}} \approx -\frac{\sqrt{C}}{2} \left(1 - \frac{C}{4}\right) \quad (3.38)$$

According to Eqs (3.26), (3.37) and (3.38) the CEPA0 energy is given by :

$$E_{\text{CEPA0}} = E_0 + n d_{\text{CEPA0}} K = E_0 + nK \left(d_{\text{FCI}} - \frac{C\sqrt{C}}{8}\right) = E_{\text{FCI}} - \frac{nK^4}{\Delta^3} \quad (3.39)$$

The result is linear in n , that is, the method is size consistent. However, the energy is lower than the Full CI energy since $\Delta > 0$. This also holds for $n = 1$, that is, CEPA0 does not

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even for 1 molecule yield the Full CI energy (DCI does). The deviation is large if $K \approx \Delta$ (near-degeneracy).

For CEPA1 we have from Eqs (3.34) and (1.27b) :

$$d^2\sqrt{C} - 2d - \sqrt{C} = 0 \quad (3.40)$$

This quadratic equation for d yields :

$$d_{\text{CEPA1}} = \frac{1 - \sqrt{1 + C}}{\sqrt{C}} \quad (3.41)$$

This is identical to the Full CI solution, Eq (3.36c)

Exercise 3.4

Show that the dissociation of the H_2 molecule may be described in a qualitative correct way by the CEPA1 method, even if the two configurations

$$|\sigma_g \bar{\sigma}_g| \text{ en } |\sigma_u \bar{\sigma}_u|$$

are degenerate in the dissociation limit. Does the CEPA0 method work for this example?
