MR CEPA

THE MULTI CONFIGURATION REFERENCE CEPA METHOD

§1 Introduction

There are several methods for generalising the CEPA method for a multi-configuration reference function, e.g. the Multi-Reference Averaged Coupled Pair Functional (MR-ACPF) (Ahlrichs). This is a generalisation of the Coupled Pair Functional method for single-configuration reference functions. These two methods use a functional (the Correlation Energy Functional instead of the Energy Expectation Value) for optimising the energy. It has the advantage that is is adapted to calculating energy gradients relatively easily. However, it appears that functionals may only be constructed for wave functions with a rather simple structure.

In the following a more direct generalisation of the CEPA method will be discussed. For this purpose we first introduce the concept of the Excitation Class.

§2 Excitation Classes

The reference function is given by :

$$| \Psi_0 > \equiv | 0 > = \frac{\sum_R c_R | R >}{[\sum_R c_R^2]^{1/2}} \qquad (4.1)$$

The MOs are divided into three subgroups :

1) The inactive MOs : these are doubly occupied in all reference functions | R >.
2) The active MOs : these are the MOs with variable occupations in the reference set.
3) The virtual or external MOs : these are the MOs which are not used (empty) in the reference set.

The Multi-Reference Coupled Cluster (MRCC) function is defined by :

$$| \Psi_{MRCC} > = \exp(T_1 + T_2) | 0 > \qquad (4.2)$$

where T_1 and T_2 represent the single and double excitations respectively. These operators include the corresponding coefficients (amplitudes).

$$T_1 = \sum_R \sum_T t_{R,T} \tau_R^T \qquad (4.3a)$$

$$T_2 = \sum_{R<S} \sum_{T<U} t_{RS,TU} \tau_{RS}^{TU} \qquad (4.3b)$$

where τ is an excitation operator and t is the corresponding coefficient.

The excitations may be classified as follows. Each class (k,ℓ) contains all configurations with k holes in the inactive MOs and ℓ particles in the virtual space. If n = the number of electrons in the

active space for $|0>$, the class (k,ℓ) configurations have $(n+k-\ell)$ electrons in the active space. In order to have a consistent framework, we have to use a Complete Active Space (CAS) reference (configuration) space, i.e. we assume that class (0,0) is complete.

By combining the excitation operators we see that :

$$\tau(k,l)\tau(k',l') = \tau(k+k',l+l') \tag{4.4}$$

In the following we will use the projection operator $\mathbf{P}_{k\ell}$. This operator projects to the space spanned by the class (k,ℓ) configurations. The space spanned by the excitations generated by $\exp(\mathbf{T}_1+\mathbf{T}_2)$ is divided into three subspaces by defining the projection operators :

$$\begin{aligned} \mathbf{P}_0 &= \mathbf{P}_{00} \\ \mathbf{P}_a &= \sum_{kl} \mathbf{P}_{kl} \qquad 0 \le k,l \le 2 \quad \text{except} \quad k = l = 0 \\ \mathbf{P}_b &= \sum_{kl} \mathbf{P}_{kl} \qquad k > 2 \quad \text{or} \quad l > 2 \end{aligned} \tag{4.5}$$

$\mathbf{P}_0$ projects to the reference space $\{|R>\}$, $\mathbf{P}_a$ projects to the interacting space of $|0>$ and $\mathbf{P}_b$ projects to all higher excitations. From the definition it follws that :

$$\mathbf{P}_0 + \mathbf{P}_a + \mathbf{P}_b = \mathbf{1} \tag{4.6}$$

We assume that the Mult-Reference CEPA (MRCEPA) function may be written as :

$$|\Psi_C> = (\mathbf{P}_0 + \mathbf{P}_a)\,|\Psi_{MRCC}> \tag{4.7}$$

This is the function for which we want to calculate the diagonal shifts needed to obtain size consistency (as far as possible).

§3 The MR CEPA diagonal shift

We start with the MR-CC equations :

$$<0|(\mathbf{H}_c - E)\exp(\mathbf{T})|0> = 0 \tag{4.8}$$

$$<\tau|(\mathbf{H}_c - E)\exp(\mathbf{T})|0> = 0 \tag{4.9}$$

where the reference function is defined by Eq (4.1). The first equation is obtained by taking a linear combitation of the secular equations for the reference configurations. In the actual calculation the coefficients c_R are varied individually. We will, however, use the contracted form Eq (4.8), since this is more useful for our purpose, i.e. the "derivation" of an expression for the diagonal shift. The contracted form, however, does not imply that the coefficients are fixed to the variationally obtained values, e.g. from a previous CASSCF calculation.

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Since $\mathcal{P}_a$ projects to the full interacting space of the reference set {| R >}, the first equation is equivalent to the first MRCEPA equation :

$$< 0 | \mathcal{H} - E | \Psi_C >= 0 \qquad (4.10)$$

Eq (4.9) may be rewritten by using Eqs (4.6) and (4.7) :

$$\begin{aligned} &< \tau | (\mathcal{H} - E)(\mathcal{P}_0 + \mathcal{P}_a + \mathcal{P}_b)\exp(\mathcal{T}) | 0 >= \\ &=< \tau | \mathcal{H} - E | \Psi_C > + < \tau | \mathcal{H}\mathcal{P}_b \exp(\mathcal{T}) | 0 >= \\ &=< \tau | \mathcal{H} - E + \Delta E_\tau | \Psi_C >= 0 \end{aligned} \qquad (4.11)$$

The last line of Eq (4.11) defines the diagonal shift ΔE_τ. We use the second term in the middle part of Eq (4.11) to calculate this shift. We see that :

$$\Delta E_\tau < \tau | \Psi_C >= \Delta E_\tau t =< \tau | \mathcal{H}\mathcal{P}_b \exp(\mathcal{T}) | 0 >= \frac{1}{2} < \tau | \mathcal{H}\mathcal{P}_b \mathcal{T}^2 | 0 > \qquad (4.12)$$

where the coefficient t of $| \tau >$ in Ψ_C is given by $< \tau | \Psi_C >$. In Eq (4.12) only the first term in the expansion of $\exp(\mathcal{T})$ contributing to the shift is kept. This result is analogous to the (Single Reference) CEPA result :

$$\Delta E_{IJ}^{AB} d_{IJ}^{AB} = \frac{1}{2} < D_{IJ}^{AB} | \mathcal{H}\mathcal{T}^2 | 0 > \qquad (4.13)$$

For the Multi Reference case, however, $\frac{1}{2}\mathcal{T}^2$ is replaced by $\frac{1}{2}\mathcal{P}_b\mathcal{T}^2$. The projection with $\mathcal{P}_b$ is needed since the interacting space configurations do not contribute to Eq (4.12). In the single reference case (and neglecting the single excitations) the projection is not needed since there the interacting space only contains the double excitations and consequently $\frac{1}{2}\mathcal{T}^2$ only contains quadruple excitations.

§4 Approximations

We start with the direct term approximation.

The H-matrix element equivalence relation is used in the following way :

$$\frac{1}{2} < \tau_{kl} | \mathcal{H}\mathcal{P}_b \mathcal{T}^2 | 0 >=< \tau_{kl} | \mathcal{H}\mathcal{P}_b \mathcal{T} | \tau_{kl} > t_{kl} =< 0 | \mathcal{H}\mathcal{P}_{\mathfrak{c}(kl)} \mathcal{T} | 0 > t_{kl} \qquad (4.14)$$

The projection operator $\mathcal{P}^b_{\mathfrak{c}(kl)}$ projects to all excitation classes which together with class (k,ℓ) generate an excitation outside the interacting space of the reference function (see Eq (4.4)). Here $\mathfrak{c}(k,\ell)$ is the complement of class (k,ℓ). For example, if $k = \ell = 1$, $\mathcal{P}_{\mathfrak{c}(kl)}$ projects to the classes (2,i) and/or (j,2) with $0 \le i,j \le 2$. For $k = \ell = 0$ $\mathcal{P}_{\mathfrak{c}(kl)}$ does not exist, i.e. there is no shift for the reference

configurations. The shift contributions which are projected out by $\mathcal{P}_{c(kl)}$ are not included since they represent interactions which are already present in the MRCI H-matrix, whereas the shifts are introduced to take account of interactions with excitations outside the interacting space of the reference function. Therefore the contributions which are projected out by $\mathcal{P}_{c(kl)}$ are called the Variationally Interacting (VI) terms. Handling the VI terms correctly is important for both obtaining accurate correlation energies and for the size consistency behaviour of the method.

Finally we use Eq (4.8) in order to express the shift $\Delta E_{k\ell}$ in terms of the correlation energy contributions of the various classes. We have :

$$E_{corr} = < 0 | \mathcal{H} | \Psi_C > = \sum_{kl} E_{kl} \qquad (4.15)$$

where

$$E_{kl} = < 0 | \mathcal{H}\mathcal{P}_{kl} | \Psi_C > \qquad (4.16)$$

represents the correlation energy contribution of the class (k,ℓ) excitations. The shift for $|\tau_{kl}>$ is then given by :

$$\Delta E(\tau_{kl}) = \sum_{k'l'} E_{k'l'} \quad k' \leq 2-k \text{ or } l' \leq 2-l \qquad (4.17)$$

These are the correlation energy contributions from all classes which combined with class (k,ℓ) correspond to a "higher" excitation.

EPV terms.

$\mathcal{T}$ always contains τ itself. Since $\tau^2 = 0$ because of the Pauli exclusion principle, the corresponding contributions from $\mathcal{T}^2$ vanish. However, in the direct term approximation these contributions are nevertheless included in the shift and therefore they are called the Exclusion Principle Violating (EPV) terms. These may be avoided in several (approximate) ways. For the inactive space it is possible to define pair correlation energies, just as in the CEPA1 method. Inactive space EPV corrections may then be calculated analogous to the CEPA1 method. For the active space, however, this is not possible. The EPV corrections corresponding to the active space excitations may, however, be incorporated in an average way, analogous to the (MR-)ACPF method. In this method a damping factor is used :

$$\Delta E_\tau = \frac{n-2}{n} E_{corr}$$

for any excitation. For the (Single Reference) ACPF method it may be proven that this choice yields size consistent results. In the MR-ACPF method, however, the correction for the VI terms

is not applied and this appears to lead to reletively large size consistency errors, in contrast to the MRCEPA results.

§5 Comments

1) By comparing our result to the original CEPA0 method, we see that the shifts depend on the excitation class of the configuration for which the shift is calculated. In the CEPA0 method we have only single (class (1,1)) and double (class (2,2)) excitations. In the original "derivation" only the double excitations appeared explicitly and the role of the single excitations in SR-CEPA is not quite clear. On the other hand, if HF MOs are used, the single excitations will not be important numerically, since then the single excitations do not contribute to the first CEPA equation (Brillouin Theorem). The only effect of the single excitations is then that they affect the coefficients of the double excitations
2) In contrast to the CEPA0 equations the MRCEPA equations are not linear. A linear system of equations would be obtained by generalising the CEPA0 equations directly :

$$E = < 0 \mid \mathcal{H} \mid \Psi_C > = E_0 + E_c \qquad (4.18)$$

$$< \tau \mid \mathcal{H} - E_0 \mid \Psi_C > = < \tau \mid \mathcal{H} - E + E_c \mid \Psi_C > = 0 \qquad (4.19)$$

In Eq (4.19) all correlation energy contributions are included into the shift. In this case the VI terms are neglected. As a result this method appears not really to perform better numerically than the MRCI method.

3) There are some formal problems with the Multi-Reference case. In Eq (4.3) the indices R and/or S may coincide with the indices T and/or U of another excitation operator if both indices correspond to active MOs. If this is the case, the corresponding excitation operators do not commute. As a consequence the expansion of $\exp(\mathcal{T})$ is not straightforward. In our method all non-zero commutators are ignored. This is in fact an important reason why it is difficult to develop the MR-CC method in a rigorous way.
4) The H-matrix element equivalence only works under the following conditions :
   a) The original matrix element only contains 2-electron contributions (the configurations are doubly excited with respect to each other)
   b) $\mathcal{T}$ and τ in Eq (4.14) have no orbital indices in common.

   The first condition is not satisfied if $\mid \tau >$ is singly excited wih respect to $\mid R >$, since the Brillouin Theorem in the Multi-Reference case only holds for certain linear combinations of the reference functions. Therefore the H-matrix element equivalence in the form of Eq (4.14) does not hold in this case.

   The second condition leads to the EPV terms.

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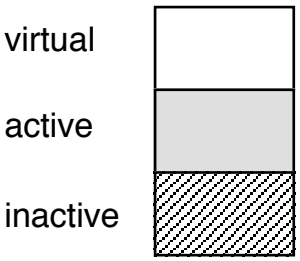
Excitation Classification in MRDCEPA



Class (k,ℓ)

k holes / ℓ particles

$0 \le k, \ell \le 2$

Excitation classes

ℓ \ k	0	1	2
0	Ref		
1		SR	
2			SR

Variationally Interacting Terms

	00	10	20	01	11	21	02	12	22
00	R	V	V	V	V	V	V	V	V
10	V	V		V	V		V	V	
20	V			V			V		
01	V	V	V	V	V	V			
11	V	V		V	V				
21	V			V					
02	V	V	V						
12	V	V							
22	V								

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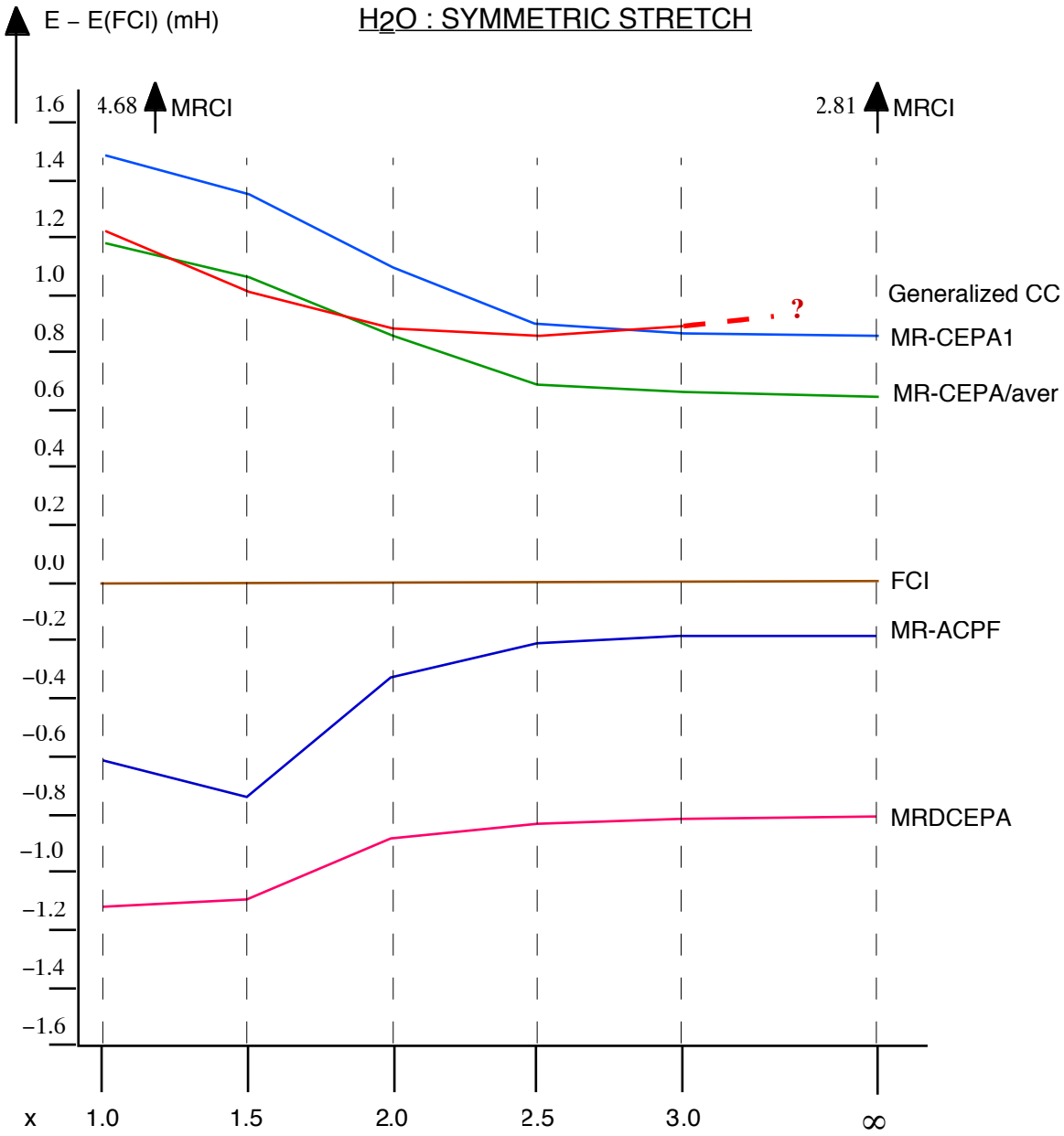

H_2O with cc-PVDZ basis, < HOH = 110.6, symmetric stretch R_{OH} = x R_e, Re = 0.9755 A,
Φ_{ref} = Proper Dissociation function (4X4 CASSCF)

MR-ACPF	Average EPV corrections (damping factor)
MRDCEPA	VI corrections
MR-CEPA/aver	VI corrections + Average EPV corrections
MR-CEPA1	VI corrections + CEPA1-type EPV corrections (inactive space) + Average EPV damping (active space)