Theoret. Chim. Acta (Berl.) 59, 487–500 (1981)

THEORETICA CHIMICA ACTA

CEPA Calculations on Open-Shell Molecules.
I. Outline of the Method

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A systematic description of an open-shell CEPA-PNO (coupled electron pair approximation using pair natural orbitals) program based on spin-adapted PNO-configurations is given which is used for the calculation of correlation energies of open-shell molecular ground and excited states. This program is an extension of our previous closed-shell CEPA-PNO program and is designed to treat doublet, triplet and open-shell singlet states. Its characteristic features are: Inclusion of all singly and doubly substituted configurations belonging to the interacting space; direct determination of pair natural orbitals; matrix element generator for automatic construction of matrix elements for prototype configurations; CEPA estimate of the contributions of unlinked clusters of singles and doubles. Applications of the program to small molecules will appear in further papers of this series.

Key words: Coupled electron pair approximation (CEPA) – Open-shell molecules – Pair natural orbitals (PNOs).

1. Introduction

Despite of the very rapid recent progress in conventional and particularly in direct CI methods–for a rather detailed, but not completely up-to-date compilation the reader is referred to [1]–the "coupled electron pair approximation" (CEPA) is one of the most efficient and powerful numerical schemes to calculate atomic and molecular correlation energies [2–8]. This is true in particular if CEPA is combined with the use of "pair natural orbitals" (PNOs) or with a "self consistent electron pairs" (SCEP) treatment [9–11].

0040-5744/81/0059/0487/$02.80

Historically, the first CEPA-paper is Meyer's famous paper on the ionization energies of H_2O [2], followed by the calculations on methane [3] and OH [4] by the same author. In Kutzelnigg's group the use of PNOs for the calculation of molecular correlation energies at different levels of sophistication started even earlier [5–7]; a detailed description of the closed-shell CEPA-PNO program [8] was published in 1975 followed by a series of applications. An extension of the CEPA method containing a more accurate treatment of the electron pairs and certain computational advantages was proposed by Meyer and Dykstra and has been termed as SCEP treatment [9–11]. The interrelations between the CEPA-model, conventional and direct CI schemes, the SCEP method and the many-body perturbation theory (MBPT) have been discussed by Ahlrichs [12, 13].

It seems to be justified to state that all these methods have been developed to a status in which they give more or less identical results; an observation that is also proved by numerical calculations, at least for closed-shell states.

In all these methods the treatment of open-shell states is much more complicated than for closed-shell states since the number and complexity of the configurations that have to be included increases rapidly with the number of unpaired electrons and the number of necessary configurations in the reference space. Therefore, most of the above mentioned methods are much less far developed for open-shell states.

This paper is the first one of a series of papers containing the results of CEPA-PNO calculations on open-shell molecules in ground or excited states. It contains a systematic description of our program which has to be looked at as an extension of our closed-shell CEPA-PNO program [8] as well as of our open-shell IEPA-PNO (independent electron pair approximation) program [7]. The discussion is mainly concerned with doublet, triplet and open-shell singlet states. But the characteristic features of our program (selection of configurations, determination of PNOs, matrix element generator) are designed to enable a straightforward extension to states which can only be described with a reference space containing more than one configuration (MC-SCF reference).

Meyer and his coworkers have applied very successfully their CEPA program for quite some time to open-shell molecules as well as to closed-shell ones ([2, 3, 4] and numerous calculations as quoted in [14]). Many of the ideas and details described in this paper are already explicitly or implicitly incorporated in Meyer's CEPA program or transferred from our closed-shell CEPA program [8]. Nevertheless, an explicit documentation of our scheme seems to be appropriate since it is more general than Meyer's (e.g. the open-shell singlet state is included), it can be generalized in a straightforward way to certain classes of multi-reference wavefunctions, and since a systematic description of many details (e.g. inclusion of singles, treatment of semiinternal doubles) has never been published.

2. Reference Wavefunction

Let Φ_0 be the reference wavefunction of the state Ψ under consideration, i.e. Φ_0 is a linear combination of those configurations which are dominant in the CI expansion of Ψ. (It is convenient to suppose that the orbitals occupied in Φ_0 and the expansion coefficients are optimized). In the simplest cases Φ_0 can be:

(A) one closed-shell RHF determinant

$$\Phi_0 = |\varphi_1\bar{\varphi}_1 \cdots \varphi_n\bar{\varphi}_n|; \tag{1}$$

(B) one open-shell RHF determinant, all singly occupied orbitals with parallel spins

$$\Phi_0 = |\varphi_1\bar{\varphi}_1 \cdots \varphi_n\bar{\varphi}_n\varphi_{n+1} \cdots \varphi_{n+p}|; \tag{2}$$

(C) a two-determinantal wavefunction for open-shell singlets (or triplets with $M_S = 0$) with two singly occupied orbitals

$$\Phi_0 = \frac{1}{\sqrt{2}}\{|\varphi_1\bar{\varphi}_1 \cdots \varphi_n\bar{\varphi}_n\varphi_{n+1}\bar{\varphi}_{n+2}| \mp |\varphi_1\bar{\varphi}_1 \cdots \varphi_n\bar{\varphi}_n\bar{\varphi}_{n+1}\varphi_{n+2}|\} \tag{3a, b}$$

(upper sign for singlet, lower for triplet);

(D) a linear combination of a few closed-shell RHF determinants differing by double substitutions, e.g.

$$\Phi_0 = C_1|\varphi_1\bar{\varphi}_1 \cdots \varphi_{n-1}\bar{\varphi}_{n-1}\varphi_n\bar{\varphi}_n| + C_2|\varphi_1\bar{\varphi}_1 \cdots \varphi_{n-1}\bar{\varphi}_{n-1}\varphi_{n+1}\bar{\varphi}_{n+1}|. \tag{4}$$

High symmetry, avoided crossings, dissociation of multiple bonds etc. can make more complicated reference wavefunctions necessary where the coefficients are given either by symmetry (as in (3)) or by energy minimization (as in (4)) by means of a MC-SCF procedure.

If we restrict our treatment to the cases (1)–(3) we will call the orbitals occupied in Φ_0 "internal orbitals" (denoted by the letters I, J, K) and distinguish between "doubly occupied" orbitals (denoted by R, S, T) and "singly occupied" orbitals (U, V, W). The remaining orbitals unoccupied in Φ_0 and orthogonal to the internal orbitals, are called "external" orbitals (A, B, C). If Φ_0 consists of more than one configuration, the terms "singly occupied" and "unoccupied" generally loose their meaning. A distinction between "inactive", "active" and "external" orbitals [16] seems to be more appropriate.

In some cases it is possible to start from a set of orbitals diagonalizing one single Fock-operator (i.e. from canonical HF orbitals)

$$(I/F/J) = \varepsilon_I\delta_{IJ}. \tag{5}$$

For the closed-shell case (1) F is the conventional Fock-operator

$$F = h + \sum_R (2J_R - K_R). \tag{6}$$

For the open-shell cases (2) and (3) F has a more complicated form; our RHF calculations are done with an operator as given by McWeeny [17] for the high-multiplicity case (2), and as proposed by us previously for the open-shell singlet [18].

In order to save computer time by making use of symmetry properties of localized equivalent orbitals we frequently transform within the sets of doubly occupied, singly occupied and external orbitals – the use of PNOs in any case amounts to a transformation in the subspace of the external orbitals. Then (5) is no longer valid in general. But as long as we start from a RHF reference wavefunction (cases (1)–(3)) Brillouin's theorem says that off-diagonal Fock operator matrix elements connecting different one-particle subspaces vanish

$$(I|F|J)\begin{cases}=0 & \text{if } I \text{ and } J \text{ belong to different subspaces}\\ \neq 0 & \text{else.}\end{cases} \tag{7}$$

We have to comment briefly on open-shell singlet states (3a) where φ_{n+1} and φ_{n+2} have the same spatial symmetry and do interact with the closed-shell configurations φ_{n+1}^2 and φ_{n+2}^2 [19]. If we discard the underlying doubly occupied orbitals for a moment and abbreviate the two singly occupied orbitals by φ_1 and φ_2 the CI matrix for a 3×3 CI [36] among the above three configurations reads

$$\begin{pmatrix} E(\varphi_1^2) & \sqrt{2}(1|h+J_1|2) & (12|21)\\ \sqrt{2}(1|h+J_1|2) & E(^1\varphi_1\varphi_2) & \sqrt{2}(1|h+J_2|2)\\ (12|21) & \sqrt{2}(1|h+J_2|2) & E(\varphi_2^2)\end{pmatrix} \tag{8}$$

if we maintain the orthogonality of the orbitals φ_1 and φ_2. There are two procedures to determine the orbitals φ_1 and φ_2:

(a) Energy minimum of $E(^1\varphi_1\varphi_2)$ with respect to a rotation between φ_1 and φ_2. This leads to the well-known condition [20]

$$(11|12)=(22|21). \tag{9}$$

Hence all off-diagonal matrix elements connecting $^1\varphi_1\varphi_2$ with φ_1^2 and φ_2^2 are identical and non-zero. $E(^1\varphi_1\varphi_2)$ is not an upper bound to the true energy of the second singlet state; a CI between φ_1^2 and $^1\varphi_1\varphi_2$ is necessary and may push the energy of the second singlet state upwards.

(b) Brillouin condition for the rotation between φ_1 and φ_2:

$$(1|F|2)=(1|h+J_1|2)=0. \tag{10}$$

Then the off-diagonal matrix element $(\varphi_1^2|H|^1\varphi_1\varphi_2)$ vanishes, but $(\varphi_2^2|H|^1\varphi_1\varphi_2)$ not. Hence this choice of the orbitals is equivalent to a CI between φ_1^2 and $^1\varphi_1\varphi_2$ and yields an upper bound to the energy of the second singlet state, provided one knows in advance whether φ_1^2 or φ_2^2 corresponds to the singlet ground state.

Since the condition (10) is most easily implemented in our RHF program for open-shell singlets we generally use the second possibility. But it has to be emphasized that in both schemes single substitutions contribute to the total energy in second order perturbation theory. The inclusion of singles in the CI treatment is therefore compulsory and will render the final CI energy independent of the choice of orbitals φ_1, φ_2.

3. Selection of Configurations

In order to account for the most important part of electron correlation we include explicitly all those configurations interacting directly with the reference wavefunction Φ_0 (interacting space [21–23]). These are all singly and doubly substituted configurations which have a non-vanishing matrix element with Φ_0. Higher substitutions and non-interacting doubles are neglected in the first step. Unlinked clusters of interacting doubles – necessary to obtain the correct dependence on the number of particles [3, 24–26] are taken care of in the final step by a CEPA-type estimate of their energy contributions.

The construction of spin-adapted configuration state function (CSFs) spanning the interacting space follows closely the lines given by McLean and Liu [21]:

(a) Set up all primitive determinants for an excitation $I \rightarrow A$ or $IJ \rightarrow AB$ etc. which belong to the same M_S value as Φ_0 and differ by the spin orientations of the singly occupied orbitals.

(b) Discard all linear combinations belonging to an S value different from that of Φ_0 and those that do not interact with Φ_0. The latter can be obtained by the procedure of McLean and Liu [21]. In most cases an inspection of the matrix elements suffices.

(c) Generally, there is more than one interacting CSF. Then, we choose them in a way as to make the matrix elements as simple as possible and to allow for a physical interpretation of the CSFs.

A compilation of the interacting singles and doubles is given in Tables 1–3, this list is complete for the reference wavefunctions (1) to (3). The classification of the prototype configurations is based on the following specifications:

(1) Type of the orbital or orbitals to be substituted. The letters D for doubly occupied and S for singly (or partly) occupied orbitals are used.

(2) Type of the orbital or orbitals into which the excitation occurs. Following Silverstone and Sinanoğlu [27] we distinguish between external, semiinternal, and internal double substitutions (corresponding to the classes $\{0, 2\}$, $\{1, 1\}$, $\{2, 0\}$ as used by McLean and Liu [21]).

(3) Order of excitation and (if necessary) spin coupling scheme of the singly occupied orbitals. The most convenient way to specify the order of the excitation is to call configurations "singly substituted" if they couple to the reference wavefunction by means of one-electron (F-operator) matrix elements, and "doubly substituted" if the coupling is via an exchange integral.

We have used a shorthand notation in writing down the CSF, by specifying only the replacements with respect to Φ_0: Φ_R^A means that in *all* determinants of Φ_0 R

Table 1. Singly substituted configurations

Nr.	Type	Φ_0	CSF	ME with Φ_0
1	D, external	(1), (2), (3)	$\frac{1}{\sqrt{2}}(\Phi_R^A+\Phi_{\bar{R}}^{\bar{A}})$	$\sqrt{2}\,(R\|F_C\|A)$
2	D, internal	(2)	$\Phi_R^{\bar{U}}$	$(R\|F_C+\frac{1}{2}K_e\|U)$
		(3a)	$\frac{1}{\sqrt{2}}(\Phi_{1,R}^U+\Phi_{2,\bar{R}}^{\bar{U}})$	$(R\|F_C+\frac{1}{2}K_U-\frac{3}{2}K_V\|U)$
3	S, external	(2)	Φ_U^A	$(U\|F_C-\frac{1}{2}K_e\|A)$
		(3a)	$\frac{1}{\sqrt{2}}(\Phi_{1,U}^A+\Phi_{2,\bar{U}}^{\bar{A}})$	$(U\|F_C-\frac{1}{2}K_U+\frac{3}{2}K_V\|A)$
4	S, internal	(3a)	$\Phi_{1,U}^V$ $\Phi_{1,\bar{V}}^{\bar{U}}$	$(U\|F_C-\frac{1}{2}K_U+\frac{1}{2}K_V\|V)$ $(U\|F_C-\frac{1}{2}K_V+\frac{1}{2}K_U\|V)$

$F_C=h+\sum_S(2J_S-K_S)+\sum_V(J_V-\frac{1}{2}K_V)$.

$K_e=\sum_V K_V$.

is to be replaced by A; the additional lower index in $\Phi_{1,R}^A$ means that this replacement has to be done only for the first determinant in Φ_0. Furthermore, since we use PNO-type expansions, Tables 2 and 3 only contain "diagonal" configurations.

The most difficult cases are the semiinternal doubles for DS pairs (Nr. 11 and 13 in Table 2). They contain formally singly substituted determinants and are responsible for the well-known spin-polarization effects [28–30]. Here the pair concept partly breaks down since the process of constructing linear independent, orthogonal CSFs mixes different pairs. In our previous IEPA scheme [7] we have chosen CSFs which preserve the pair concept as much as possible, but lead to rather complicated matrix elements and effective operators. In Table 3 another alternative is chosen which seems to be simpler and more symmetric. The difference between these different possibilities is expected to be small as soon as all nondiagonal CI-blocks are included in the final CI matrix.

The operators appearing in the matrix elements in Tables 1–3 are given by

$$F_c=h+\sum_S(2J_S-K_S)+\sum_V(J_V-\tfrac{1}{2}K_V) \tag{11}$$

$$K_e=\sum_V K_V \tag{12}$$

$$(A|K_{RS}^{\pm}|B)=\tfrac{1}{2}[(AR|SB)\pm(AS|RB)]. \tag{13}$$

If we start from RHF wavefunctions of the types (1)–(3) – type (3a) only if φ_{n+1} and φ_{n+2} have different spatial symmetry – all singly substituted configurations satisfy Brillouin's theorem and do not belong to the interacting space. In most

Table 2. "Interacting" doubly substituted configurations

Nr.	Type		Φ_0	CSF	ME with Φ_0
1	DD	external	(1)–(3)	$\Phi^{A\bar{A}}_{R\bar{R}}$	$(A\vert K_R\vert A)$
2		semiint.	(2)	$\Phi^{BU}_{R\bar{R}}$	$(A\vert K_R\vert U)$
			(3a)	$\frac{1}{\sqrt{2}}(\Phi^{B\bar{U}}_{1,R\bar{R}}+\Phi^{U\bar{B}}_{2,R\bar{R}})$	
3		internal	(3a)	$\Phi^{U\bar{V}}_{1,R\bar{R}}$	$\sqrt{2}\,(U\vert K_R\vert V)$
4	DD′ singlet	external	(1)–(3)	$\frac{1}{\sqrt{2}}(\Phi^{A\bar{A}}_{R\bar{S}}+\Phi^{\bar{A}A}_{\bar{R}S})$	$\sqrt{2}\,(A\vert K^{+}_{RS}\vert A)$
5		semiint.	(2)	$\frac{1}{\sqrt{2}}(\Phi^{B\bar{U}}_{R\bar{S}}+\Phi^{\bar{U}B}_{\bar{R}S})$	$\sqrt{2}\,(B\vert K^{+}_{RS}\vert U)$
			(3a)	$\frac{1}{2}(\Phi^{U\bar{B}}_{1,R\bar{S}}+\Phi^{\bar{B}U}_{1,\bar{R}S}-\Phi^{B\bar{U}}_{2,R\bar{S}}-\Phi^{\bar{U}B}_{2,\bar{R}S})$	
6		internal	(3a)	$\frac{1}{\sqrt{2}}(\Phi^{\bar{U}V}_{1,\bar{R}S}-\Phi^{U\bar{V}}_{2,R\bar{S}})$	$2(U\vert K^{+}_{RS}\vert V)$
7	DD′ triplet	external	(1)–(3)	$\frac{1}{\sqrt{12}}(2\Phi^{AB}_{RS}+2\Phi^{\bar{A}\bar{B}}_{RS}+\Phi^{A\bar{B}}_{R\bar{S}}-\Phi^{B\bar{A}}_{R\bar{S}}+\Phi^{\bar{A}B}_{\bar{R}S}-\Phi^{\bar{B}A}_{\bar{R}S})$	$2\sqrt{3}\,(A\vert K^{-}_{RS}\vert B)$
8		semiint.	(2)	$\frac{1}{\sqrt{6}}(2\Phi^{\bar{U}\bar{C}}_{\bar{R}\bar{S}}+\Phi^{\bar{U}C}_{\bar{R}S}-\Phi^{C\bar{U}}_{R\bar{S}})$	$\sqrt{6}\,(C\vert K^{-}_{RS}\vert U)$
			(3a)	$\frac{1}{\sqrt{12}}(2\Phi^{UC}_{1,RS}-2\Phi^{\bar{U}\bar{C}}_{2,\bar{R}\bar{S}}+\Phi^{U\bar{C}}_{1,R\bar{S}}+\Phi^{C\bar{U}}_{2,R\bar{S}}-\Phi^{\bar{U}C}_{1,\bar{R}S}-\Phi^{\bar{C}U}_{2,\bar{R}S})$	
9		internal	(2)	$\Phi^{\bar{U}\bar{V}}_{\bar{R}\bar{S}}$	$2(U\vert K^{-}_{RS}\vert V)$
10	DS singlet	external	(2)	$\Phi^{\bar{A}A}_{\bar{R}U}$	$(A\vert K^{+}_{RU}\vert A)$
			(3a)	$\frac{1}{\sqrt{2}}(\Phi^{\bar{A}A}_{1,\bar{R}U}-\Phi^{A\bar{A}}_{2,R\bar{U}})$	
11		semiint.		Table 3	
12	DS triplet	external	(2)	$\frac{1}{\sqrt{6}}(2\Phi^{AB}_{RU}+\Phi^{\bar{A}B}_{\bar{R}U}-\Phi^{\bar{B}A}_{\bar{R}U})$	$\sqrt{6}\,(A\vert K^{-}_{RU}\vert B)$
			(3a)	$\frac{1}{\sqrt{12}}(2\Phi^{AB}_{1,RU}-2\Phi^{\bar{A}\bar{B}}_{2,\bar{R}\bar{U}}+\Phi^{\bar{A}B}_{1,\bar{R}U}+\Phi^{B\bar{A}}_{2,R\bar{U}}-\Phi^{\bar{B}A}_{1,\bar{R}U}-\Phi^{A\bar{B}}_{2,R\bar{U}})$	
13		semiint.		Table 3	
14	SS′ singlet	external	(3a)	$\Phi^{A\bar{A}}_{1,U\bar{V}}$	$\sqrt{2}\,(A\vert K^{+}_{UV}\vert A)$
15	SS′ triplet	external	(2)	Φ^{AB}_{UV}	$2(A\vert K^{-}_{UV}\vert B)$

$(A\vert K^{\pm}_{RS}\vert B)=\frac{1}{2}[(AR\vert SB)\pm(AS\vert RB)]$

Table 3. Semiinternal DS substitutions

Φ_0	Excitation	CSF	ME with Φ_0
(2) $p=1$	$RU \to UA$	$\frac{1}{\sqrt{6}}(2\Phi^{\bar{U}A}_{\bar{R}U} - \Phi^{A}_{R} + \Phi^{\bar{A}}_{\bar{R}})$	$\sqrt{3/2}\,(R\|K_U\|A)$
(2) $p=2$	$RU \to UA$	$1/2(-\Phi^{A}_{R} + \Phi^{\bar{A}}_{\bar{R}} + \Phi^{\bar{U}A}_{\bar{R}u} + \Phi^{\bar{V}A}_{\bar{R}V})$	$(R\|K_U + K_V\|A)$
	$RV \to VA$	$1/\sqrt{2}\,(\Phi^{\bar{U}A}_{\bar{R}U} - \Phi^{\bar{V}A}_{\bar{R}V})$	$1/\sqrt{2}\,(R\|K_U - K_V\|A)$
	$RU \to VA$	$1/\sqrt{2}\,(\Phi^{\bar{V}A}_{\bar{R}U} + \Phi^{\bar{U}A}_{\bar{R}V})$	$\sqrt{2}(R\|K^{-}_{UV}\|A)$
	$RV \to UA$	$1/\sqrt{2}\,(\Phi^{\bar{V}A}_{\bar{R}U} - \Phi^{\bar{U}A}_{\bar{R}V})$	$\sqrt{2}\,(R\|K^{+}_{UV}\|A)$
(2) $p>2$		Compare Ref. 7	
(3a)	$RU \to UA$ $RV \to VA$	$1/\sqrt{12}\,(2\Phi^{U\bar{A}}_{1,R\bar{U}} - 2\Phi^{\bar{U}A}_{2,\bar{R}U} + \Phi^{A}_{1,R} + \Phi^{A}_{2,R} - \Phi^{\bar{A}}_{1,\bar{R}} - \Phi^{\bar{A}}_{2,\bar{R}})$	$\sqrt{3/2}\,(R\|K_U - K_V\|A)$
	$RU \to VA$	$\frac{1}{2}(\Phi^{\bar{A}V}_{2,\bar{R}U} + \Phi^{AV}_{2,RU} - \Phi^{\bar{A}\bar{U}}_{1,\bar{R}\bar{V}} - \Phi^{A\bar{U}}_{1,R\bar{V}})$	$\sqrt{2}\,(R\|K^{-}_{UV}\|A)$
	$RV \to UA$	$\frac{1}{2}(\Phi^{\bar{A}V}_{2,\bar{R}U} + \Phi^{AV}_{2,RU} + \Phi^{\bar{A}\bar{U}}_{1,\bar{R}\bar{V}} + \Phi^{A\bar{U}}_{1,R\bar{V}})$	$\sqrt{2}\,(R\|2J_{UV} - K^{+}_{UV}\|A)$

cases they contribute only little to the total correlation energy as well as to excitation energies. But we have found some examples where their coupling with certain doubly substituted configurations is large and changes dramatically along a potential curve or surface. Their inclusion is also compulsary whenever correlation corrections to the expectation values of one-particle operators are to be calculated [31].

4. Determination of PNOs

Maintaining the ideas of pair theories of electron correlation as reviewed by Kutzelnigg [15] we combine all excitations from a specified pair of occupied orbitals (characterized by their indices I and J and the spin coupling between them) into a "pair CI". This contains in general CSFs for a) external doubles ($IJ \to AB$), b) semiinternal doubles ($IJ \to UA$), c) internal doubles ($IJ \to UV$). (We have indicated the different pairs by horizontal lines in Table 2). The dimension of pair CI is determined by the orbital basis set: if M' is the number of external orbitals there are $M'(M'+1)/2$ external doubles for each pair if one does not work in a PNO expansion; there are $M'p$ semiinternal doubles and so on.

In order to reduce the dimensions of the pair CI (and the final CI) matrices we generally use pair natural orbitals (PNOs). The *external doubles* are treated in the same way as described previously in our closed-shell program [8] using the approximate Ahlrichs – Driessler scheme [32], the only modification is that the effective one-electron operators occuring in the generalized Brillouin conditions (compare Table IV of Ref. [8]) are much more complicated than in the closed-shell case. So far they have been coded explicitly for the cases (1)–(3) in order to keep the computer time for this step as low as possible but their automatic generation with the matrix element generator (compare Sect. 5.) is in progress. By using PNOs the maximum number of external doubles per pair is reduced to M' or $M'/2$ in triplet excitations.

The *semiinternal doubles* can be included completely, their number per pair is only in the order of $M'p$ (p being the number of singly occupied orbitals). Alternatively, one can use "semiinternal PNOs", determined perturbationally or optimized by means of a Brillouin-theorem as proposed previously [7]. (See Appendix for details). In a series of pilot calculations we have found that these alternative treatments lead to virtually identical results (deviations in the order of $5 \cdot 10^{-6}$ a.u. at most). The main drawback of an expansion in virtual SCF orbitals is that one cannot truncate the one-particle space without considerable loss in energy, using the PNOs of the external doubles of the same pair a truncation to about $M'/2$ configurations is possible.

The *external singles* belonging to a fixed occupied orbital I are again considered as one "pair". Here a reduction of the dimension of the pair CI from M' to 1 analogously to the one for the semiinternal doubles is not possible – at least as long as one starts from a RHF Φ_0 – because the coefficients C_A vanish in first order. Instead we use the PNOs of the corresponding intraorbital pair $R\bar{R}$ if I is doubly occupied and virtual SCF orbitals if I is singly occupied.

The *internal doubles* and *internal singles* have to be included explicitly; their number is generally very small.

After the determination of the PNOs for each individual pair a pair CI is performed yielding a total pair energy E_{IJ} and a pair correlation energy

$$\varepsilon_{IJ} = E_{IJ} - E_0, \qquad \varepsilon_I = E_I - E_0. \tag{14}$$

The sum of the pair correlation energies of the individual pairs is the total correlation energy in the "independent electron pair approximation" (IEPA):

$$E^{\text{corr}}_{\text{IEPA}} = \sum_{IJ} \varepsilon_{IJ} + \sum_{I} \varepsilon_I. \tag{15}$$

As in our closed-shell program [8] we make frequent use of symmetry properties of localized equivalent orbitals: PNOs, diagonal and off-diagonal CI-blocks and CI coefficients of equivalent pairs can be generated by symmetry operations rather than by recalculation. In highly symmetric molecules one can save more than 50% of computer time by this procedure.

5. Matrix Element Generator

The matrix elements between configurations belonging to the same pair and particularly those for different pairs are so complicated that it is almost impossible to code all of them explicitly as we have done before in the closed-shell program [8]. We have rather written a general matrix element generator for an automatic construction and evaluation of CI matrix elements. It goes back to various studies in our own institute [33, 34] and is based on the following ideas:

(a) Since the PNOs belonging to different pairs and the PNOs of the external and semiinternal doubles belonging to the same pair are not orthogonal to each other, nonorthogonality has to be included explicitly.

(b) Since the CSFs used do not belong to one of the nice spin coupling schemes which allow for an analytical form of matrix elements [35] we have used the determinantal forms of the CSFs as given in the Tables 1–3 and applied Wick's algebra for a symbolic matrix element tape.

(c) Each symbolic matrix element is constructed only once for a pair of prototype CSFs. It is stored and used whenever these prototypes occur.

(d) The program is general enough as to allow application to more complicated reference wavefunctions Φ_0 as those given in (1)–(4).

The construction of the symbolic matrix element tape in terms of prototypes needs about 5–60 min computer time (Telefunken 440, Univac 1108) for the three cases (1) to (3). It can be stored once for all on a permanent file (about 100K Bytes), or the construction can be repeated for each individual calculation. The number of stored prototype matrix elements is 27 (closed-shell, [8]), 245 (doublet), 789 (triplet), 787 (open-shell singlet).
In constructing a full CI matrix using our matrix element generator it is necessary to emphasize the following points which are of fundamental importance for our treatment and which hold for the open-shell states treated here as well as for our previous closed-shell program:

(1) Despite of the fact that the PNOs of different pairs are non-orthogonal [14] all the CSFs remain orthogonal to each other.
(2) Two-electron integrals involving more than two external orbitals (SCF virtual orbitals, PNOs) do occur almost exclusively in the pair CI blocks, i.e. in the diagonal blocks of the full CI matrix. Furthermore, they are of the type

$(AB|BA) = (A|K_B|A)$ ext. doubles in singlet pairs

$(AB|BU) = (A|K_B|U)$ external vs semiint. doubles in singlet pairs, similar expressions in triplet pairs and between singles and doubles

$(AB|B'A') - (AB'|BA') = 2\ (A|K_{\bar{B}B'}|A')$ ext. doubles in triplet pairs

(A,A', B,B' are the two partners in a triplet pair function).

Since the dimension of a pair CI in general is only 20–30, the 4-index transformation is replaced by about 20 P (P = number of pairs) sweeps through the AO integral tape.

(3) For the matrix elements involving CSFs of different pairs, there are only two-electron integrals of the form

$(RA|BS)$

which are most easily evaluated using the $K^{\pm}$ operator of the occupied orbitals R and S. Since these operators are already necessary for the construction of the PNOs of the pair RS they are calculated and stored prior to the determination of the PNOs and are read into the core storage whenever they are asked for in off-diagonal matrix elements.

(4) Some additional difficulties arise in calculations including single substitutions: There are matrix elements containing two-electron integrals with three external orbital indices in off-diagonal blocks connecting single substitutions from the orbital R and joint doubles $R\bar{R}$, ${}^1RS$, ${}^3RS$, i.e. doubles involving the same orbital R. If we use the intraorbital PNOs of the pair $R\bar{R}$ as external orbitals for the singles from R then these matrix elements can be calculated immediately after the diagonal pair CI matrix for the pair $R\bar{R}$. Thus, no additional sweeps through the AO integral tape are necessary and the calculation of these matrix elements is primarily a problem of book-keeping.

In any case, the inclusion of singles greatly increases the number and types of off-diagonal matrix blocks, thus leading to a considerable increase in the computer time. Since they belong to the non-interacting space and generally contribute little to the total correlation energy one has to decide for each system whether or not they can be excluded.

6. The CEPA Scheme

The diagonal and off-diagonal CI blocks as constructed by means of the matrix element generator for the PNO configurations can be combined into a final CI matrix. Its dimension is roughly given by

$$N_{\mathrm{CI}} \approx N_{\mathrm{C}}^2 \cdot N_{\mathrm{PNO}} + N_{\mathrm{C}} \cdot N_{\mathrm{PNO}} \tag{16}$$

with

N_{C} = number of occupied orbitals to be correlated

N_{PNO} = average number of PNOs per pair; generally 20–30.

The second term of the right hand side is only effective if singles are included. The small number of internal and semiinternal configurations is neglected in (16). The diagonalization of the CI matrix (using the procedure given in [8]) yields a strictly variational total CI-energy denoted by $E_{\mathrm{PNO\text{-}CI}}$.

It is well known nowadays that any CI treatment including only singles and doubles has not the correct dependence on the number of electrons [24–26]. This defect has to be remedied by the inclusion of "unlinked clusters" of singles and doubles. The CEPA method amounts to an approximate scheme how to take care of these effects without calculating new matrix elements.

We are not going into details concerning different CEPA models [12]. For the open-shell cases (1)–(3) we have used the CEPA-2 model [4] which in the case of singles and doubles leads to the following equations (μ denotes one pair, IJ

say, I the single substitutions from the occupied orbital I, C_μ and C_I the vectors of the respective CI coefficients):

$$E = E_0 + \sum_\mu \varepsilon_\mu + \sum_I \varepsilon_I \tag{17}$$

$$\varepsilon_I = (\Phi_0|H|\Phi_I)C_I \tag{18}$$

$$\varepsilon_\mu = (\Phi_0|H|\Phi_\mu)C_\mu \tag{19}$$

$$H_{\mu 0} + H_{\mu\mu}C_\mu + \sum_\nu^{\neq\mu} H_{\mu\nu}C_\nu + \sum_J H_{\mu J}C_J + \sum_{J<K} H_{\mu,JK}\, C_J C_K = (E_0 + \varepsilon_\mu + \varepsilon_I + \varepsilon_J)C_\mu \tag{20}$$

$$H_{I0} + H_{II}C_I + \sum_J^{\neq I} H_{IJ}C_J + \sum_\nu H_{I\nu}C_\nu = \left(E_0 + \varepsilon_I + \sum_\mu^{I\mu} \varepsilon_\mu\right) C_I. \tag{21}$$

The notation is completely analogous to the one used in the closed shell case [8].

The contributions ε_I of the singly substituted configurations, as defined in (18), vanish if one starts from an SCF wavefunction, the corresponding coefficients C_I are small, but finite, since the non-zero second order terms $H_{I\nu}C_\nu$ enter into (21). By means of the coupling elements $H_{\mu J}C_J$ the singles enter into (20) and influence the coefficients $C\mu$ and pair correlation energies ε_μ. The last term on the left hand side of (20) represents unlinked clusters of singles and is neglected in the present version of our program, as are higher-order terms. Finally, the last term on the right hand side of (21) is the sum of all pair correlation energies ε_μ in which the pair index μ contains the orbital index I.

For all pairs μ, ε_μ contains the contribution of external doubles as well as semiinternal and internal doubles if the latter do exist. In the case of *DS* pairs with $p = 2$ (compare Table 3 and Sect. 3.) we have distributed the contributions of the three (open-shell singlet) or four (triplet) semiinternal excitations equally among the two pairs *RU* and *RV*. There is a certain degree of arbitrariness in this procedure, but at least the symmetry is preserved if *U* and *V* are equivalent, e.g. for π^2, ${}^3\Sigma^-$ and ${}^1\Delta$ states.

It has to be stressed that the justification of the CEPA model is based on certain complete and incomplete compensations of unlinked cluster contributions [15]. By sticking to CEPA-2 [4] and using the ε_μ as energy denominator shifts one may introduce non-negligible errors, in particular if some internal or semiinternal contributions are large (Pauli principle violations). This is apparently the reason for the rather poor CEPA value of the energy difference between ${}^3\Sigma_g^-$ and ${}^1\Delta_g$ in O_2 (part II of this series). An improved version of the CEPA scheme is currently in progress; a thorough discussion of this point is necessary for the multiple reference CEPA.

Appendix

Since the CSFs of semiinternal doubles for the pair IJ contain only one external orbital at a time we have the equivalence

$$\sum_{A}^{\text{ext.}} C_A \Phi_{IJ}(\cdots U \cdots A \cdots) = C_{A'} \Phi_{IJ}(\cdots U \cdots A \cdots) \tag{1}$$

$$C_{A'} \varphi_{A'} = \sum_{A} C_A \varphi_A \tag{2}$$

irrespectively, which set of external orbitals φ_A is used. That means, the use of a single "semiinternal PNO" $\varphi_{A'}$ is equivalent to the CI with all CSFs Φ_{IJ} $(\cdots U \cdots A \cdots)$ on the left hand side of (1). The coefficient $C_{A'}$ has been added since $\varphi_{A'}$ is normalized.

The C_A are the CI coefficients of the semiinternal doubles in the pair CI. They can be estimated perturbationally to first order by

$$\mathrm{C}_{\mathrm{A}} = \frac{(\Phi_0|H|\Phi_{IJ}(\cdots U \cdots A \cdots))}{E[\Phi_{IJ}(\cdots U \cdots A \cdots)] - E_0}. \tag{3}$$

A slightly better optimization for $\varphi_{A'}$ is obtained using the Brillouin condition

$$(\Phi_0 + C_{A'} \Phi_{IJ}(\cdots U \cdots A' \cdots)|H|\Phi_{IJ}(\cdots U \cdots A'' \cdots)) = 0 \quad \text{for all } \varphi_{A''} \perp \varphi_{A'} \tag{4}$$

i.e. the requirement that CSFs with $\varphi_{A''}$ instead of $\varphi_{A'}$ don't lead to any energy improvement. (4) leads to an inhomogeneous pseudo-eigenvalue equation for $\varphi_{A'}$ which is solved iteratively since the unknown coefficient $C_{A'}$ enters explicitly, in each iteration $C_{A'}$ is determined by the formula (3) [7]. In most cases the two procedures lead to almost identical results; the reason is that the matrix elements $(\Phi_0|H|\Phi_{IJ}$ $(\cdots U \cdots A \cdots))$ and the energy $E[\Phi_{IJ}(\cdots U \cdots A \cdots)]$ can be obtained easily since two-electron integrals involving more than one external orbital do not occur.

It has to be mentioned that the replacement (1, 2) is only possible when the C_A don't vanish in first order. Noninteracting configurations and singles for which the Brillouin theorem holds cannot be simplified in this manner.

Acknowledgement. We are indebted to Prof. Kutzelnigg and Dr. Kollmar for numerous stimulating discussions on this subject.

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Received July 15, 1980/March 13, 1981