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Molecular Orbital Calculations Based on Linear Combinations of Fragment Orbitals

I. Basic Theory and Interpretation of PE Spectra of π Systems

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A semiempirical MO method based on localized fragment orbitals has been developed, which is particularly suited for the construction of orbital correlation diagrams for the discussion of the electronic structure of complex molecules in terms of fragments and their interactions. The method allows for the inclusion of experimental ionization potentials and electron affinities of the fragments within the calculation of the Fock matrix elements and may thus form the basis of an interpretation of photoelectron spectra, comparable to the interpretation of UV spectra by means of the MIM method of Longuet-Higgins and Murrell. Several levels of approximation are discussed using the acrolein molecule as an example.

Key words: Photoelectron spectra, interpretation of ~

1. Introduction

The interpretation of complicated wave functions in a way which is illuminating and suggestive to a chemist requires concepts such as localized pairs or groups of electrons and which stresses additivity and transferability of the properties of individual bonds or distinct parts or fragments of complex systems. Thus a considerable effort has been devoted to the interpretation of wave functions of molecules in terms of localized orbitals [1–7] and to building up the wave function by starting from wave functions associated with its pieces or fragments [8–11]. The transferability of localized orbitals has been studied in detail [2, 12–14], and several methods have been designed to save computer time by making use of the transferability of results or Fock-matrix elements from calculations on smaller molecules [15–19]. A method which proceeds from chemical formulae towards exact solutions without assuming transferability is the PCILO method which uses localized bonding and antibonding orbitals as a basis for a perturbative expansion

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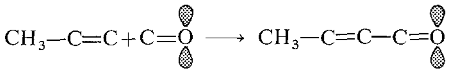
equivalent to a CI treatment [10, 20]. A discussion of excited states of composite molecules in relation to excited states of separate fragments became possible through the MIM approach of Longuet-Higgins and Murrell [21], whereas a generalization of the MIM method has been presented by v. Niessen [22]. Other schemes are especially designed for the interpretation of complex wave functions either by projection [6] or by decomposition of the molecular energy into local contributions [14, 23–26]. Perturbational methods have been applied mainly to study intermolecular interaction energies [27–30] and to the treatment of conformational problems [11, 31–33]. Recently fragment orbitals have been used for a perturbational analysis of molecular orbitals and energetics of composite systems [34]. Donor-acceptor interactions were discussed by means of self-consistent linear combinations of molecular orbitals [35], whereas linear combinations of bond orbitals were used to interpret "through-bond" interactions [36].

The present paper is concerned with the development of a semiempirical SCF MO method based on linear combinations of localized fragment orbitals (LCFO) and especially designed to compute the changes in orbital energies and wave functions which occur if two or more small systems or fragments are combined to form a new larger system. Thus we may consider the formal process

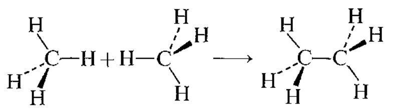
$$\text{A–X} + \text{B–Y} \longrightarrow \text{A–U–B},$$

where A and B are those parts of the fragments which remain essentially undisturbed (e.g. cores or substituents) and X and Y are those parts which interact to yield the system U. As an example we may consider the combination of the π systems of propene (X) and formaldehyde (Y) to yield the π system of acrolein (U), with A being the methyl group and B the oxygen lone pair:



$$CH_3{-}C{=}C + C{=}O \longrightarrow CH_3{-}C{=}C{-}C{=}O$$

As another example we consider the combination of two CH_4 molecules to form ethane:



Here we may take either the two CH-bonds as X and Y to form the CC bond U, A and B being the CH_3 groups, or else the whole ethane molecule may be taken as the combined system U. In the present paper we give an outline of the theory for both the combination of π and σ systems, with an application of the equations for π systems to the acrolein molecule. The detailed discussion of σ systems will be given in a subsequent paper [37].

The main application of this method of linear combination of fragment orbitals (LCFO) will be the interpretation of PE spectra of complex molecules on the basis of correlation diagrams which relate the orbital energies of fragments to those of the system under investigation. Correlation diagrams of this kind have proved very valuable in empirical assignments of PE spectra [38]. The method is therefore formulated in a way which allows for the systematic estimation of the inductive perturbation of one fragment by another such that it becomes possible to include in the calculation experimental values of ionization potentials and electron affinities of the fragments in a way comparable to that in which experimental data are included in the discussion of excited states within the MIM approach [21]. Furthermore, within the framework of the ZDO integral scheme [42] several levels of approximations are discussed, ranging from the complete LCFO-MO-SCF method, which of course is connected to the usual LCAO-MO-SCF method simply by an unitary transformation, to the LCBO model in the HMO approximation [39, 40]. It is this possibility of introducing approximations and of including experimental data which justifies the derivation of the full SCF equations in the way described in the following section and which distinguishes the present approach from previous work on self-consistent LCMO methods [35].

2. The Method of Linear Combination of Fragment Orbitals

2.1. *The Generalized Product Approach*

A convenient starting point for the development of an MO method based on linear combinations of fragment orbitals is the theory of generalized product functions [9]. We therefore write the wave function

$$\Psi(1,\dots N)=\mathscr{A}\Phi_{\mathrm{A}}(1,\dots N_{\mathrm{A}})\Phi_{\mathrm{B}}(N_{\mathrm{A}}+1,\dots N_{\mathrm{A}}+N_{\mathrm{B}})\dots \tag{2.1}$$

as a generalized product of antisymmetrized wave functions Φ_{A}, $\Phi_{\mathrm{B}},\dots$ of the fragments A, B, ..., with $\mathscr{A}$ being an antisymmetrizer giving a fully antisymmetrical N-electron function. Strong orthogonality [8] in the sense

$$\int \Phi_{\mathrm{R}}^{*}(1,i,j\dots)\Phi_{\mathrm{S}}(1,k,l,\dots)\,d\tau_1=0\ (\mathrm{R}\neq\mathrm{S}) \tag{2.2}$$

is assumed, which may be ensured by using orthogonal basis orbitals ϕ_I^{R}:

$$\int \phi_I^{\mathrm{R}}(1)\phi_J^{\mathrm{S}}(1)\,d\tau_1=\delta_{IJ}\quad \text{(all R, S).} \tag{2.3}$$

An effective Hamiltonian for the electrons of group R in the field of all other groups may be defined as

$$\mathscr{H}_{\mathrm{eff}}^{\mathrm{R}}(1,\dots N_{\mathrm{R}})=\sum_{i=1}^{N_{\mathrm{R}}} h_{\mathrm{eff}}^{\mathrm{R}}(i)+\tfrac{1}{2}\sum_{i,j=1}^{N_{\mathrm{R}}} g(i,j), \tag{2.4}$$

where

$$h_{\mathrm{eff}}^{\mathrm{R}}(i)=h(i)+\sum_{\mathrm{S}(\neq\mathrm{R})}\mathscr{G}^{\mathrm{S}}(i)=h^{\mathrm{R}}(i)+\sum_{\mathrm{S}(\neq\mathrm{R})}[\mathscr{V}^{\mathrm{S}}(i)+\mathscr{G}^{\mathrm{S}}(i)] \tag{2.5}$$

with

$$\mathscr{h}^{\mathrm{R}}(i) = -\tfrac{1}{2}\nabla^2(i) + \mathscr{V}^{\mathrm{R}}(i) \tag{2.5a}$$

and

$$\mathscr{G}^{\mathrm{S}}(i) = \mathscr{J}^{\mathrm{S}}(i) - \mathscr{K}^{\mathrm{S}}(i) \tag{2.5b}$$

is an effective one-electron operator for the group R electrons. $\mathscr{V}^{\mathrm{R}}(i)$ is the operator of the potential energy due to the nuclei (or cores) of fragment R and $\mathscr{J}^{\mathrm{S}}(i)$ and $\mathscr{K}^{\mathrm{S}}(i)$ are the Coulomb and exchange operators describing the effective field at point i due to the electrons of groups S.

If the groups R and S are described by a one-determinant wave function

$$\Phi_{\mathrm{R}}(1,\ldots N_{\mathrm{R}}) = |\psi_1^{\mathrm{R}}(1)\bar{\psi}_1^{\mathrm{R}}(2)\ldots| \tag{2.6}$$

of doubly occupied MO's

$$\psi_k^{\mathrm{R}}(i) = \sum a_{Ik}^{\mathrm{R}} \phi_I^{\mathrm{R}}(i), \tag{2.7}$$

which are obtained from a set of SCF equations

$$\boldsymbol{F}^{\mathrm{R}}\boldsymbol{a}_i^{\mathrm{R}} = \varepsilon_i^{\mathrm{R}}\boldsymbol{a}_i^{\mathrm{R}} \tag{2.8}$$

with $\boldsymbol{F}^{\mathrm{R}} = \boldsymbol{h}_{\mathrm{eff}}^{\mathrm{R}} + \boldsymbol{G}^{\mathrm{RR}}(\boldsymbol{P}^{\mathrm{R}})$, (2.9)

the one-electron density matrix $\boldsymbol{P}^{\mathrm{R}}$ is simply the charge density-bond order matrix with elements

$$(\boldsymbol{P}^{\mathrm{R}})_{IJ} = 2\sum_{i\,(\mathrm{occ})} a_{Ii}^{\mathrm{R}} a_{Ji}^{\mathrm{R}}, \tag{2.10}$$

and the energy of group R is given by

$$H_{\mathrm{eff}}^{\mathrm{R}} = \mathrm{tr}\,\boldsymbol{h}_{\mathrm{eff}}^{\mathrm{R}}\boldsymbol{P}^{\mathrm{R}} + \tfrac{1}{2}\mathrm{tr}\,\boldsymbol{G}^{\mathrm{RR}}\boldsymbol{P}^{\mathrm{R}}, \tag{2.11}$$

while the total energy of the system is

$$E_0 = \sum_{\mathrm{R}}\left[H_{\mathrm{eff}}^{\mathrm{R}} - \sum_{\mathrm{S}(\neq \mathrm{R})} \mathrm{tr}(\boldsymbol{G}^{\mathrm{RS}} + \boldsymbol{V}^{\mathrm{S}})\boldsymbol{P}^{\mathrm{S}}\right]. \tag{2.12}$$

According to Eq. (2.5) $\boldsymbol{G}^{\mathrm{RS}}$ is essentially a generalization of the total electron interaction matrix of Roothaan [40] with elements

$$(\boldsymbol{G}^{\mathrm{RS}})_{IJ} = \sum_{K,L}\left[(\phi_I^{\mathrm{R}}\phi_J^{\mathrm{R}}\,|\,\phi_K^{\mathrm{S}}\phi_L^{\mathrm{S}}) - \tfrac{1}{2}(\phi_I^{\mathrm{R}}\phi_L^{\mathrm{S}}\,|\,\phi_J^{\mathrm{R}}\phi_K^{\mathrm{S}})\right](\boldsymbol{P}^{\mathrm{S}})_{KL}, \tag{2.13}$$

and the elements of $\boldsymbol{h}_{\mathrm{eff}}^{\mathrm{R}}$ are given by

$$(\boldsymbol{h}_{\mathrm{eff}}^{\mathrm{R}})_{IJ} = (\boldsymbol{h}^{\mathrm{R}})_{IJ} + \sum_{\mathrm{S}(\neq \mathrm{R})} (\boldsymbol{V}^{\mathrm{S}} + \boldsymbol{G}^{\mathrm{RS}})_{IJ}. \tag{2.14}$$

2.2. *π-Systems*

If AX and BY are two fragments with n_{X} and n_{Y} π-electrons, and the interaction between the π systems X and Y is small, the combined system may be described by a generalized product function Eq. (2.1), and from Eqs. (2.13) and (2.14) one obtains for the SCF matrix elements of the π group X in the field of BY:

$$
\begin{aligned}
(\boldsymbol{F}^{\mathrm{X}})_{IJ} &= (\boldsymbol{h}^{\mathrm{X}}_{\mathrm{eff}})_{IJ} + \boldsymbol{G}^{\mathrm{XX}}(\boldsymbol{P}^{\mathrm{X}})_{IJ} \\
&= [\boldsymbol{h}^{\mathrm{X}} + \boldsymbol{V}^{\mathrm{A}} + \boldsymbol{G}^{\mathrm{XA}}(\boldsymbol{P}^{\mathrm{A}}_0)]_{IJ} + [\boldsymbol{V}^{\mathrm{B}} + \boldsymbol{G}^{\mathrm{XB}}(\boldsymbol{P}^{\mathrm{B}}_0) + \boldsymbol{V}^{\mathrm{Y}} + \boldsymbol{G}^{\mathrm{XY}}(\boldsymbol{P}^{\mathrm{Y}}_0)]_{IJ} \\
&\qquad + \boldsymbol{G}^{\mathrm{XX}}(\boldsymbol{P}^{\mathrm{X}})_{IJ} \\
&= (\boldsymbol{F}^{\mathrm{X}}_0)_{IJ} + [\boldsymbol{V}^{\mathrm{B}} + \boldsymbol{G}^{\mathrm{XB}}(\boldsymbol{P}^{\mathrm{B}}_0) + \boldsymbol{V}^{\mathrm{Y}} + \boldsymbol{G}^{\mathrm{XY}}(\boldsymbol{P}^{\mathrm{Y}}_0)]_{IJ} + \boldsymbol{G}^{\mathrm{XX}}(\boldsymbol{P}^{\mathrm{X}} - \boldsymbol{P}^{\mathrm{X}}_0)_{IJ} \qquad (2.15)
\end{aligned}
$$

where $\boldsymbol{F}^{\mathrm{X}}_0$ and $\boldsymbol{P}^{\mathrm{X}}_0$ are the SCF matrix and the one-electron density matrix respectively of the π system X in the isolated fragment AX, i.e. in the field of group A alone. If we use as basis functions $\phi^{\mathrm{R}}_I(i)$ (R = X, Y, A and B) the MO's of group R in the isolated fragment, i.e. just those MO's which diagonalize $\boldsymbol{F}^{\mathrm{R}}_0$ and which may therefore be called fragment orbitals (FO's), we have

$$
(\boldsymbol{P}^{\mathrm{R}}_0)_{KL} = \begin{cases} 2\delta_{KL} & \text{for } \phi^{\mathrm{R}}_K \text{ occ.} \\ 0 & \text{for } \phi^{\mathrm{R}}_K \text{ unocc.} \end{cases} \qquad (2.16)
$$

In order that the strong orthogonality requirement Eq. (2.2) be fulfilled, the FO's ϕ^{R}_I and ϕ^{S}_J are assumed to be linear combinations of different sets of orthogonal AO's χ^{R}_ρ and χ^{S}_σ [9]. If furthermore the zero-differential overlap (ZDO) approximation [42] commonly used in semiempirical work is invoked, we have

$$
\phi^{\mathrm{R}}_I \phi^{\mathrm{S}}_J \equiv 0 \quad \text{for} \quad \mathrm{R} \neq \mathrm{S}, \qquad (2.17)
$$

as for $\mathrm{R} \neq \mathrm{S}$ the FO's ϕ^{R}_I and ϕ^{S}_J are localized in different fragments. From Eqs. (2.16) and (2.17) we have

$$
\boldsymbol{I}^{\mathrm{R}}_{IJ} = [\boldsymbol{V}^{\mathrm{R}} + \boldsymbol{G}^{\mathrm{XR}}(\boldsymbol{P}^{\mathrm{R}}_0)]_{IJ} = \boldsymbol{V}^{\mathrm{R}}_{IJ} + \sum_{P\,(\mathrm{occ})} 2(\phi^{\mathrm{X}}_I \phi^{\mathrm{X}}_J \mid \phi^{\mathrm{R}}_P \phi^{\mathrm{R}}_P) \qquad (2.18)
$$

and Eq. (2.15) becomes

$$
\begin{aligned}
(\boldsymbol{F}^{\mathrm{X}})_{IJ} = \varepsilon^{\mathrm{X}}_I \, \delta_{IJ} + \boldsymbol{I}^{\mathrm{B}}_{IJ} + \boldsymbol{I}^{\mathrm{Y}}_{IJ} + \sum_{K,\,L} (\boldsymbol{P}^{\mathrm{X}} - \boldsymbol{P}^{\mathrm{X}}_0)_{KL} [(\phi^{\mathrm{X}}_I \phi^{\mathrm{X}}_J \mid \phi^{\mathrm{X}}_K \phi^{\mathrm{X}}_L) \\
- \tfrac{1}{2}(\phi^{\mathrm{X}}_I \phi^{\mathrm{X}}_K \mid \phi^{\mathrm{X}}_J \phi^{\mathrm{X}}_L)] \qquad (2.19)
\end{aligned}
$$

where $\varepsilon^{\mathrm{X}}_I$ is the I'th eigenvalue of $\boldsymbol{F}^{\mathrm{X}}_0$ (as only the eigenvalues of $\boldsymbol{F}^{\mathrm{X}}_0$ are needed, they will be designated by $\varepsilon^{\mathrm{X}}_I$, a subscript 0 is not needed).

Equation (2.18) may be taken as a definition of the π inductive perturbation of group X due to the field of the fragment BY; the perturbations $\boldsymbol{I}^{\mathrm{R}}_{IJ}$ are seen to be small, as the nuclear attraction terms $\boldsymbol{V}^{\mathrm{R}}_{IJ}$ and the electron repulsion terms $\sum_{P\,(\mathrm{occ})} 2(\phi^{\mathrm{X}}_I \phi^{\mathrm{X}}_J \mid \phi^{\mathrm{R}}_P \phi^{\mathrm{R}}_P)$ are of the same magnitude but of opposite sign. Obviously, the π inductive effect can cause just a shift of the π levels of group X in fragment AX, if only the perturbations of the diagonal elements are non-zero, or generally a shift as well as a mixing of the π levels.

For larger interactions the groups X and Y may be combined to form a new group U with $n_{\mathrm{U}} = n_{\mathrm{X}} + n_{\mathrm{Y}}$ π electrons. The SCF matrix of this group U has elements

$$
(\boldsymbol{F}^{\mathrm{U}})_{IJ} = (\boldsymbol{h}^{\mathrm{U}})_{IJ} + [\boldsymbol{V}^{\mathrm{A}} + \boldsymbol{G}^{\mathrm{UA}}(\boldsymbol{P}^{\mathrm{A}}_0) + \boldsymbol{V}^{\mathrm{B}} + \boldsymbol{G}^{\mathrm{UB}}(\boldsymbol{P}^{\mathrm{B}}_0)]_{IJ} + \boldsymbol{G}^{\mathrm{UU}}(\boldsymbol{P}^{\mathrm{U}}). \qquad (2.20)
$$

Taking into account the fact that

$$\boldsymbol{h}^{\mathrm{U}}=\left(\begin{array}{c:c}\boldsymbol{h}^{\mathrm{X}}+\boldsymbol{V}^{\mathrm{Y}} & \boldsymbol{h}^{\mathrm{XY}}\\ \hdashline \boldsymbol{h}^{\mathrm{YX}} & \boldsymbol{h}^{\mathrm{Y}}+\boldsymbol{V}^{\mathrm{X}}\end{array}\right) \tag{2.21}$$

and that $\boldsymbol{F}^{\mathrm{U}}$ and $\boldsymbol{P}^{\mathrm{U}}$ may be written in the form

$$\boldsymbol{F}^{\mathrm{U}}=\left(\begin{array}{c:c}\boldsymbol{F}^{\mathrm{U}}_{(\mathrm{X})} & \boldsymbol{F}^{\mathrm{U}}_{(\mathrm{XY})}\\ \hdashline & \boldsymbol{F}^{\mathrm{U}}_{(\mathrm{Y})}\end{array}\right) \quad \text{and} \quad \boldsymbol{P}^{\mathrm{U}}=\left(\begin{array}{c:c}\boldsymbol{P}^{\mathrm{U}}_{(\mathrm{X})} & \boldsymbol{P}^{\mathrm{U}}_{(\mathrm{XY})}\\ \hdashline & \boldsymbol{P}^{\mathrm{U}}_{(\mathrm{Y})}\end{array}\right), \tag{2.22}$$

indicating that $\boldsymbol{F}^{\mathrm{U}}_{(\mathrm{X})}$ consists of matrix elements between the orbitals ϕ_I^{X} localized in group X etc., one obtains by means of Eqs. (2.15) and (2.19).

$$\begin{aligned}(\boldsymbol{F}^{\mathrm{U}}_{(\mathrm{X})})_{IJ}&=(\boldsymbol{h}^{\mathrm{U}}_{(\mathrm{X})})_{IJ}+[\boldsymbol{V}^{\mathrm{A}}+\boldsymbol{G}^{\mathrm{XA}}(\boldsymbol{P}_0^{\mathrm{A}})+\boldsymbol{V}^{\mathrm{B}}+\boldsymbol{G}^{\mathrm{XB}}(\boldsymbol{P}_0^{\mathrm{B}})]_{IJ}+\boldsymbol{G}^{\mathrm{XX}}(\boldsymbol{P}^{\mathrm{U}}_{(\mathrm{X})})_{IJ}\\ &\qquad +\boldsymbol{G}^{\mathrm{XY}}(\boldsymbol{P}^{\mathrm{U}}_{(\mathrm{Y})})_{IJ}+\boldsymbol{G}^{\mathrm{XU}}(\boldsymbol{P}^{\mathrm{U}}_{(\mathrm{XY})}+\boldsymbol{P}^{\mathrm{U}}_{(\mathrm{YX})})_{IJ}\\ &=(\boldsymbol{F}^{\mathrm{X}})_{IJ}+\sum_{K,L}(\boldsymbol{P}^{\mathrm{U}}_{(\mathrm{X})}-\boldsymbol{P}^{\mathrm{X}})_{KL}[(\phi_I^{\mathrm{X}}\phi_J^{\mathrm{X}}\mid\phi_K^{\mathrm{X}}\phi_L^{\mathrm{X}})-\tfrac{1}{2}(\phi_I^{\mathrm{X}}\phi_K^{\mathrm{X}}\phi_J^{\mathrm{X}}\phi_L^{\mathrm{X}})]\\ &\qquad +\sum_{K,L}(\boldsymbol{P}^{\mathrm{U}}_{(\mathrm{Y})}-\boldsymbol{P}^{\mathrm{Y}})_{KL}(\phi_I^{\mathrm{X}}\phi_J^{\mathrm{X}}\mid\phi_K^{\mathrm{Y}}\phi_L^{\mathrm{Y}})\end{aligned} \tag{2.23}$$

Substituting Eq. (2.18) for $(\boldsymbol{F}^{\mathrm{X}})_{IJ}$ yields

$$\begin{aligned}(\boldsymbol{F}^{\mathrm{U}}_{(\mathrm{X})})_{IJ}&=\varepsilon_I^{\mathrm{X}}\,\delta_{IJ}+[\boldsymbol{I}^{\mathrm{B}}+\boldsymbol{I}^{\mathrm{Y}}]_{IJ}+\sum_{K,L}(\boldsymbol{P}^{\mathrm{U}}_{(\mathrm{X})}-\boldsymbol{P}_0^{\mathrm{X}})_{KL}[(\phi_I^{\mathrm{X}}\phi_I^{\mathrm{X}}\mid\phi_K^{\mathrm{X}}\phi_L^{\mathrm{X}})\\ &\qquad -\tfrac{1}{2}(\phi_I^{\mathrm{X}}\phi_K^{\mathrm{X}}\mid\phi_J^{\mathrm{X}}\phi_L^{\mathrm{X}})]+\sum_{K,L}(\boldsymbol{P}^{\mathrm{U}}_{(\mathrm{Y})}-\boldsymbol{P}_0^{\mathrm{Y}})_{KL}(\phi_I^{\mathrm{X}}\phi_J^{\mathrm{X}}\mid\phi_K^{\mathrm{Y}}\phi_L^{\mathrm{Y}}).\end{aligned} \tag{2.24}$$

Finally,

$$(\boldsymbol{F}^{\mathrm{U}}_{(\mathrm{XY})})_{IJ}=(\boldsymbol{h}^{\mathrm{U}}_{(\mathrm{XY})})_{IJ}-\tfrac{1}{2}\sum_{K,L}(\boldsymbol{P}^{\mathrm{U}}_{(\mathrm{XY})})_{KL}(\phi_I^{\mathrm{X}}\phi_K^{\mathrm{X}}\mid\phi_J^{\mathrm{Y}}\phi_L^{\mathrm{Y}}). \tag{2.25}$$

Eqs. (2.24) and (2.25) may be taken as a justification of the LCMO model in the HMO approximation [39], for $\boldsymbol{P}^{\mathrm{U}}_{(\mathrm{X})}=\boldsymbol{P}_0^{\mathrm{X}}$ and $\boldsymbol{P}^{\mathrm{U}}_{(\mathrm{Y})}=\boldsymbol{P}_0^{\mathrm{Y}}$, which is a reasonable starting point for the SCF calculations, makes all the electron interaction terms disappear. Within the framework of Koopmans' approximation [42] experimental ionization potential (IP) and electron affinities (EA) may be introduced by

$$-\varepsilon_I^{\mathrm{X}}=\begin{cases}\mathrm{IP}_I(\mathrm{X}) & \text{for} \quad \phi_I^{\mathrm{X}} \text{ occ.}\\ \mathrm{EA}_I(\mathrm{X}) & \text{for} \quad \phi_I^{\mathrm{X}} \text{ unocc.}\end{cases} \tag{2.26}$$

Further simplifications may be obtained by truncating the basis set so that only the occupied or the occupied and the lowest unoccupied fragment orbitals ϕ_I are used. In the following section these approximations will be studied by means of a numerical example and by comparison with results from the more complete expressions in Eqs. (2.24) and (2.25).

To complete this subsection we will give the SCF matrix elements for group A (and B) after union of X and Y to form U:

$$\begin{aligned}(\boldsymbol{F}^{\mathrm{A}'})_{IJ} &= \boldsymbol{h}_{IJ}^{\mathrm{A}} + \boldsymbol{I}_{IJ}^{\mathrm{X}} + \boldsymbol{I}_{IJ}^{\mathrm{Y}} + \boldsymbol{I}_{IJ}^{\mathrm{B}} + \boldsymbol{G}^{\mathrm{AX}}(\boldsymbol{P}_{(\mathrm{X})}^{\mathrm{U}} - \boldsymbol{P}_0^{\mathrm{X}})_{IJ} \\ &\qquad + \boldsymbol{G}^{\mathrm{AY}}(\boldsymbol{P}_{(\mathrm{Y})}^{\mathrm{U}} - \boldsymbol{P}_0^{\mathrm{Y}})_{IJ} + \boldsymbol{G}^{\mathrm{AA}}(\boldsymbol{P}^{\mathrm{A}'} - \boldsymbol{P}^{\mathrm{A}})_{IJ} \\ &= (\boldsymbol{F}^{\mathrm{A}})_{IJ} + \sum_{K,L} (\boldsymbol{P}_{(\mathrm{X})}^{\mathrm{U}} - \boldsymbol{P}_0^{\mathrm{X}})_{KL} (\phi_I^{\mathrm{A}} \phi_J^{\mathrm{A}} \mid \phi_K^{\mathrm{X}} \phi_L^{\mathrm{X}}) \\ &\quad + \sum_{K,L} (\boldsymbol{P}_{(\mathrm{Y})}^{\mathrm{U}} - \boldsymbol{P}_0^{\mathrm{Y}})_{KL} (\phi_I^{\mathrm{A}} \phi_J^{\mathrm{A}} \mid \phi_K^{\mathrm{Y}} \phi_L^{\mathrm{Y}}) \\ &\quad + \sum_{K,L} (\boldsymbol{P}^{\mathrm{A}'} - \boldsymbol{P}^{\mathrm{A}})_{KL} [(\phi_I^{\mathrm{A}} \phi_J^{\mathrm{A}} \mid \phi_K^{\mathrm{A}} \phi_L^{\mathrm{A}}) - \tfrac{1}{2} (\phi_I^{\mathrm{A}} \phi_K^{\mathrm{A}} \mid \phi_J^{\mathrm{A}} \phi_L^{\mathrm{A}})] \end{aligned} \tag{2.27}$$

2.3. σ-Systems

If two σ systems A–X and B–Y are to be combined to form a new system A–U–B some additional problems arise, because the total number of electrons and nuclei may change. E.g. if two CH_4 molecules are to be combined to form CH_3–CH_3, the CC bond U with two electrons is formed from the two CH bonds X and Y with two electrons each. Due to this change in the number of electrons and nuclei a term $-I_{IJ}^{\mathrm{X}}$ appears in the expression for the matrix elements of group A and group B equivalent to Eq. (2.18), i.e.

$$\begin{aligned}(\boldsymbol{F}^{\mathrm{A}})_{IJ} &= (\boldsymbol{h}^{\mathrm{A}})_{IJ} + [\boldsymbol{V}^{\mathrm{X}} + \boldsymbol{G}^{\mathrm{AX}}(\boldsymbol{P}_0^{\mathrm{X}})]_{IJ} + \boldsymbol{G}^{\mathrm{AA}}(\boldsymbol{P}_0^{\mathrm{A}})_{IJ} \\ &\quad + [\boldsymbol{V}^{\mathrm{B}} + \boldsymbol{G}^{\mathrm{AB}}(\boldsymbol{P}_0^{\mathrm{B}}) + \boldsymbol{V}^{\mathrm{U}} + \boldsymbol{G}^{\mathrm{AU}}(\boldsymbol{P}_0^{\mathrm{U}})]_{IJ} + \boldsymbol{G}^{\mathrm{AA}}(\boldsymbol{P}^{\mathrm{A}} - \boldsymbol{P}_0^{\mathrm{A}})_{IJ} \\ &= \varepsilon_I^{\mathrm{A}} \, \delta_{IJ} + \boldsymbol{I}_{IJ}^{\mathrm{B}} + \boldsymbol{I}_{IJ}^{\mathrm{U}} - \boldsymbol{I}_{IJ}^{\mathrm{X}} + \sum_{K,L} (\boldsymbol{P}^{\mathrm{A}} - \boldsymbol{P}_0^{\mathrm{A}}) \\ &\qquad \times [(\phi_I^{\mathrm{A}} \phi_J^{\mathrm{A}} \mid \phi_K^{\mathrm{A}} \phi_L^{\mathrm{A}}) - \tfrac{1}{2} (\phi_I^{\mathrm{A}} \phi_K^{\mathrm{A}} \mid \phi_J^{\mathrm{A}} \phi_L^{\mathrm{A}})] \end{aligned} \tag{2.28}$$

In Eq. (2.28) it has been assumed that Eq. (2.16) holds also for $\boldsymbol{P}^{\mathrm{U}}$, i.e. that the orbitals ϕ_K^{U} diagonalize $\boldsymbol{F}^{\mathrm{U}}$ given by

$$(\boldsymbol{F}^{\mathrm{U}})_{ij} = (\boldsymbol{h}^{\mathrm{U}})_{ij} + \boldsymbol{I}_{ij}^{\mathrm{A}} + \boldsymbol{I}_{ij}^{\mathrm{B}} + \sum_{k,l} (\boldsymbol{P}_0^{\mathrm{U}})_{kl} \, [(\tilde{\phi}_i^{\mathrm{U}} \tilde{\phi}_j^{\mathrm{U}} \mid \tilde{\phi}_k^{\mathrm{U}} \tilde{\phi}_l^{\mathrm{U}}) - \tfrac{1}{2} (\tilde{\phi}_i^{\mathrm{U}} \tilde{\phi}_k^{\mathrm{U}} \mid \tilde{\phi}_j^{\mathrm{U}} \tilde{\phi}_l^{\mathrm{U}})] \tag{2.29}$$

In the case of the ethane molecule the two sp^3 hybrid AO's χ_μ^{X} and χ_ν^{Y} may be used to form the basis orbitals

$$\begin{aligned}\tilde{\phi}_i^{\mathrm{U}} &= \frac{1}{\sqrt{2}} (\chi_\mu^{\mathrm{X}} + \chi_\nu^{\mathrm{Y}}) \\ \tilde{\phi}_j^{\mathrm{U}} &= \frac{1}{\sqrt{2}} (\chi_\mu^{\mathrm{X}} - \chi_\nu^{\mathrm{Y}}), \end{aligned} \tag{2.30}$$

which in this case already diagonalize $\boldsymbol{F}^{\mathrm{U}}$ for reasons of symmetry, so that $\phi_I^{\mathrm{U}} = \tilde{\phi}_i^{\mathrm{U}}$.

If there is an interaction between all parts of the molecule, the use of a generalized product function may no longer be justified. As an example we take again the ethane molecule, including the through-space interaction between the two CH_3

groups. In this case, the SCF-matrix and the density matrix of the whole interacting system AUB may be written similarly as in Eq. (2.22) in the form

$$\boldsymbol{F}=\left(\begin{array}{c:c:c} \boldsymbol{F}_{(\mathrm{A})} & \boldsymbol{F}_{(\mathrm{AU})} & \boldsymbol{F}_{(\mathrm{AB})} \\ \hdashline & \boldsymbol{F}_{(\mathrm{U})} & \boldsymbol{F}_{(\mathrm{UB})} \\ \hdashline & & \boldsymbol{F}_{(\mathrm{B})} \end{array}\right) \quad \text{and} \quad \boldsymbol{P}=\left(\begin{array}{c:c:c} \boldsymbol{P}_{(\mathrm{U})} & \boldsymbol{P}_{(\mathrm{AU})} & \boldsymbol{P}_{(\mathrm{AB})} \\ \hdashline & \boldsymbol{P}_{(\mathrm{U})} & \boldsymbol{P}_{(\mathrm{UB})} \\ \hdashline & & \boldsymbol{P}_{(\mathrm{B})} \end{array}\right) \tag{2.31}$$

with

$$\begin{aligned}(\boldsymbol{F}_{(\mathrm{A})})_{IJ} &= \boldsymbol{h}^{\mathrm{A}}_{IJ}+\boldsymbol{V}^{\mathrm{U}}_{IJ}+\boldsymbol{V}^{\mathrm{B}}_{IJ}+\boldsymbol{G}^{\mathrm{AA}}(\boldsymbol{P}_{(\mathrm{A})})_{IJ}+\boldsymbol{G}^{\mathrm{AB}}(\boldsymbol{P}_{(\mathrm{B})})_{IJ}+\boldsymbol{G}^{\mathrm{AU}}(\boldsymbol{P}_{(\mathrm{U})})_{IJ} \\ &\quad +\boldsymbol{G}(\boldsymbol{P}_{(\mathrm{AU})}+\boldsymbol{P}_{(\mathrm{UA})})_{IJ}+\boldsymbol{G}(\boldsymbol{P}_{(\mathrm{AB})}+\boldsymbol{P}_{(\mathrm{BA})})_{IJ}+\boldsymbol{G}(\boldsymbol{P}_{(\mathrm{UB})}+\boldsymbol{P}_{(\mathrm{BU})})_{IJ} \\ &= (\boldsymbol{F}^{\mathrm{A}})_{IJ}+\boldsymbol{G}^{\mathrm{AA}}(\boldsymbol{P}_{(\mathrm{A})}-\boldsymbol{P}^{\mathrm{A}})_{IJ}+\boldsymbol{G}^{\mathrm{AB}}(\boldsymbol{P}_{(\mathrm{B})}-\boldsymbol{P}^{\mathrm{B}}_{0})_{IJ}+\boldsymbol{G}^{\mathrm{AU}}(\boldsymbol{P}_{(\mathrm{U})}-\boldsymbol{P}^{\mathrm{U}}_{0})_{IJ},\end{aligned} \tag{2.32}$$

where we used Eq. (2.28) as well as the fact, that $\boldsymbol{G}(\boldsymbol{P}_{(\mathrm{RS})}+\boldsymbol{P}_{(\mathrm{SR})})_{IJ}=0$ for all values of I and J. Substituting Eq. (2.28) into Eq. (2.32) yields

$$\begin{aligned}(\boldsymbol{F}_{(\mathrm{A})})_{IJ} &= \varepsilon^{\mathrm{A}}_{I}\,\delta_{IJ}+\boldsymbol{I}^{\mathrm{B}}_{IJ}+\boldsymbol{I}^{\mathrm{U}}_{IJ}-\boldsymbol{I}^{\mathrm{X}}_{IJ}+\sum_{K,L}(\boldsymbol{P}_{(\mathrm{A})}-\boldsymbol{P}^{\mathrm{A}}_{0})_{KL}[(\phi^{\mathrm{A}}_{I}\phi^{\mathrm{A}}_{J}\mid\phi^{\mathrm{A}}_{K}\phi^{\mathrm{A}}_{L}) \\ &\qquad\qquad -\tfrac{1}{2}(\phi^{\mathrm{A}}_{I}\phi^{\mathrm{A}}_{K}\mid\phi^{\mathrm{A}}_{J}\phi^{\mathrm{A}}_{L})] \\ &\quad +\sum_{K,L}(\boldsymbol{P}_{(\mathrm{B})}-\boldsymbol{P}^{\mathrm{B}}_{0})_{KL}(\phi^{\mathrm{A}}_{I}\phi^{\mathrm{A}}_{J}\mid\phi^{\mathrm{B}}_{K}\phi^{\mathrm{B}}_{L})+\sum_{K,L}(\boldsymbol{P}_{(\mathrm{U})}-\boldsymbol{P}^{\mathrm{U}}_{0})_{KL}(\phi^{\mathrm{A}}_{I}\phi^{\mathrm{A}}_{J}\mid\phi^{\mathrm{U}}_{K}\phi^{\mathrm{U}}_{L}).\end{aligned} \tag{2.33}$$

Finally

$$(\boldsymbol{F}_{(\mathrm{AU})})_{IJ}=(\boldsymbol{h}_{(\mathrm{AU})})_{IJ}-\tfrac{1}{2}\sum_{K,L}(\boldsymbol{P}_{(\mathrm{AU})})_{KL}(\phi^{\mathrm{A}}_{I}\phi^{\mathrm{A}}_{K}\mid\phi^{\mathrm{U}}_{J}\phi^{\mathrm{U}}_{L}).$$

The rest of the paper will be concerned with π systems only. The formulae for σ systems are given here for the sake of completeness. They will be discussed in more detail and applied to a variety of molecular systems in a forthcoming paper of this series [37].

3. An Example: Acrolein

As an example the application of the method of linear combinations of fragment orbitals to the π systems of the acrolein molecule is given in some detail. As localized group orbitals ϕ^{R}_{I} of the fragments AX and Y, where A and X refer to the lone-pair and the π system of formaldehyde and Y to the π system of ethylene, we use the π MO's π_{CO}, π^{*}_{CO}, π_{CC}, π^{*}_{CC} and the oxygen lone-pair orbital n_{O}. These orbitals ϕ^{R}_{I} are expressed in terms of AO's χ^{R}_{μ} by means of the relation

$$(\phi^{\mathrm{A}}_{1},\ldots,\phi^{\mathrm{R}}_{I},\ldots)=(\chi^{\mathrm{A}}_{1},\ldots,\chi^{\mathrm{R}}_{\mu},\ldots)\boldsymbol{C} \tag{3.1}$$

where the matrix $\boldsymbol{C}$ of the LCAO coefficients $c_{\mu I}$ contains non-zero blocks only along the diagonal, so that in our example

$$\boldsymbol{C}=\begin{pmatrix} \boldsymbol{C}_{(\mathrm{A})} & & 0 \\ & \boldsymbol{C}_{(\mathrm{X})} & \\ 0 & & \boldsymbol{C}_{(\mathrm{Y})} \end{pmatrix}. \tag{3.2}$$

By means of this matrix, the one-electron integrals $(\boldsymbol{h}_\chi)_{\mu\nu}$ over AO's χ_μ are transformed into integrals $(\boldsymbol{h})_{IJ}$ over FO's ϕ_I^{R} according to

$$\boldsymbol{h}=\boldsymbol{C}^\dagger \boldsymbol{h}_\chi \boldsymbol{C}, \tag{3.3}$$

where due to the structure of $\boldsymbol{C}$ the blocks belonging to different groups of the fragments may be transformed separately, i.e.

$$\boldsymbol{h}_{(\mathrm{RS})}=\boldsymbol{C}^\dagger_{(\mathrm{R})} \boldsymbol{h}_\chi^{(\mathrm{RS})} \boldsymbol{C}_{(\mathrm{S})}. \tag{3.4}$$

The two-electrons integrals over FO's are obtained by means of the relation

$$\tilde{\boldsymbol{\Gamma}}=\tilde{\boldsymbol{T}}^\dagger \boldsymbol{g} \tilde{\boldsymbol{T}}, \tag{3.5}$$

$\tilde{\boldsymbol{T}}$ being a matrix of dimension $n \times n(n+1)/2$ with elements

$$\tilde{T}_{\mu,IJ}=c_{\mu I}\, c_{\mu J}. \tag{3.6}$$

Columns IJ with I referring to an FO localized in R and J to one localized in S vanish, so that $\tilde{\boldsymbol{T}}$ can be reduced to an $n \times m$ matrix $\boldsymbol{T}$ with $m=\sum_{\mathrm{R}} n_{\mathrm{R}}(n_{\mathrm{R}}+1)/2$ of the form

$$\boldsymbol{T}=\begin{pmatrix} \boldsymbol{T}_{(\mathrm{A})} & & 0 \\ & \boldsymbol{T}_{(\mathrm{X})} & \\ 0 & & \boldsymbol{T}_{(\mathrm{Y})} \end{pmatrix} \tag{3.7}$$

leading to a matrix

$$\boldsymbol{\Gamma}=\boldsymbol{T}^\dagger \boldsymbol{g} \boldsymbol{T}=\begin{pmatrix} \boldsymbol{\Gamma}_{(\mathrm{AA})} & \boldsymbol{\Gamma}_{(\mathrm{AX})} & \boldsymbol{\Gamma}_{(\mathrm{AY})} \\ \boldsymbol{\Gamma}_{(\mathrm{XA})} & \boldsymbol{\Gamma}_{(\mathrm{XX})} & \boldsymbol{\Gamma}_{(\mathrm{XY})} \\ \boldsymbol{\Gamma}_{(\mathrm{YA})} & \boldsymbol{\Gamma}_{(\mathrm{YX})} & \boldsymbol{\Gamma}_{(\mathrm{YY})} \end{pmatrix} \tag{3.8}$$

with

$$\boldsymbol{\Gamma}_{(\mathrm{SR})}=\boldsymbol{T}^\dagger_{(\mathrm{S})} \boldsymbol{g}_{(\mathrm{SR})} \boldsymbol{T}_{(\mathrm{R})}=(\boldsymbol{T}^\dagger_{(\mathrm{R})} \boldsymbol{g}^\dagger_{(\mathrm{SR})} \boldsymbol{T}_{(\mathrm{S})})^\dagger=\boldsymbol{\Gamma}^\dagger_{(\mathrm{RS})} \tag{3.9}$$

because of $\boldsymbol{g}_{(\mathrm{RS})}=\boldsymbol{g}^\dagger_{(\mathrm{SR})}$, so that again each block may be transformed separately. It follows that once the integrals for the separate fragments are known, only interaction integrals, i.e. the blocks $\boldsymbol{h}_{(\mathrm{RS})}$ and $\boldsymbol{\Gamma}_{(\mathrm{RS})}$ with $\mathrm{R} \neq \mathrm{S}$ have to be calculated. In the case of the two-electron integrals of the present example instead of the 15×15 matrix $\tilde{\boldsymbol{\Gamma}}$ only the 3×3 block $\boldsymbol{\Gamma}_{(\mathrm{XY})}$ and two 1×3 blocks $\boldsymbol{\Gamma}_{(\mathrm{AX})}$ and $\boldsymbol{\Gamma}_{(\mathrm{AY})}$ are needed.

The following results were obtained for geometries with $r_{\mathrm{CO}}=0.1241$, $r_{\mathrm{C=C}}=0.1375$ and $r_{\mathrm{C-C}}=0.1425$ nm and 120° for all angles by using standard parameters and integral values within the Pariser–Parr–Pople approximation [44]. The one-electron integrals over AO's χ_μ are calculated from

$$\begin{aligned}(\boldsymbol{h}_\chi)_{\mu\mu} &= \alpha_\mu = \mathrm{U}_\mu + \sum_{\nu\neq\mu} Z'_\mu \gamma_{\mu\nu} \\ (\boldsymbol{h}_\chi)_{\mu\nu} &= \beta_{\mu\nu} \quad \text{or } 0 \quad (\mu \neq \nu),\end{aligned} \tag{3.10}$$

where the valence state ionization potentials U_μ are taken to be $\mathrm{U_C}=-9.85$ eV, $\mathrm{U_0^{(\pi)}}=-18.25$ eV and $\mathrm{U_O^{(n)}}=-24.75$ eV and the two-electron integrals $\gamma_{\mu\nu}$ where calculated from the Mataga relation [45] using $\gamma_{\mathrm{CC}}=11.08$ eV and $\gamma_{\mathrm{OO}}=14.52$ eV for the n and the π electrons.

Results of a complete LCFO-MO calculation for acrolein are given in Table 1. It is seen that ψ_1 and ψ_2 are essentially the π_{CO} and π_{CC} FO's with a small admixture of the π^*_{CO} FO mainly to ψ_2, whereas the coefficient of π^*_{CC} is small for both occupied MO's. The virtual MO's on the other hand are mixtures of nearly equal amounts of the π^*_{CO} and π^*_{CC} FO's. Thus, as long as one is interested in the occupied MO's only, it may be sufficient to use the π_{CO}, π_{CC} and π^*_{CO} FO's as basis orbitals for the LCFO-MO calculation, as is verified in the lower part of Table 1.

Table 1. Results of LCFO MO calculations for the π system of acrolein (energies in eV)

Eigenvalue	LCFO coefficients a_{Ik}			
ε_I	$k=\pi_{\mathrm{CO}}$	π_{CC}	π^*_{CO}	π^*_{CC}
4 Basis orbitals				
1.48	0.064	−0.127	−0.616	−0.775
−1.51	0.039	0.198	0.752	−0.627
−10.29	−0.239	0.929	−0.226	−0.004
−13.37	0.953	0.286	−0.059	0.079
3 Basis orbitals				
−0.39	−0.016	0.228	0.974	—
−10.34	−0.284	0.933	−0.223	—
−13.30	0.959	0.280	−0.049	—

Much more detailed information may be obtained by considering the orbital energies ε_I and occupation number P_{II} given in Table 2 for different levels and different approximation of the LCFO calculations. It is seen that the CO group does not experience any π inductive perturbation from the CC group, due to the uniform charge distribution of the latter which together with the Goeppert-Mayer and Sklar approximation [46] of Eq. (3.10) leads to an exact cancellation of all core-attraction and the corresponding electron-interaction terms. By the same arguments the lone-pair does not influence the CC group, whereas the π inductive effect of the CO groups stabilizes both the π_{CC} and the π^*_{CC} orbitals by

Table 2. Orbital energies ε_I (in eV) and populations P_{II} as well as $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$, $S = (\varepsilon_1 + \varepsilon_2)/2$ and total π electron energy E from LCFO MO calculations for the π system of acrolein at different stages and approximations[a]

	I	*II*	*III*(HMO)		*IV*(LCFO)		*V*(3 × 3-LCFO)		*VI*(LCBO)	
	ε_I^*	$\varepsilon_I^* + \sum I_{II}^{\mathrm{R}}$	ε_I	P_{II}	ε_{II}	P_{II}	ε_I	P_{II}	ε_I	P_{II}
$\psi_4(\pi_{\mathrm{CC}}^*)$	0.97	0.50	1.39	0.01	1.48	0.01	—	—	—	—
$\psi_3(\pi_{\mathrm{CO}}^*)$	−0.93	−0.93	−1.52	0.04	−1.51	0.11	−0.39	0.10	—	—
$\psi_2(\pi_{\mathrm{CO}})$	−9.59	−10.06	−10.08	1.96	−10.29	1.89	−10.34	1.90	−9.91	2.00
$\psi_1(\pi_{\mathrm{CC}})$	−13.49	−13.49	−13.69	1.99	−13.37	1.99	−13.30	2.00	−13.64	2.00
$\psi_0(n_{\mathrm{O}})$	−10.40	−10.40	−9.75[b]	2.00	−9.75[b]	2.00	−9.75[b]	2.00	−10.40	2.00
$\Delta\varepsilon$	3.90	3.43	3.61		3.08		2.96		3.73	
S	11.54	11.78	11.89		11.83		11.82		11.78	
E	−54.07	—	—		−54.82		−54.70		−54.07	

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[a] Columns *I* and *II* refer to isolated fragments without and with π inductive perturbation (see Eq. (2.19)), column *III* to a calculation neglecting electron interaction terms (see discussion after Eq. (2.25)) and columns *IV*–*VI* to LCFO MO calculations with 4, 3 and 2 basis orbitals respectively.

[b] Change of lone-pair energy due to charge redistribution calculated from Eq. (2.27).

equal amounts and also leads to a slight mixing of these MO's, as may be seen from the inductive perturbation matrix

$$I^{\mathrm{CO}}_{(\mathrm{CC})}=\begin{pmatrix}-0.470 & -0.076\\ & -0.470\end{pmatrix} \tag{3.11}$$

From Eq. (2.27) the change in the lone-pair energy F^{A} due to the redistribution of the π electrons in the combined π system is calculated to amount to $+0.65$ eV, corresponding to a destabilization of the n_{O} orbital by this value.

As mentioned before, the HMO approximation may be a fair approximation in the case of the LCMO or LCFO model, as all electron interaction terms in the Fock matrix elements Eqs. (2.24) and (2.25) are due only to the redistribution of π electrons after combination of the fragments. In the case of unsaturated carbonyl compounds however, this redistribution is not negligible, so that individual matrix elements $(F_{(\mathrm{XY})})_{IJ}$ may differ considerably in the HMO and SCF approximations, as is particularly true for the interaction element between π_{CC} and π^*_{CO} (see below). If only occupied FO's are taken into account as in the LCBO model, no charge redistribution can occur and HMO- and SCF-approximations become identical. Orbital energies of LCFO calculations without and with inclusions of electron interaction are given in columns III and IV of Table 2.

From the π electron redistribution in unsaturated carbonyl compounds together with the contribution of the π^*_{CO} FO to the occupied MO's it is to be expected that the LCBO model, which has been extremely successful with the interpretation of the PE spectra of hydrocarbons [46], is not applicable to carbonyl compounds [47]. This is confirmed by the data in Table 2: whereas from the LCFO results in column IV it is seen that due to the conjugative π interaction ψ_2 (π_{CC}) is stabilized and the difference $\Delta\varepsilon=\varepsilon_2-\varepsilon_1$ is reduced with respect to the values of the isolated fragments, the opposite, i.e. a destabilization of ψ_2 and an increase of $\Delta\varepsilon$, is predicted by the LCBO model.

Finally, the results obtained for crotonaldehyde, 2,4-hexadienal and 2,4,6-octatrienal by using experimental values for the fragment IP's and EA's within the

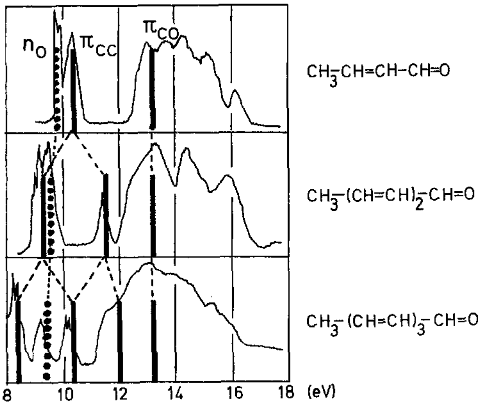

Fig. 1. Crotonaldehyde, 2,4-hexadienal and 2,4,6-octatrienal: π MO energies (solid bars) and n_{O} MO energies (broken bars) as calculated by the LCFO MO method based on experimental IP's and EA's of acetaldehyde as well as IP's of propene, pentadiene and heptatriene together with a schematic representation of the PE spectra [48]

LCFO approach with truncated basis are shown in Fig. 1 together with the experimental PE spectra [48]. As the present approach is restricted to the π electrons, only the π inductive effect can be calculated. A σ inductive effect, which may be appreciable particularly for the carbonyl group, has therefore to be taken into account by choosing the experimental values for the fragment IP's judiciously. The results of Fig. 2 are based on the choice $\mathrm{IP}(\pi_{\mathrm{CO}}) = +13.5$ eV, $\mathrm{IP}(n_0) = +10.26$ eV from the PE spectrum of acetaldehyde [49] and $\mathrm{IP}(\pi_{\mathrm{CC}})$ values from the PE spectra of propene, 1,3-butadiene and 1,3,5-heptatriene [40]. As the results are not very sensitive to the value of $\mathrm{EA}(\pi^*_{\mathrm{CO}})$, the value $\mathrm{EA}(\pi^*_{\mathrm{CO}}) = -1.5$ eV obtained from the half-wave potential of formaldehyde [50] was chosen. This choice of data is justified by the very good agreement between calculated orbital energies and those obtained from the experimental PE spectrum by means of Koopmans' approximation, as may be seen from Fig. 1. A further justification based on a similar LCFO calculation which includes all valence-electrons so that the π inductive as well as the σ inductive effect can be calculated will be given in a forthcoming paper.

4. Discussion

The LCFO SCF method described in the present paper is quite closely related to previous work, in particular to the LCMO method of Flurry [35], the MIM method of v. Niessen [22] and the group orbital method of Whangbo and Wolfe [33, 34]. If no approximations are introduced, all four methods reproduce the LCAO MO SCF results, i.e. they differ in the formulations of the SCF equations which allow for different approximations corresponding to the purpose for which each method was developed. Thus Flurry as well as v. Niessen confine the calculation to a few orbitals, leaving some orbitals or parts of the system unchanged, and Wolfe *et al.* apply perturbation theory in order to analyze the results for composite systems in terms of its constituents, whereas we are mainly interested in using Koopmans' approximation [43] in order to introduce experimental ionization potentials and electron affinities of fragments into the calculation of the combined system. Thus the vital point in our formulation of the LCFO SCF equations is the explicit expression for the inductive perturbation, i.e. for the changes of the Fock matrix elements for one fragment in the field of another fragment, which we obtained from the generalized product approach [9].

As long as we use semi-empirical integral schemes based on the zero differential overlap approximation no orthogonality problems arise. If the method is to be extended to *ab initio* type calculations, projection techniques could be applied as in the work of v. Niessen [22]. On the other hand, an orthogonalization procedure could be included without additional labour in the transformation of the integrals from the AO basis to the FO basis, as long as the full transformation is carried out, i.e. if not only the interaction integrals, but also the integrals of the individual fragments are to be recalculated.

Although we are not aiming at saving computer time, the calculation can profitably be simplified by truncating the basis of the FO's. Results for the acrolein molecule indicate that it will be quite sufficient to include the lowest unoccupied FO of each fragment or even only just one unoccupied FO for the whole system, and that the results are not very sensitive to the actual value of the orbital energies of these unoccupied FO's. Thus, only very few values of electron affinities are needed, which could also be estimated or treated as parameters of the method if no experimental values were available.

Furthermore, if experimental ionization potentials and electron affinities are used in calculating the diagonal elements of the Fock matrix, the results are nearly independent of the values chosen for heteroatom parameters like $U_O^{(\pi)}$ [48]. Thus by an appropriate choice of the fragments the only variable parameters are the β's for the union of the fragments, similarly to the situation for the LCBO model of hydrocarbons [39].

In conclusion we may say, that from a limited number of fragments as building blocks energies and wave functions of a large number of composite systems may be calculated in a very simple manner by computing interaction integrals over the occupied and the few unoccupied FO's and solving the truncated SCF problem.

The orbital correlation diagrams obtained by this method may be very useful in discussing the electronic structure of complex molecules and in assigning the PE spectra. Thus the results of the present paper suggest that within the framework of the π approximation unsaturated carbonyl compounds should be described by an orbital correlation diagram shown schematically in Fig. 2. In contrast to hydrocarbons, where the LCBO model may be applied and the splitting of the occupied orbitals is a measure for the interaction of the fragment orbitals, the orbital splitting may be smaller for the interacting system than for the fragment orbitals in spite of considerable conjugative interaction between the C=C and C=O π bond.

There are three reasons for the different behaviour of the carbonyl compounds and the hydrocarbons: 1) due to the difference in the C=C and C=O π bond energies, their interaction is a second-order effect if described by perturbation theory, whereas the interaction of two (degenerate) C=C bonds is a first-order effect; 2) the π^*_{CO} orbital lies energetically lower than the π^*_{CC} orbital, making second-order contributions more important, and 3) the interaction element F_{IJ} between the π_{CC} and the π^*_{CO} FO (which has the value $F_{\pi\pi^*} = +2.23$ eV in the case

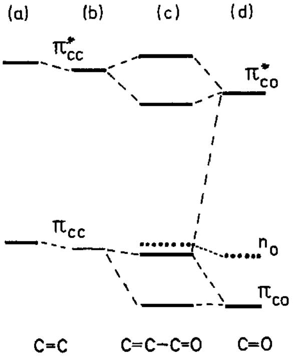

Fig. 2. Schematic orbital correlation diagram for unsaturated carbonyl compounds; (a) and (d) isolated fragments, (b) including inductive perturbation and (c) including conjugative interaction

of acrolein) is considerably larger than the one between the π^*_{CC} and the π_{CC} FO ($F_{\pi\pi^*} = +1.68$ eV for butadiene), whereas the opposite is true for the interaction elements between the occupied FO's. This is due to the unsymmetrical electron distribution in π_{CO} and π^*_{CO}, which increases the one-electron and to an even larger extent also the two-electron contribution to the antibonding interaction element.

In the case of the tropone molecule, similar results are obtained [52], which indicate a non-negligible contribution of the π^*_{CO} FO to the ground state electronic structure. These findings are at variance with the results of Schweig *et al.* [53] who from MINDO/2 calculations with conjugative interruptions [54] conclude that the inductive stabilization and consequently also the conjugative destabilization of the π_{CC} level are much larger. But such differences are not unexpected since Schweig *et al.* did not use the π approximation but were working within an all-valence electron scheme, and since the magnitude of inductive and conjugative effects naturally depends on their definition which is quite arbitrary.

The definition of the inductive perturbation based on the generalized product approximation appears to be consistent and physically meaningful. This will be demonstrated in forthcoming papers by applying the method to the interpretation of a wide range of carbonyl compounds including tropone and related compounds [52], to unsaturated ethers [55] and to other compounds.

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