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Author's Review

Fragment Molecular Orbitals for Molecules and Interacting Systems

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Different approaches to describe the structure and properties of molecules as well as reactions between molecules in terms of localized fragment orbitals and their interactions are briefly reviewed and the method of fragments-in-molecules (FIM) is delineated. The FIM method is formulated entirely in terms of strictly transferable fragment orbitals (FO's) which makes it possible to reduce the basis set in order to simplify the calculations, to save computer time and to make the results even more visual. Calculations within the CNDO/2 approximation on $\text{CH}_3\text{-S}$ molecules with $\text{S} = \text{CH}_3$, NH_2 , OH , F , CN , $\text{CH}=\text{CH}_2$ and $\text{CH}=\text{O}$ are used to demonstrate the effect of limiting the number of virtual orbitals taken into account and to analyse inductive and mesomeric interactions. It appears that the same orbital interactions between occupied and virtual FO's of different fragments which are responsible for the rotational barrier also have the largest effect on the total energies of the systems under consideration. A partitioning of the energy of interaction between molecular fragments based on the formulation of the FIM approach yields definitions of inductive and mesomeric effects which are in good accord with chemical experience and is closely connected with other energy partitioning schemes.

INTRODUCTION

Chemical experience shows that many global properties of a molecule may be obtained in an additive way from contributions of individual bonds or groups, and that the properties of a complex molecule may be discussed in terms of its constituent fragments, *i. e.* in terms of a hydrocarbon skeleton and functional groups or other substituents. Of particular interest, however, are deviations from additivity, which may be conveniently described by orbital interactions. Thus, interactions of orbitals localized in different subsystems may be used to elucidate the structure and properties of molecules as well as to describe reactions between molecules.

The determination of orbital interactions and the calculation of interaction energies is therefore one of the principal goals of quantum organic chemistry. The direct calculation of an interaction energy as the difference of two total energies is unsatisfactory, as usually the error is too large compared with the required energy difference¹. The only way of meeting this difficulty is to separate theoretically the energy of a system into terms which refer to

its component parts supplemented by extra terms which directly represent the interaction.

The approaches which have been developed to solve these problems may be divided essentially into three groups. Perturbation theory has most often been utilized to determine the interaction of fragment orbitals and to estimate the interaction energies²⁻¹⁵. Another possibility is to analyse wave functions for energies of the composite system in terms of localized orbitals and their contributions to the energy¹⁶⁻²⁴. Finally, one may build up the wave function by starting from wave functions associated with the fragments²⁵⁻³⁶. In the present paper, these three approaches will be reviewed briefly and some applications of fragment orbital calculations will be reported and compared with conclusions from other methods if available. Thus, the scope of the various methods designed to describe molecules and interacting systems on the basis of fragment orbitals will be outlined and limitations of these approaches will be indicated.

THE THEORETICAL DESCRIPTION OF INTERACTING FRAGMENTS

(a) Separability of a System into Fragments

The discussion of the electronic structure of a molecular system on the basis of its component parts or fragments and their interactions must be based on a physically meaningful separation into subsystems. Although such a separation is readily formulated, serious mathematical difficulties can arise due to the use of non-orthogonal wave functions for the fragments¹.

If the total Hamiltonian can be written as

$$H(1, \dots, N) = H_A(1, \dots, N_A) + H_B(N_A + 1, \dots, N_A + N_B) + \dots \quad (1)$$

as the sum of Hamiltonians of the subsystems, the total energy

$$E = E_A + E_B + \dots \quad (2)$$

is the sum of the energies of the subsystems, *i. e.* the total energy is strictly additive.

In the more interesting case that $H(1, \dots, N)$ contains interaction terms H_{AB} , for systems which overlap only slightly some degree of separation can be achieved on the basis of the strong orthogonality assumption³⁷

$$\int \Phi_R(1, i \dots) \Phi_S(1, j \dots) d\tau_1 = 0 \quad (R \neq S) \quad (3)$$

where Φ_R and Φ_S are the wave functions of different subsystems of fragments and the integration is over the coordinates of only one of the electrons. The wave function of the combined system may then be written as the antisymmetrized product of fragment wave functions²⁵

$$\Psi(1, \dots, N) = \hat{A} \Phi_A(1, \dots, N_A) \Phi_B(N_A + 1, \dots, N_A + N_B) \dots \quad (4)$$

For this wave function the spinless one-electron density matrix is given²⁵ in the form

$$\mathbf{P} = \mathbf{P}_A + \mathbf{P}_B + \dots \quad (5)$$

which expresses the separability of the system into fragments. Introducing an effective Hamiltonian

$$H_{\text{eff}}^{\text{R}}(1, \dots, N_{\text{R}}) = \sum_{i=1}^{N_{\text{R}}} h_{\text{eff}}^{\text{R}}(i) + \frac{1}{2} \sum_{i,j=1}^{N_{\text{R}}} g(i, j)$$

with

$$h_{\text{eff}}^{\text{R}}(i) = h(i) + \sum_{\text{S}(\neq \text{R})} \mathbf{G}^{\text{S}}(i) = h^{\text{R}}(i) + \sum_{\text{S}(\neq \text{R})} [\mathbf{V}^{\text{S}}(i) + \mathbf{G}^{\text{S}}(i)], \quad (6)$$

which describes the fragment R in the field of all other fragments S³⁸, the total energy of the system may be written^{26,32} as

$$E_0 = \sum_{\text{R}} [E_{\text{eff}}^{\text{R}} - \sum_{\text{S}(\neq \text{R})} \text{tr}(\mathbf{G}^{\text{RS}} + \mathbf{V}^{\text{S}}) \mathbf{P}^{\text{S}}], \quad (7)$$

where \mathbf{G}^{RS} is essentially a generalization of the electron interaction matrix of Roothaan³⁹ and \mathbf{V}^{S} represents the potential due to the cores of fragment S.

From this formulation it is apparent that deviations from additivity will be smaller the better the attractive and repulsive interactions between different fragments compensate.

The extension of the generalized product function approach to non-orthogonal group functions³³ does not change these patterns: The generalized product of unperturbed group functions Φ_{R}^0 describes Coulomb and exchange effects, whereas the product of self-consistent group functions yields polarization effects as well, and the standard HF—SCF wave function also includes charge transfer effects between different fragments. The decomposition of the interaction energy into coulomb, exchange, polarisation and charge transfer effects can also be applied to other properties as *e. g.* dipole moments⁴⁰.

(b) *The Perturbational Treatment of Interacting Fragments*

Perturbational methods for the evaluation of interaction energies have been discussed both within the framework of an independent-electron model³⁻⁸ and on various levels of self-consistent field theory⁹⁻¹⁵. Salem³ pointed out that the inclusion of overlap is an essential feature of an independent-electron treatment as otherwise no repulsion energy whatsoever is obtained. Using a perturbational formalism including overlap based on extended Hückel theory, Libit and Hoffmann⁷ gave a detailed analysis of substituent effects; they showed that charge transfer between the fragments is a first-order effect, whereas in the second-order of perturbation theory the initially orthogonal fragment orbitals begin to be mixed up with each other, polarizing the fragment by accumulating electron density at one or several centers.

In a self-consistent perturbation theory electron repulsion is taken into account explicitly; therefore the neglect of overlap, although certainly amounting to an approximation, cannot have the disastrous effect it has in the independent-electron model¹⁴. If not only one-electron perturbations are considered¹³, but also two-electron perturbations are taken into account within the framework of the INDO-approximation⁴¹, the first-order interaction energy is entirely attributable to the electrostatic interaction, whereas the second-order energy may be broken up into local one-electron and two-electron contributions which approximately cancel for non-polar fragments, and a one-electron cross-term which corresponds to the second-order energy change in Hückel per-

turbation theory¹⁴. If non-orthogonality effects are taken into account, purely repulsive exchange terms modify the Coulomb interaction¹⁵ and lead to an electron redistribution through orbital mixing.

A similar partitioning of the second-order perturbation contribution was obtained when expressions for the delocalization and polarization energies were derived on the basis of antisymmetrized products of fragment MOs including monoexcitations within fragments and between fragments (monotransferred configurations)⁹.

(c) *The Interpretation of MO Wavefunction in Terms of Interacting Fragments*

On the basis of *ab initio* SCF theory a scheme has been proposed¹⁶ in which the interaction energy of the fragments of a complex system is decomposed into electrostatic (ES), polarization (PL), exchange repulsion (EX), charge transfer (CT) and coupling (MIX) terms, in order to gain insight into the origin of molecular interaction; these components are calculated as differences between energy expectation values for appropriate wave functions. In the same fashion as for the energy, the total change in electron density $\Delta\rho$ and its components ρ_{PL} , ρ_{EX} , ρ_{CT} and $\rho_{\text{MIX}} = \Delta\rho - (\rho_{\text{PL}} - \rho_{\text{EX}} - \rho_{\text{CT}})$ can be defined.

Another way of analysing the bond formation between two species consists of expanding the molecular orbitals of the combined systems in terms of the MO's of the fragments, as originally proposed for the interpretation of UV spectra in terms of localized and charge-transfer transitions¹⁸. Such a procedure is easy to apply to interacting closed-shell fragments such as *e.g.* electron donator-acceptor complexes¹⁹, but other methods may be necessary in more general cases. Thus, transformation of the canonical SCF—MO's into localized MO's has been put forward²⁰ and a method to decompose the canonical MO's into local bond orbitals²¹, which are constructed simply as in-phase and out-of-phase combinations of directed hybrids, has been proposed. Another scheme uses group orbitals, obtained by diagonalising appropriate blocks of the Fock matrix²³.

These analyses of the wave functions allow interaction energies to be discussed in terms of bond-bond and bond-antibond or two-electron stabilizing and four-electron destabilizing interactions respectively⁸. The energy component analysis may give different results, depending on whether orthogonal or non-orthogonal basis sets are being used. In a nonorthogonal basis there is no clear distinction between the contributions of different basis functions, and the determinantal product of nonorthogonal bond orbitals will implicitly bring in some of those interactions, which in an orthonormal basis will be classified as bond-antibond interactions²³.

(d) *The Method of Fragments-in-Molecules*

Using fragment MO's $\varphi_{\text{I}}^{\text{R}}$ (FO's) instead of AOs χ_{I} in the expansion

$$\psi_i = \sum_{\text{I}} c_{\text{I}}^{\text{R}} \varphi_{\text{I}}^{\text{R}} + \sum_{\text{J}} c_{\text{J}}^{\text{S}} \varphi_{\text{J}}^{\text{S}} + \dots \quad (8)$$

of the MO's of a system composed of fragments, R, S... corresponds to a unitary basis transformation and thus does not yield new results, although it constitutes a powerful method of analysing weak and moderately strong inter-

actions. Of particular importance are interactions between the frontier orbitals of the fragments, and the concepts of interaction frontier orbitals³⁴ and coupled fragment MO's³⁵ have been proposed for the discussion of interactions between different fragments.

The use of fragment orbitals not only has advantages for the interpretation of results, but also makes it possible to include in the calculation experimental data for the fragments and to evaluate explicitly only the interaction energies, thus leading to much more accurate total energies. This possibility was first recognized by Moffitt in his method of atoms-in-molecules⁴² and was used later in the molecules-in-molecules (MIM) approach of Murrell and Longuet-Higgins to calculate the excited states of complex π -systems starting from the spectroscopic data of the fragment molecules²⁸. The same principles were qualitatively used in interpreting the PE spectra of complex molecules on the basis of correlation diagrams which relate the orbital energies of fragments to those of the system under investigation⁴³. In order to be able theoretically to calculate such orbital correlation diagrams, a fragments-in-molecules method (FIM) has been developed^{32,44}, which is based on the linear combination of localized fragment orbitals (LCFO-MO) and which allows for a systematic calculation of the inductive perturbation of one fragment by another. This is the key step which makes it possible to include into the calculation experimental data of the unperturbed fragments.

In the FIM method developed previously^{32,44}, the Fock matrix $\mathbf{F}^U = \mathbf{h}^U + \mathbf{G}(\mathbf{P}^U)$ and the density matrix \mathbf{P}^U of the composite system U built up from fragments R, S, ... are written in the form

$$\mathbf{F}^U = \begin{pmatrix} \mathbf{F}^U_{(R)} & \mathbf{F}^U_{(RS)} & \cdots \\ \cdots & \mathbf{F}^U_{(S)} & \cdots \\ \cdots & \cdots & \cdots \end{pmatrix} \quad \text{and} \quad \mathbf{P}^U = \begin{pmatrix} \mathbf{P}^U_{(R)} & \mathbf{P}^U_{(RS)} & \cdots \\ \cdots & \mathbf{P}^U_{(S)} & \cdots \\ \cdots & \cdots & \cdots \end{pmatrix} \quad (9)$$

where the diagonal blocks

$$\mathbf{F}^U_{(R)} = \mathbf{F}^{R_0} + \Delta \mathbf{F}^U_{(R)} \quad (10)$$

and

$$\mathbf{P}^U_{(R)} = \mathbf{P}^{R_0} \Delta \mathbf{P}^U_{(R)}$$

may be decomposed into two parts corresponding to the isolated fragments and representing the effect of combining the fragments to form the composite system U. As basis functions fragment orbitals (FO's) φ^R_I are used which diagonalise the corresponding Fock matrix \mathbf{F}^{R_0} of the isolated fragment R, the diagonal elements being the orbital energies ε^R_I , and which make the density matrix of the isolated fragment R diagonal with

$$(\mathbf{P}^{R_0})_{KK} = \begin{cases} 2 & \text{for } \varphi^R_K \text{ occupied} \\ 0 & \text{for } \varphi^R_K \text{ unoccupied} \end{cases} \quad (11)$$

In terms of these FO's the elements of the diagonal block of the Fock matrix are given by

$$\begin{aligned} (\mathbf{F}^U_{(R)})_{IJ} = & \varepsilon^R_I \delta_{IJ} + \sum_{K,L} (\mathbf{P}^U_{(R)} - \mathbf{P}^{R_0})_{K,L} [(\varphi^R_I \varphi^R_J | \varphi^R_K \varphi^R_L) - \frac{1}{2} (\varphi^R_I \varphi^R_K | \varphi^R_J \varphi^R_L)] + \\ & + \sum_{S(\neq R)} [(\mathbf{I}^{RS})_{IJ} + \sum_{K,L} (\mathbf{P}^U_{(S)} - \mathbf{P}^{S_0})_{K,L} (\varphi^R_I \varphi^R_J | \varphi^S_K \varphi^S_L)], \end{aligned} \quad (12)$$

where

$$(\mathbf{I}^{\text{RS}})_{\text{IJ}} = [\mathbf{V}^{\text{RS}} + \mathbf{G}^{\text{RS}}(\mathbf{P}_0^{\text{S}})]_{\text{IJ}} = (\mathbf{V}^{\text{RS}})_{\text{IJ}} + \sum_{\text{K(occ)}} 2(\varphi_{\text{I}}^{\text{R}} \varphi_{\text{J}}^{\text{R}} | \varphi_{\text{K}}^{\text{S}} \varphi_{\text{K}}^{\text{S}}) \quad (13)$$

may be identified with the inductive perturbation⁴⁵ of fragment R due to fragment S, as may be seen if the wave function is written as a generalized product (Eq. (4)) which describes each fragment R in the field of all other fragments S. \mathbf{V}^{RS} contains the one-electron terms due to the cores of fragment S which are not contained in \mathbf{h}^{R} , and $\mathbf{G}^{\text{RS}}(\mathbf{P}_0^{\text{S}})$ represents the interaction with the electron distribution \mathbf{P}_0^{S} in fragment S. If core attraction and electron repulsion cancel each other, the inductive perturbations \mathbf{I}^{RS} disappear; this is true for non-polar systems where the screening of the core charges due to the electron distribution is just about complete⁴⁵.

The off-diagonal blocks cannot contain contributions from the isolated fragments and may thus be written in standard form as

$$(\mathbf{F}^{\text{U}}_{(\text{RS})})_{\text{IJ}} = (\mathbf{h}^{\text{U}}_{(\text{RS})})_{\text{IJ}} - \frac{1}{2} \sum_{\text{K,L}} (\mathbf{P}^{\text{U}}_{(\text{RS})})_{\text{KL}} (\varphi_{\text{I}}^{\text{R}} \varphi_{\text{K}}^{\text{R}} | \varphi_{\text{J}}^{\text{S}} \varphi_{\text{L}}^{\text{S}}), \quad (14)$$

where $(\mathbf{h}^{\text{U}}_{(\text{RS})})_{\text{IJ}} = \langle \varphi_{\text{I}}^{\text{R}} | h^{\text{U}} | \varphi_{\text{J}}^{\text{S}} \rangle$ is the one electron term. In evaluating the two-electron term $(\mathbf{G}(\mathbf{R}))_{\text{IJ}}$ in Eqs. (12)–(14) the fact was used that

$$\varphi_{\text{K}}^{\text{R}} \varphi_{\text{L}}^{\text{S}} \equiv 0 \quad \text{for } \text{R} \neq \text{S}, \quad (15)$$

as for $\text{R} \neq \text{S}$ for FO's $\varphi_{\text{K}}^{\text{R}}$ and $\varphi_{\text{L}}^{\text{S}}$ are localized in different fragments and are therefore linear combinations of different sets of AO's χ_{ρ}^{R} and χ_{ρ}^{S} which are assumed to satisfy the ZDO approximation⁴⁶.

In the following some representative results are presented which were obtained using the CNDO/2 approximation and standard geometries. sp^3 and sp^2 hybridization has been assumed for saturated groups and for the vinyl and carbonyl group respectively. Unless otherwise stated the molecules were dissected into three fragments corresponding to the CH_3 group, the substituent S and the $\sigma(\text{CX})$ bond between the C atom of the CH_3 group and the X atom of the substituent. The effect of different dissections and of the use of experimental data for the fragment orbital energies $\varepsilon_{\text{I}}^{\text{R}}$ were discussed elsewhere⁴⁴.

The FIM method was formulated in such a way that any chemically interesting group may be chosen as the basic fragment. It has proven most practicable to consider each newly formed σ bond as one fragment, and to obtain the FO's, using a basis of appropriate hybrid AO's, from an SCF calculation on the closed-shell system, which in the case of groups like CH_3 is obtained from the corresponding radical $\text{CH}_3\cdot$ by assuming that the radical electron compensates just for one unit of core charge. In the case of σ bonds uniting two fragments, the FO's are obtained by assuming that all valence electrons other than the radical electron compensate for the corresponding number of core charge units. Thus the FO's $\varphi_{\text{I}}^{\text{R}}$ and FO energies $\varepsilon_{\text{I}}^{\text{R}}$ are characteristic for the fragment and strictly transferable from molecule to molecule; the dependence on the environment of the fragment in the molecule is taken into account by the \mathbf{I}^{RS} terms as well as by the electron reorganization terms in Eq. (12).

RESULTS AND DISCUSSION

(a) Rotational Barriers and the Effect of Virtual Orbitals

The results of an FIM calculation including all occupied and all virtual FO's, which may be denoted as full linear combination of fragment orbitals (LCFO) calculation, are identical with the solution of the SCF problem in the original AO basis; by including only a limited number of virtual FO's the dimension of the FO-SCF problem may be reduced considerably, so that the method may become even faster than the standard SCF calculation without losing much of the accuracy. This is evident from the data in Table I which shows the dependence of the total energies on the number of FO's used in the calculation. The effect of including virtual orbitals is small, though not unimportant.

TABLE I

Total Electronic Energies (a. u.) of CH₃-S Molecules Computed with FO Basis Sets of Different Size^a

	CH ₃ CH ₃	CH ₃ F	CH ₃ CN	CH ₃ CH=CH ₂
I (full LCFO)	-45.40526	-59.98724	-58.52115	-66.42967
II	-45.40141	-59.97644	-58.50759	-66.38965
III	-45.35859	-59.95928	-58.45917	-66.38171
IV	-45.35761	-59.95807	-58.45562	-66.34992
V	-45.35569	-59.94988	-58.45013	-66.37232
VI (min LCFO)	-45.35465	-59.94873	-58.44038	-66.34115

^a The basis sets differ in the number of virtual FO's; basis I includes all virtual FO's, whereas basis II contains all virtual orbitals of π symmetry and basis III-V contain only virtual orbitals of σ symmetry, *i. e.* $\sigma_{\text{CH}_3}^*$, σ_{CX}^* and σ_{S}^* (III), σ_{CX}^* (IV) and $\sigma_{\text{CH}_3}^*$ and σ_{S}^* (V), respectively; the minimal basis VI consists only of FO's occupied in the fragments.

The minimal basis FO (min-LCFO) calculations take into account only bonding (or occupied) orbitals and are therefore equivalent to a Hückel-type approach sometimes called linear combination of bonding orbitals (LCBO)⁴⁷. Although this approximation corresponds simply to a unitary transformation of occupied orbitals among themselves, the total energy of the composite system is not just the sum of the fragment energies, as may be seen for ethane from the SCF values $E(\text{CH}_3) = -12.1177$ a. u., $E(\sigma\text{CC}) = -2.3577$ a. u. and the min-LCFO-SCF energy $E(\text{C}_2\text{H}_6) = -45.3617$ a. u.. There are two reasons for the non-additivity: Electron interaction, which according to Eq. (12) cancels within the min-LCFO approximation because $\mathbf{P}^{\text{U}}_{(\text{R})} = \mathbf{P}^{\text{R}}_0$, comes in indirectly through the diagonal elements of the Fock matrix and has to be taken into account in evaluating the fragment energies $E = 1/2 \text{tr } \mathbf{P}(\mathbf{F} + \mathbf{h})$ by using the same one-electron integrals \mathbf{h} as for the united system, which yields $E(\text{CH}_3) = -19.1166$ a. u. and $E(\sigma\text{CC}) = -7.1574$ a. u.; and the difference between the sum of these additive fragment energies and the min-LCFO-SCF energy is due to the inductive perturbations according to Eq. (13), which are included in the FO

calculation and which in the case of the interaction of two methyl groups to yield the ethane molecule lead to a destabilization (cf. the following section).

If the fragment energies were strictly additive, the electronic energies would be the same for all configurations and conformations of a given molecule. Thus within the min-LCFO-SCF approximation the conformational energy is due to two electronic terms, the electron-core attraction and the inductive perturbation, as well as to the nuclear repulsion. From the data in Table II it is seen, that the inductive perturbation is to a good approximation independent of the molecular conformation, whereas electron-core attraction and core-core repulsion nearly cancel, their difference being due only to the difference between the point-charge and the charge-distribution model⁴⁸.

These results may be used to analyse the origin of rotational barriers. Based on the additivity of fragment energies no barriers at all are to be expected. The min-LCFO-SCF approximation yields small values for the barriers due to the three contributions mentioned above. The main contribution to the rotational barriers must thus come from orbital interactions between occupied orbitals of one fragment and virtual orbitals of another fragment. As it is possible to apply the FIM method with different numbers of virtual orbitals included in the basis of FO's, the effect of the interactions with each of the virtual orbitals can be studied separately. Some representative results are collected in Table II. As expected, orbitals with σ symmetry have no influence on the calculated barrier of $\text{CH}_3\text{-S}$ molecules. The effect of the virtual π^* orbitals is to stabilize the staggered conformation of ethane, methyl amine and methanol and the eclipsed conformation of propene and acetaldehyde. In both series of compounds the stabilization decreases with increasing polarity of the substituent due to the reduced interaction of the occupied substituent orbitals with the $\pi_{\text{CH}_3}^*$ FO's as well as due to the reduced number of virtual substituent orbitals available.

This picture of the origin of rotational barriers is in agreement with other treatments⁴⁹, although its simplicity is essentially due to the use of orthogonal basis functions. A detailed discussion of these problems will be given elsewhere⁵⁰.

TABLE II
Contributions (in kJ/mol) to the Rotational Barrier $\Delta E = E_{\text{ecl}} - E_{\text{stag}}$ of $\text{CH}_3\text{-X}$ Molecules

	CH_3CH_3	CH_3NH_2	CH_3OH	$\text{CH}_3\text{-CH=CH}_2$	$\text{CH}_3\text{-CH=O}$
Core repulsion	+19.6	14.1	6.5	41.0	22.2
Core attraction	-18.5	-12.5	-3.2	-39.4	-22.2
Inductive perturb.	-0.1	-0.7	-2.7	-0.4	+0.2
Orbital interactions	8.1	5.8	2.4	-6.4	-2.9
Total	9.2	6.7	3.0	-5.2	-2.7
Individual orbital contributions					
σ_{CX}^*	0.0	0.0	0.0	0.0	0.0
$\Sigma \sigma^*$	-0.3	+0.6	+0.9	-0.5	+0.3
$\Sigma \pi^*$	+8.3	+5.4	+1.7	-5.9	-2.9

(b) Inductive and Mesomeric Effects

The quantities I^{RS} in Eq. (13) were called inductive perturbations⁴⁵, because they were derived in such a way as to describe the difference in one-electron integrals between the isolated fragment R and the fragment R in the field of fragment S. Thus in discussing molecules $\text{CH}_3\text{—S}$, where S denotes a substituent bound to the CH_3 group through atom X, each of the three groups CH_3 , $\sigma(\text{CH})$ and S is inductively perturbed by the other two groups. This is not the way inductive substituent effects are commonly defined⁵¹, but nevertheless the data supports chemical intuition, as may be seen *e.g.* from the inductive perturbations of the $\sigma(\text{CX})$ group, which are shown in Table III. The influence of the CH_3 fragment on the $\sigma(\text{CX})$ fragment is small and destabilizing, as can be seen from the data for ethane. With more electronegative substituents like NH_2 or OH the destabilizing effect is greater, and the off-diagonal perturbations $I_{\sigma\sigma}^{\text{TS}}$ become appreciable, thus changing the polarity of the CX bond by mixing the FO's φ_π and φ_π^* . These effects are only small and disappear if the charge distribution in the substituent group is uniform as for F in CH_3F , where the polarity of the $\sigma(\text{CX})$ bond is the same as in the isolated fragment. From the data for propene, acetaldehyde and acetonitrile it is seen that the effect of the vinyl group is comparable to that of a methyl group, and that an electronegative atom in the β position, as in acetaldehyde and acetonitrile leads to an inductive stabilisation of $\sigma(\text{CC})$.

TABLE III

Substituent Effects in $\text{CH}_3\text{—S}$ Molecules; Inductive and Mesomeric Contributions ΔE_{ind} and ΔE_{mes} to the Total Energy (in a. u.), Inductive Perturbations (I^{RS})_{II} of the σ_{CX} and σ_{CH_3} FO's (in a. u.) and Total Inductive Substituent Effects $\Sigma(\text{S})$

	ΔE_{ind}	ΔE_{mes}	R = σ_{CX}			R = CH_3^a		$\Sigma(\text{S})^b$
			$I_{\sigma\sigma}^{\text{RS}}$	$I_{\sigma\sigma^*}^{\text{RS}}$	$I_{\sigma^*\sigma^*}^{\text{RS}}$	$I_{\text{KK}}^{\text{RS}}$	$I_{\text{KK}}^{\text{R}\sigma_{\text{CX}}}$	
$\text{CH}_3\text{—CH}_3$	0.0289	—0.0506	0.005	0.001	0.005	0.003	0.0	8
$\text{CH}_3\text{—NH}_2$	0.1048	—0.0426	0.031	—0.013	0.029	0.012	—0.015	5
$\text{CH}_3\text{—OH}$	0.1883	—0.0399	0.037	—0.019	0.032	0.011	—0.030	50
$\text{CH}_3\text{—F}$	0.2596	—0.0385	0.0	0.0	0.0	0.0	—0.042	110
$\text{CH}_3\text{—CN}$	0.0021	—0.0748	—0.019	0.002	—0.019	—0.014	—0.014	74
$\text{CH}_3\text{—CH=CH}_2$	0.0343	—0.0879	0.006	—0.002	0.006	0.003	—0.004	3
$\text{CH}_3\text{—CH=O}$	—0.0566	—0.0868	—0.028	0.007	—0.028	—0.016	—0.004	53

^a Only the inductive perturbations of the σ_{CH_3} FO, denoted by K, are given; off-diagonal values $I_{\text{KK}^*}^{\text{RS}}$ as well as differences between $I_{\text{LL}}^{\text{RS}}$ with $\text{L} = \pi_{\text{CH}_3}$ or $\pi_{\text{CH}_3}^*$ and values quoted are negligible.

^b $\Sigma(\text{S}) = I_{\text{KK}}^{\text{RS}} + I_{\text{KK}}^{\text{RT}}$ in kJ/mol.

Table III also gives the inductive perturbations of the CH_3 FO's due to the substituent and to the $\sigma(\text{CX})$ bond. The $\sigma(\text{CC})$ bond between sp^3 hybridized carbons is non-polar and does not give rise to any inductive perturbation, whereas the non-uniform charge distribution in a σ bond between sp^3 and sp^2 or even more so between sp^3 and sp carbons stabilizes the CH_3 FO's although to a lesser degree than the more polar $\sigma(\text{CX})$ bonds with $\text{X} = \text{N}, \text{O}$ or F , with

σ (CF) being the only case which leads to appreciable off-diagonal contributions. The sum $\Sigma(S) = I_{\sigma\sigma}^{RS} + I_{\sigma\sigma}^{RT}$ of the effects due to the σ (CX) bond and the substituent group (in kJ/mol) given in the last column of Table III, are in very good agreement with chemical ideas about inductive effects. This shows that the inductive perturbations defined in Eq. (13) may well be used to get quantitative estimations of substituent effects.

Table III gives also sums of contributions to the total energies from inductive perturbations as well as from mesomeric interactions. From this data it is seen that the total interaction energy between a CH_3 group and a substituent can be partitioned into inductive and mesomeric contributions, which can either partially cancel each other as for ethane, or which can both be stabilizing as in the case of the carbonyl group in acetaldehyde. As was shown in the previous section about rotational barriers, the mesomeric stabilization stems mainly from interactions of occupied orbitals of one fragment with virtual orbitals of another fragment. The fact that for molecules like CH_3F the sum of inductive and mesomeric contributions is positive or destabilizing, is due to the fact that the isolated fragment energies, which are not calculated according to a variational criterion, very much overestimate the stability as is indicated by the large inductive destabilizations of the FO's.

Calculated inductive and mesomeric effects depend according to Eq. (13) on the choice of FO's. Thus, if a σ/π separation is introduced and four fragments [CH_3 , $\sigma(\text{CC})$, $\sigma(\text{CHO})$ and $\pi(\text{CO})$] are used instead of three to discuss the acetaldehyde molecule, the π_{CO} changes from

$$\pi_{\text{CO}} = 0.6574 p_{\text{C}} + 0.7536 p_{\text{O}} \quad \text{to} \quad \pi'_{\text{CO}} = 0.6396 p_{\text{C}} + 0.7687 p_{\text{O}};$$

if σ/π interaction is allowed for in the latter case, the polarity of the σ framework induces a mixing of π'_{CO} and π'^*_{CO} FO's via the inductive perturbations,

TABLE IV

Inductive and Mesomeric Contributions to the Matrix Elements $(\mathbf{F}_{(\text{CH}_3)}^{\text{U}})_{\text{KK}}$ of the CH_3 Group in Acetaldehyde and to the Total Energy Calculated without and with σ/π Separation (in a. u.)^a

	$\text{K} = \sigma_{\text{CH}_3}$	π_{CH_3}	π	ΔE
No σ/π separation (3 fragments)				
$I(\sigma + \pi)_{\text{KK}}$	-0.017	-0.016	-0.018	
$I(\sigma_{\text{CC}})_{\text{KK}}$	-0.004	-0.004	-0.004	$\Delta E_{\text{ind}} = -0.0566$
M_{KK}	-0.003	+0.006	+0.002	$\Delta E_{\text{mes}} = -0.0368$
With σ/π separation (4 fragments)				
$I(\sigma)_{\text{KK}}$	-0.016	-0.015	-0.017	
$I(\pi)_{\text{KK}}$	-0.010	-0.009	-0.011	
$I(\sigma_{\text{CC}})_{\text{KK}}$	-0.004	-0.004	-0.004	$E_{\text{ind}} = +0.0691$
M_{KK}	+0.006	+0.015	+0.012	$E_{\text{mes}} = -0.0912$

^a $I(S)$ denotes the inductive perturbation $\mathbf{I}_{\text{KK}}^{\text{RS}}$ of the FO K of the CH_3 group by group S, $\mathbf{M}_{\text{KK}} = \sum_{\text{T}} [\text{G}(\mathbf{P}_{(\text{T})}^{\text{T}} - \mathbf{P}_{(\text{T})}^{\text{T}_0})]_{\text{KK}}$ denotes the contributions to \mathbf{F}_{KK} due to the charge redistribution.

which therefore exhibit comparatively high values for the off-diagonal elements, and conversely, the polarity of the π_{CO} bond induces a mixing of the σ orbitals. Charge redistributions are also appreciably dependent on the choice of FO's, so that there is no simple additivity of σ and π inductive effects in this scheme. In fact, from Table IV it is seen that the higher stabilizing inductive perturbations in the case of σ/π separation are compensated for by higher destabilizing contributions from the electron redistribution.

CONCLUSION

The results discussed in the previous sections demonstrate some of the interpretational advantages of the fragment orbital approach. The interpretation of rotational barriers was used to show the effect of limiting the number of virtual orbitals taken into account. It was shown that the barrier is essentially due to a π_R/π^*_S orbital interaction between occupied and virtual orbitals of different fragments. This is in line with the analysis of Lowe⁵² based on a one-electron model and with that of Brunck and Weinhold²¹, which traced the barrier to the differential stabilizing effects of cis- and trans bond-antibond interactions, and with the conclusion obtained from calculations using Hartree products of bond orbitals⁵³, that electrostatic interactions between bonds are not an important factor in rotational barriers. In calculations based on non-orthogonal orbitals, the conformational dependence of localized orbital coefficients in the vicinal tail of CH bonds corresponding to the bond-antibond mixing of orthogonal bond orbitals was found to be most important⁵⁴; therefore, a determinantal product of nonorthogonal bond orbitals may give reasonable rotational barriers even if delocalization is not allowed for⁵⁵.

This brief discussion shows that results from FIM calculations are comparable to results from other MO methods; the main difference being the great intuitive appeal of the interactions of localized orthogonal fragment orbitals. The discussion of the propene and acetaldehyde barrier demonstrates how well known ideas about the effect of electronegative atoms can be accommodated within the model. In addition to the way the results lend themselves to an interpretation in chemical terms, it is of great importance that the FIM method is not used to analyse the results of a given SCF calculation, but rather to perform the calculation, using strictly transferable FO's as basis orbitals. This makes it possible to restrict the basis, which not only increases the interpretability of the results, but also reduces the computer time considerably so that the calculations may become much faster than conventional SCF calculations without losing much of the accuracy. Table I showed that the same orbital interactions which are responsible for the rotational barrier also have the largest effect on the total energies.

The analysis of inductive and mesomeric interactions may be taken as another partitioning of the interaction energy between molecular fragments. It is closely connected not only with the energy partitioning in the group function method³³, which has been discussed in the literature in connection with the SCF scheme of Morokuma¹⁶, but also with the energy partitioning based on SCF perturbation theory¹⁴, which attributes first-order terms to electrostatic interactions and second-order terms to local contributions corresponding to the inductive perturbations in the FIM model, and to a one-electron cross-term corresponding to elements in the off-diagonal block Eq.

(14) of the FIM Fock matrix. The connection with Hückel perturbation theory⁷ is less clear-cut, due to non-orthogonality effects as well as to the neglect of two-electron contributions.

In summarizing one may say that most features of the different models proposed to discuss the interaction of fragments in molecules or reacting systems show up also in the FIM method. The important advantage is that the FIM method makes use of the separation of a complex system into fragments right from the beginning and that it is formulated entirely in terms of fragment orbitals. This introduces the possibility of reducing the basis set in order to simplify the calculations, to save computer time and to make the results even more visual. It also makes it possible to introduce experimental data into the calculation and thereby to increase the absolute accuracy of the method; this aspect will be taken up elsewhere⁵⁶. Both the use of small basis sets and of experimental data will make these calculations especially useful in discussing chemical reactivity and reaction mechanisms as we hope to show in forthcoming papers.

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SAŽETAK

Opis molekula i njihovih interakcija s pomoću molekulskih orbitala njihovih fragmenata

Martin Klessinger

Dan je kratak prikaz različitih pristupa za opis strukture i svojstava molekula koji se osnivaju na lokaliziranim orbitalama fragmenata. Posebna pažnja posvećena je izvornoj metodi molekulskih fragmenata (FIM). Ona je formulirana na osnovnom skupu orbitala fragmenata (FO) koje su potpuno transferabilne. To bitno smanjuje broj osnovnih funkcija i pojednostavnjuje račune. Metoda je ilustrirana CNDO/2-računima izvedenim na nizu spojeva $\text{CH}_3\text{-X}$ ($\text{X}=\text{CH}_3, \text{NH}_2, \text{OH}, \text{F}, \text{CN}, \text{CH}=\text{CH}_2$ i $\text{CH}=\text{O}$) kod kojih su analizirani induktivni i mezomerni efekti. Pokazano je da interakcije zaposjednutih i nezaposjednutih FO orbitala, koje određuju visinu barijera interne rotacije, istovremeno najviše pridonose ukupnoj stabilnosti razmatranih molekula. Izračunani induktivni i mezomerni efekti u skladu su s kemijskim iskustvom.