

CCA-1387

YU ISSN 0011-1643

UDC 541

*Original Scientific Paper*

## The Fragments-in-Molecules Method III. Inductive and Mesomeric Effects\*

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Received August 30, 1982

Within the framework of the recently developed FIM method the interaction of FO's is evaluated in two steps: inductive perturbations are calculated on the basis of the generalized product approach treating each fragment in the field of all other fragments. The mesomeric interactions in the composite system are then obtained from SCF calculations based on these FO's. Applications to  $\pi$  systems based on the PPP approximation as well as applications based on the CNDO/2 approach show that this definition of inductive and mesomeric effects is quite natural and useful in discussing the electronic structure of organic molecules.

### INTRODUCTION

In recent years several quantum chemistry programmes have become available which enable routine calculations to be performed in order to solve structural problems or to discuss chemical reactions. A number of schemes have been proposed for the interpretation of the results of such calculations in a way which is illuminating and suggestive to a chemist and which allows for generalizations, e. g. the construction of localized orbitals<sup>1</sup> or the use of bond orbitals<sup>2</sup> or fragment orbitals<sup>3</sup>. But each of these examples require the knowledge of the SCF-MOs, so that correlations with molecular structure may be obtained only by the analysis of the results of distinct calculations on specific systems of interest.

The FIM method<sup>4,5</sup> on the other hand emphasizes throughout the structure of the system in terms of chemically significant groups or fragments and their interactions. It has been formulated in terms of transferable fragment orbitals  $\Phi_I$  and their energies  $\epsilon_I$  in such a way, that in a first step the perturbations of these FO's due to the presence of the other fragments are calculated, whereas the interactions of these FO's in the composite system are treated in a second step. In the present paper it will be shown that this subdivision of the calculation may form the basis of a natural and non-arbitrary definition of inductive and mesomeric effects.

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\* Presented at *The IUPAC International Symposium on Theoretical Organic Chemistry*, held in Dubrovnik, Croatia, August 30 — September 3, 1982.

## THE FIM-METHOD

The wave function of a system made up of several independent fragments may be written as a generalized product of antisymmetrized functions  $\Phi_R$  of the fragments R (R = A, B...) which are assumed to fulfill the strong orthogonality requirement<sup>6</sup>:

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

If the functions  $\Phi_R$  are Slater determinants of doubly occupied FO's  $\Phi_I^R$ , the matrix elements of the Fock-Operator in the basis of the  $\Phi_I^R$  read

$$\begin{aligned} (F^R)_{IJ} &= (h_{\text{eff}}^R)_{IJ} + G^{\text{RR}}(P^R)_{IJ} \\ &= \varepsilon_I^R \delta_{IJ} + \sum_{S (\neq R)} (I^{\text{RS}})_{IJ} + \end{aligned} \quad (2)$$

$$\sum_{K, L} (P^R - P^R)_{KL} [(\Phi_I^R \Phi_J^R | \Phi_K^R \Phi_L^R) - \frac{1}{2} (\Phi_I^R \Phi_K^R | \Phi_J^R \Phi_L^R)], \quad (2)$$

where  $\varepsilon_I^R$  is the I'th SCF-eigenvalue of the isolated fragment R and

$$(I^{\text{RS}})_{IJ} = [V^{\text{RS}} + G^{\text{RS}}(P^S)_{IJ}]_{IJ} = V_{IJ}^{\text{RS}} + \sum_{K (\text{occ})} 2 (\Phi_I^R \Phi_J^R | \Phi_K^S \Phi_K^S) \quad (3)$$

is the contribution of fragment S to the effective one-electron Hamiltonian  $h_{\text{eff}}^R(i)$  of group R, with  $V^{\text{RS}}$  denoting the core attraction due to fragment S and  $G^{\text{RS}}(P^S)$  denoting the Roothaan electron interaction matrix, which depends on the one-electron density matrix  $P^S$ . For the isolated fragments with doubly occupied FO's one has

$$(P^R)_{KL} = \begin{cases} 2\delta_{KL} & \text{for } \Phi_K^R \text{ occ} \\ 0 & \text{for } \Phi_K^R \text{ unocc.} \end{cases} \quad (4)$$

If the wave function of the composite system is written as a Slater determinant of MO's  $\psi_i$  built up from the FO's of all fragments

$$\Psi(1, \dots, N) = \left| \psi_1 \psi_1 \dots \psi_{\frac{N}{2}} \psi_{\frac{N}{2}} \right|, \quad (5)$$

the matrix elements of the Fock operator of the united system U in the basis of the  $\Phi_I^R$  may be written as

$$\begin{aligned} (F^U)_{IJ} &= (F^R)_{IJ} + \sum_{K, L} (P^U)_{KL} [(\Phi_I^R \Phi_J^R | \Phi_K^R \Phi_L^R) - \frac{1}{2} (\Phi_I^R \Phi_K^R | \Phi_J^R \Phi_L^R)] + \\ &+ \sum_{S (\neq R)} \sum_{K, L} (P^U)_{KL} (\Phi_I^R \Phi_J^R | \Phi_K^S \Phi_L^S) \end{aligned} \quad (6)$$

and

$$(F^U)_{IJ} = (h^U)_{IJ} - \frac{1}{2} \sum_{K, L} (P^U)_{KL} (\Phi_I^R \Phi_K^R | \Phi_J^S \Phi_L^S) \quad (7)$$

where the subscripts (R) etc. indicate whether the FO's  $\Phi_I$  and  $\Phi_J$  belong to same fragment R or to different fragments RS, and  $(h^U)_{IJ}$  contains one electron interactions between the fragments which may be expressed in terms of resonance integrals  $\beta_{\sigma\sigma}$ .

## INDUCTIVE AND MESOMERIC EFFECTS

The wave functions Eq. (1) and Eq. (5) characterize the two steps of the FIM calculation: The generalized product function of the first step takes into account only those interactions which arise just from the presence of the other fragments,  $F^R$  of Eq. (2) differs from the Fock matrix  $F_o^R$  of the isolated fragment R by the one-electron terms  $I^{RS}$  and the electron interaction terms which depend on the rearrangement ( $P^R - P_o^R$ ) of the electrons of group R in the field of the other groups. According to Eq. (3) the one-electron terms are given by the core attraction  $V^{RS}$  of the electrons of fragment R due to the cores of fragment S plus the electron-electron repulsion between the electrons of fragment R and the charge distribution  $P_o^S$  of fragment S. Thus  $I^{RS}$  represents just the inductive perturbation of fragment R due to fragment S, which disappears, if core attraction and electron repulsion cancel each other. Within the framework of the usual  $\pi$ -electron approximation this is true for alternant hydrocarbons as a consequence of the Coulson-Rushbrooke theorem<sup>8</sup>, but it is also valid to a very good approximation for semiempirical all-valence electron calculations on saturated and unsaturated hydrocarbons, as may be seen from the results in the next section. It should be pointed out, that the off-diagonal elements of  $I^{RS}$  are in general non-zero, i. e. the inductive perturbation has not only the effect of shifting the orbital energies  $\epsilon_{I}^R$ , but due to the off-diagonal elements it also causes a mixing of the FO's  $\Phi_I^R$ . Furthermore, this orbital mixing leads to a charge redistribution which gives rise to the electron interaction term in Eq. (2). In general, the off-diagonal elements of the perturbation matrix will be small, so that the orbital mixing and the electron interaction will be only higher order effects.

If the wave function of the composite system is written according to Eq. (5) as antisymmetrized product of the FO's  $\Phi_I^R$  of all fragments R, MO's are obtained which are delocalized over the whole system and charge transfer from one fragment to another becomes possible. This may be described as a typically mesomeric effect. From Eq. (7) it is seen, that the mixing of the FO's from different fragments is due to contributions from resonance integrals  $\beta_{\sigma\rho}$  corresponding to bonds between atom  $\rho$  of fragment R and atom  $\sigma$  of fragment S, as well as to electron-electron interaction terms due to non-zero off-diagonal elements  $(P^{R(RS)})_{KL}$  of the one-electron density matrix. According to Eq. (6) the elements  $(F^U_{(R)})_{IJ}$  of the Fock matrix which correspond to fragment R differ from the corresponding Fock matrix elements  $(F^R)_{IJ}$  of the inductively disturbed fragment R only by electron interaction terms due to the charge redistribution.

## RESULTS AND DISCUSSION

In Table I results are collected for acrolein<sup>4</sup> as a typical example of an application of the FIM method within the framework of the PPP type  $\pi$  electron approximation<sup>9</sup>. Due to the uniform charge distribution the CC fragment does not exert a  $\pi$  inductive effect upon the CO fragment, whereas the  $\pi_{CC}$  orbitals are stabilized by 0.5 eV due to the presence of the polar  $\pi_{CO}$  group. Since the off-diagonal element of the inductive perturbation matrix

$$I^{RS} = \begin{pmatrix} -0.47 & -0.08 \\ & -0.47 \end{pmatrix}$$

is nearly one order of magnitude smaller than the diagonal element, and since

TABLE I

*Acrolein, FO Energies  $\varepsilon_I^R$ , Inductive Perturbations  $I_{II}^{RS}$ , Orbital Energies  $\varepsilon_i$ ,  $\pi$  Electron Energies  $E_\pi$  (in eV) and FO Populations  $P_{II}$  from PPP Type FIM Calculations*

| <i>I</i>                            | Isol. fragments<br>$\varepsilon_I^R$ | Inductive perturbation<br>$I_{II}^{RS}$ |       | FIM results<br>$P_{II}$ |
|-------------------------------------|--------------------------------------|---|-------|-------------------------|
| $\pi_{CC}^*$                        | 0.97                                 | —                                       | —0.47 | 0.01                    |
| $\pi_{CC}$                          | — 9.59                               | —                                       | —0.47 | 1.89                    |
| $\pi_{CO}^*$                        | — 0.93                               | 0.0                                     | —     | 0.11                    |
| $\pi_{CO}$                          | —13.49                               | 0.0                                     | —     | 1.99                    |
| $\varepsilon_2 - \varepsilon_1$     | 3.90                                 | 3.43                                    |       | 3.08                    |
| $(\varepsilon_1 + \varepsilon_2)/2$ | —11.54                               | —11.78                                  |       | —11.83                  |
| $E_\pi$                             | —53.13                               | —54.07                                  |       | —54.82                  |

the FO energies  $\varepsilon_\pi = -10.06$  eV and  $\varepsilon_{\pi^*} = 0.50$  eV differ appreciably, the orbital mixing and the charge redistribution due to the off-diagonal inductive perturbation is negligible. The mesomeric effect mixes mainly the bonding FO  $\pi_{CC}$  with the antibonding FO  $\pi_{CO}^*$ , as may be seen from the FO populations  $P_{II}$ . From Table 1 it is also seen that mean value  $(\varepsilon_1 + \varepsilon_2)/2$  of the  $\pi$  orbital energies is decreased and the difference  $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$  is reduced with respect to the values of the isolated fragments both by  $\pi$  inductive and mesomeric interactions. This latter effect is in agreement with PE spectroscopic results but at variance with expectations based on a simple LCBO model<sup>10</sup>.

Similar results for methyl fluoride as an example of a FIM calculation on a  $\sigma$  system<sup>5</sup> within the CNDO/2 approximation<sup>11</sup> are shown in Table II. The

TABLE II

*Methyl Fluoride, FO Energies  $\varepsilon_I^R$ , Inductive Perturbations  $I_{II}^{RS}$  (in eV), Total Energies (in a. u.) and FO Populations  $P_{II}$  from CNDO/2 Type FIM Calculations*

| <i>I</i>          | Isol. fragm.<br>$\varepsilon_I^R$ | Inductive perturbations<br>$I_{II}^{RS}$ |       |     | FIM results<br>$P_{II}$ |
|-------------------|-----------------------------------|--|-------|-----|-------------------------|
| $\pi_{CH_3}^*$    | 8.80                              | —  | —0.11 | 0.0 | 0.019                   |
| $\sigma_{CH_3}^*$ | 8.54                              | —  | —0.11 | 0.0 | 0.001                   |
| $\pi_{CH_3}$      | —19.78                            | —  | —0.11 | 0.0 | 2.000                   |
| $\sigma_{CH_3}$   | —30.88                            | —  | —0.11 | 0.0 | 1.993                   |
| $\sigma_{CF}^*$   | 8.60                              | 0.16                                     | —     | 0.0 | 0.009                   |
| $\sigma_{CF}$     | —31.65                            | 0.16                                     | —     | 0.0 | 1.999                   |
| $\pi_F$           | —23.92                            | 0.14                                     | 3.32  | —   | 1.981                   |
| $\pi_F$           | —39.84                            | 0.14                                     | 3.32  | —   | 2.070                   |
| <i>E</i>          | —37.315                           | —37.054                                  |       |     | —37.092                 |

inductive perturbations due to the unpolar  $\text{CH}_3$  group are small, whereas the  $\text{CF}$   $\sigma$  bond destabilizes mainly the lone-pairs as is to be expected from the non-uniform charge distribution within this bond, which leads to an increased electron density on the F atom. The mesomeric stabilization, which amounts to 100 kJ/mol and is thus much smaller than the destabilization due to inductive perturbations, is mainly due to an interaction of the F lone pairs with the antibonding  $\pi_{\text{CH}_3}^*$  FO's and of the  $\sigma_{\text{CH}_3}$  FO with the antibonding  $\sigma_{\text{CF}}^*$  FO, as may be seen from the one-electron density matrix

$$P = \begin{pmatrix} \sigma_{\text{CH}_3} & \pi_{\text{CH}_3} & \sigma_{\text{CH}_3}^* & \pi_{\text{CH}_3}^* & \sigma_{\text{CF}} & \sigma_{\text{CF}}^* & n_{\text{F}} & n_{\text{F}}' \\ \left( \begin{array}{cccccccc} 1.99 & 0.0 & -0.02 & 0.0 & 0.0 & -0.11 & 0.0 & 0.0 \\ & 2.00 & 0.0 & 0.02 & 0.0 & 0.0 & 0.0 & 0.0 \\ & & 0.0 & 0.0 & 0.03 & 0.0 & 0.03 & 0.0 \\ & & & 0.02 & 0.0 & 0.0 & 0.0 & 0.19 \\ & & & & 2.00 & 0.02 & 0.0 & 0.0 \\ & & & & & 0.01 & 0.0 & 0.0 \\ & & & & & & 2.00 & 0.0 \\ & & & & & & & 1.98 \end{array} \right) \end{pmatrix}$$

Neglecting the deviations of the matrix elements  $P_{II}$  from 2.00 and 0.0 respectively is equivalent to neglecting all mesomeric effects and yields the simplest model which describes the molecule just in terms of doubly occupied FO's<sup>5</sup>. In principle, the inductive perturbations depend on the distance and orientation of the fragments with respect to each other. In ethane, this effect is negligible, as may be seen from the data for the rotational barrier collected in Table III.

TABLE III

Ethane, Total Energy  $E$  (in a. u.) and Rotational Barrier (in kJ/mol) from CNDO/2 Type FIM Calculations

|                  | $E_{\text{stagg}}$ | $E_{\text{ecl}}$ | $\Delta E$ |
|------------------|--------------------|------------------|------------|
| isol. fragments  | -18.7833           | -18.7829         | 1.0        |
| induct. perturb. | -18.7558           | -18.7554         | 1.0        |
| FIM results      | -18.8064           | -18.8039         | 6.6        |

In fact, the inductive perturbations do not contribute at all to the barrier which is mainly due to mesomeric effects which stem from interactions between the  $\pi_{\text{CH}_3}$  FO's of one  $\text{CH}_3$  group with the antibonding  $\pi_{\text{CH}_3}^*$  FO's of the other  $\text{CH}_3$  group.

Finally the data for propene and acetaldehyde in Table IV and 5 illustrate the effect of replacing the unpolar vinyl group by the carbonyl group. The inductive perturbations  $I^{\text{RS}}$  due to the methyl group and the  $\text{CC}$   $\sigma$  bond are very much the same in both molecules. The vinyl group slightly destabilizes the methyl group and the  $\text{CC}$   $\sigma$  bond through the  $\sigma$  framework, whereas the  $\pi$  system with uniform charge distribution does not give rise to any inductive effect. The carbonyl group on the other hand stabilizes the methyl group and the  $\text{CC}$   $\sigma$  bond by fairly large inductive perturbations due to the  $\sigma$  as well as the  $\pi$  system. The mesomeric stabilization being mainly due to the interaction between the  $\pi_{\text{CH}_3}$  and the  $\pi_{\text{CC}}^*$  or  $\pi_{\text{CO}}^*$  FO's and between bonding and antibonding methyl and vinyl or carbonyl  $\sigma$  FO's amounts to approximately 230 kJ/mol for both molecules, but due to the larger mutual destabilization

TABLE IV

Propene, FO Energies  $\varepsilon_I^R$ , Inductive Perturbations  $I_{II}^{RS}$  (in eV), Total Energies  $E$  (in a. u.) and FO Populations  $P_{II}$  from CNDO/2 Type FIM Calculations

|                 | Isol. fragm.<br>$\varepsilon_I^R$ |      | Inductive perturbation<br>$I_{II}^{RS}$ |      | FIM results<br>$P_{II}$ |         |
|-----------------|-----------------------------------|------|---|------|-------------------------|---------|
| $\pi_{CH_3}$    | -19.78                            | —    | -0.11                                   | 0.08 | 0.0                     | 1.99    |
| $\pi_{CH_3}$    | -19.78                            | —    | -0.11                                   | 0.05 | 0.0                     | 1.97    |
| $\sigma_{CH_3}$ | -30.88                            | —    | -0.11                                   | 0.08 | 0.0                     | 2.00    |
| $\sigma_{CC}$   | -26.99                            | 0.14 | —                                       | 0.14 | 0.0                     | 1.98    |
| $\varphi_V''$   | -17.38                            | 0.05 | 0.08                                    | —    | 0.0                     | 2.00    |
| $\varphi_V''$   | -21.03                            | 0.05 | 0.08                                    | —    | 0.0                     | 2.00    |
| $\varphi_V'$    | -26.31                            | 0.05 | 0.08                                    | —    | 0.0                     | 1.99    |
| $\varphi_V$     | -37.20                            | 0.05 | 0.08                                    | —    | 0.0                     | 1.99    |
| $\pi_{CC}$      | -16.27                            | 0.08 |   |      |                         | 1.98    |
| $E$             | -25.724                           |      | -25.683                                 |      |                         | -25.771 |

TABLE V

Acetaldehyde, FO Energies  $\varepsilon_I^R$ , Inductive Perturbations  $I_{II}^{RS}$  (in eV), Total Energies  $E$  (in a. u.) and FO Populations  $P_{II}$  from CNDO/2 Type FIM Calculations

|                 | Isol. fragm.<br>$\varepsilon_I^R$ |      | Inductive perturbations<br>$I_{II}^{RS}$ |       |       | FIM results<br>$P_{II}$ |
|-----------------|-----------------------------------|------|--|-------|-------|-------------------------|
| $\pi_{CH_3}$    | -19.78                            | —    | -0.11                                    | -0.27 | -0.54 | 1.94                    |
| $\pi_{CH_3}$    | -19.78                            | —    | -0.11                                    | -0.22 | -0.49 | 1.98                    |
| $\sigma_{CH_3}$ | -30.88                            | —    | -0.11                                    | -0.24 | -0.52 | 2.00                    |
| $\sigma_{CC}$   | -26.99                            | 0.14 | —  | -0.44 | -0.90 | 1.99                    |
| $n'_O$          | -17.49                            | 0.05 | 0.11                                     | —     | 1.71  | 1.99                    |
| $n_O$           | -21.09                            | 0.05 | 0.11                                     | —     | 1.50  | 1.99                    |
| $\sigma_{CHO}$  | -26.56                            | 0.08 | 0.11                                     | —     | -0.11 | 2.00                    |
| $\sigma_{CHO}$  | -41.14                            | 0.08 | 0.11                                     | —     | 1.50  | 2.00                    |
| $\pi_{CO}$      | -16.65                            | 0.05 | 0.11                                     | 0.68  | —     | 1.99                    |
| $E$             | -35.515                           |      | -35.441                                  |       |       | -35.528                 |

of the  $\sigma$  and  $\pi$  systems of the carbonyl group the sum of the inductive and mesomeric interactions is only 35 kJ/mol for acetaldehyde, but 130 kJ/mol for propene.

## CONCLUSION

The results discussed in the present paper show that the inductive and mesomeric effects defined on the basis of the FIM approach may be very

useful in discussing the electronic structure of organic molecules. Forthcoming papers<sup>12</sup> will be concerned with the discussion of rotational barriers based on these concepts, and with the interpretation of temperature-dependent PE spectra of methyl vinyl ether and related molecules<sup>13</sup> on the basis of interactions of fragment orbitals.

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## SAŽETAK

**Metoda molekularnih fragmenata III. Induktivni i mezomerni efekti**

M. Klessinger

U okviru nedavno razvijene metode molekularnih fragmenata izvedena je interakcija fragmentnih orbitala u dva koraka: Induktivne perturbacije računane su pomoću poopćenog produkta tretirajući svaki fragment u polju svih ostalih fragmenata. Zatim su mezomerne interakcije u sastavljenom sistemu dobivene iz SCF računa zasnovanih na ovim fragmentnim orbitalama. Primjene na  $\pi$ -sisteme na temelju PPP aproksimacije kao i primjene bazirane na CNDO/2 pristupu pokazuju da je ova definicija induktivnih i mezomernih efekata potpuno prirodna i korisna u razmatranju elektronske strukture organskih molekula.