

# ORGANIC QUANTUM CHEMISTRY PROBLEMS

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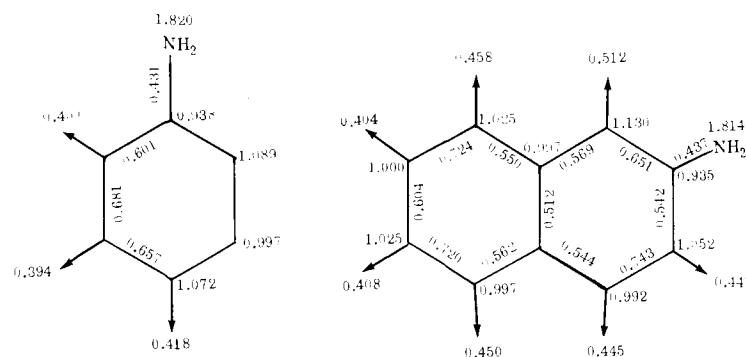
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## INTRODUCTION

This collection of examples of the application of quantum-chemical methods in the solution of various chemical problems (mainly in organic chemistry) is based on an arrangement of the materials used by the first author in his lectures on organic quantum chemistry and molecular constitution, delivered since 1959 at the Science Department of Charles University, as well as in courses of quantum chemistry and, finally, in his lectures on the fundamentals of quantum chemistry held in the years 1965–1967 at the universities of Würzburg, Groningen, and Giessen, and at the Technical University of Munich.

This collection is regarded as a supplement to existing textbooks on organic chemistry. Whereas the situation is satisfactory as regards the number and the standard of textbooks and monographs in this field are concerned, this cannot be said of the collections of examples. Although in some books<sup>1-4</sup> a certain number of examples are presented, we believe, in view of the great importance of quantum-chemical calculations, that a separate publication of examples would be useful. A similar subject has been dealt with in the recently published book by A. and O. Julg<sup>5</sup> and in the first part of a book to be published by Heilbronner and Bock.<sup>6</sup>

In his work with this collection of examples, the student will undoubtedly utilize some of the standard textbooks, but nevertheless, we have summarized quantum-chemical data in Part III, and presented some frequently employed quantum-chemical relationships in Part IV. Part III contains only the formulation of the problems, while Part IV contains the procedures of the calculation and gives the results. Part V is devoted to the solutions (as well as the formulas in Part IV) and is regarded only as aids facilitating



## IV. Appendix

### 1. FORMULAS, SOME FUNDAMENTAL RELATIONS, AND DEFINITIONS

#### 1. A. HMO Characteristics

Total  $\pi$ -electron energy:

$$W = \sum_{i=1}^m n_i E_i = \sum_{i=1}^m n_i (\alpha + k_i \beta) \quad (1)$$

Here  $m$  is the number of occupied molecular orbitals,  $n$  the number of electrons in the respective molecular orbital, ( $n = 1$  or  $2$ ), and  $E$  the orbital energy.

Delocalization energy (resonance energy):

$$DE = W - m W_{Et} = W - m (2\alpha + 2\beta) \quad (2)$$

where  $m$  is the number of double bonds, and  $W_{Et}$ , the  $\pi$ -electron energy of ethylene.

Specific delocalization energy:

$$DE_n = \frac{DE}{n} \quad (3)$$

where  $n$  is the number of atoms.

$$DE_m = \frac{DE}{m} \quad (4)$$

where  $m$  is the number of C-C  $\sigma$ -bonds.

N → V<sub>1</sub> excitation energy:

$$E(N \rightarrow V_1) = E_n - E_{n+1} = \alpha + k_n \beta - (\alpha + k_{n+1} \beta) \\ = (k_n - k_{n+1}) \beta$$

$$[\text{or } E_1 - E_{-1} = (k_1 - k_{-1}) \beta] \quad (5)$$

π-electron densities:

$$q_\mu = \sum_{i=1}^m n_i c_{i\mu}^2 \quad (6)$$

where m is the number of occupied molecular orbitals.

π-charges

$$f_\mu = n_\mu - q_\mu \quad (7)$$

where  $n_\mu$  is the number of the electrons which the  $\mu$ -th atom contributes to a conjugation.

Bond order:

$$p_{\mu\nu} = \sum_{i=1}^m n_i c_{i\mu} c_{i\nu} \quad (8)$$

Free valence:

$$F_\mu = N_{\max} - \sum_{\text{neighboring } \nu} p_{\mu\nu} \quad (9)$$

For the  $sp^2$  carbon atom  $N_{\max} = \sqrt{3}$ .

Atom localization energy (Wheland):

$$A_\mu = W - \sum_T W_T \quad (10)$$

where  $W_T$  is the  $\pi$ -electron energy of torso.

Superdelocalizabilities for electrophilic substitutions (Fukui et al.), accurate (S), approximate (S'):

$$S_{\mu,e} = 2 \sum_{i=1}^m \frac{c_{i\mu}^2}{k_i}; \quad S'_{\mu,e} = 2 \frac{c_{m\mu}^2}{k_m} \quad (11)$$

where m is the index of the highest occupied molecular orbital (HOMO).

For nucleophilic substitution

$$S_{\mu,n} = -2 \sum_{l=m+1}^n \frac{c_{l\mu}^2}{k_l}; \quad S'_{\mu,n} = -2 \frac{c_{(m+1)\mu}^2}{k_{m+1}} \quad (12)$$

where (m + 1) is the index of the lowest free molecular orbital (LFMO).

For radical substitution

$$S_{\mu,r} = \frac{1}{2} (S_{\mu,e} + S_{\mu,n}); \quad S'_{\mu,r} = \frac{1}{2} (S'_{\mu,e} + S'_{\mu,n}) \quad (13)$$

Polarizabilities (Coulson and Longuet-Higgins):

atom-atom

$$\pi_{\mu\nu} = 4 \sum_{j=1}^m \sum_{k=m+1}^n \frac{c_{j\mu} c_{j\nu} c_{k\mu} c_{k\nu}}{k_j - k_k} \quad (14)$$

bond-atom\*

$$\pi_{\mu\nu,\rho} = 2 \sum_{j=1}^m \sum_{k=m+1}^n \frac{c_{j\rho} c_{k\rho} (c_{j\mu} c_{k\nu} + c_{j\nu} c_{k\mu})}{k_j - k_k} \quad (15)$$

$$\pi_{\mu\nu,\rho} = \frac{1}{2} \pi_{\rho,\mu\nu}$$

bond-bond

$$\pi_{\mu\nu,\rho\sigma} = 2 \sum_{j=1}^m \sum_{k=m+1}^n \frac{(c_{j\rho} c_{k\sigma} + c_{j\sigma} c_{k\rho})(c_{j\mu} c_{k\nu} + c_{j\nu} c_{k\mu})}{k_j - k_k}$$

\*For alternant hydrocarbons the atom-bond and bond-atom polarizabilities are zero.

### 1.B. Relations between E, p, q, $\alpha$ , and $\beta$ and Some Checks of the HMO Calculations

MO's as a linear combination of atomic orbitals:

$$\varphi_i = \sum_{\mu=1}^n c_{i\mu} \lambda_{\mu} \quad (17)$$

From the Schrödinger equation follows directly (after multiplying by  $\varphi_i$  and integrating) for the orbital energy:

$$E_i = \frac{\int \varphi_i H \varphi_i d\tau}{\int \varphi_i^2 d\tau} \quad (18)$$

Using Equations (17) and (18) and applying variational method,

$$E_i = \sum_{\mu} c_{i\mu}^2 \alpha_{\mu} + 2 \sum_{\mu < \nu} c_{i\mu} c_{i\nu} \beta_{\mu\nu} \quad (19)$$

If the summation is carried out over the occupied MO's, the following equation is obtained:

$$W = \sum_{i=1}^m n_i E_i = \sum_{\mu=1}^n q_{\mu} \alpha_{\mu} + 2 \sum_{\mu < \nu} p_{\mu\nu} \beta_{\mu\nu} \quad (20)$$

Changes in  $\pi$ -electron densities and bond orders caused by changing the values of  $\alpha$  and  $\beta$ :

$$\Delta q_{\mu} = \sum_{\nu} \pi_{\mu\nu} \Delta \alpha_{\nu} \quad (21)$$

$$\Delta q_{\mu} = \sum_{\rho\sigma} \pi_{\mu,\rho\sigma} \Delta \beta_{\rho\sigma} \quad (22)$$

$$\Delta p_{\mu\nu} = \sum_{\rho\sigma} \pi_{\mu\nu,\rho\sigma} \Delta \beta_{\rho\sigma} \quad (23)$$

$$\Delta p_{\mu\nu} = \sum_{\rho} \pi_{\mu\nu,\rho} \Delta \alpha_{\rho} \quad (24)$$

Check:

$$\sum_{\nu} \pi_{\mu\nu} = 0 \quad (25)$$

$$\sum_{\mu\nu} \pi_{\mu\nu,\rho} = 0 \quad (26)$$

$$\sum_{\mu\nu} \pi_{\mu\nu,\rho\sigma} = 0 \quad (27)$$

$$\sum_{\mu=1}^n q_{\mu} = l \quad (\text{total number of } \pi\text{-electrons}) \quad (28)$$

$$\sum_{\mu=1}^n F_{\mu} = n \sqrt{3} - 2 \sum_{i=1}^m k_i \quad (29)$$

$$\sum_{\mu=1}^n S_{\mu,e} = 2 \sum_{\text{occupied}} \frac{1}{k_i} \quad (30)$$

$$\sum_{\mu=1}^n S_{\mu,n} = -2 \sum_{\text{unoccupied}} \frac{1}{k_i} \quad (31)$$

$$\sum_{\mu=1}^n S'_{\mu,e} = \frac{2}{k_m} \quad (32)$$

$$\sum_{\mu=1}^n S'_{\mu,n} = -\frac{2}{k_{m+1}} \quad (33)$$

$$\sum_{i=1}^n k_i = \sum_{\mu=1}^n a_{\mu\mu} \quad (\text{matrix trace}) \quad (34)$$

$a_{\mu\mu}$  are diagonal matrix elements

$$\sum_{i=1}^n k_i^2 = \sum_{\mu} \sum_{\nu} a_{\mu\nu}^2 \quad (35)$$

$a_{\mu\nu}$  are nondiagonal and diagonal matrix ( $\mu = \nu$ ) elements; for hydrocarbons the sum of the squares of the matrix elements is equal to double the number of C-C bonds.