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An Improved Semi-empirical Hückel-Method for the Study of Physico-Chemical Properties of Aromatic Systems

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This work describes an improved semi-empirical Hückel-method for the study of physico-chemical properties of aromatic systems. Coherent heteroatomic coulomb- and exchange parameters are calculated according to McWeeny's theory [30]. The variation of the exchange integrals β_{ij} with bond length is introduced in the calculations by means of an iterative "self-consistent β"-procedure. A new iteration function for the aromatic $C=C$ link and a general method to obtain similar relations for several heteroatomic bonds are described. A simple computer program calculating various molecular properties is presented.

Eine Hückelmethode für aromatische Systeme mit Heteroatomen wird beschrieben, wobei die Heteroparameter nach McWeeny [30] berechnet werden. Eine neue selbstkonsistente β-Methode wird angegeben. Ein entsprechendes Programm zur Berechnung verschiedener Molekülgrößen ist bei den Autoren erhältlich.

Ce travail décrit une méthode LCAO semi-empirique améliorée dans l'approximation de Hückel. Les paramètres hétéroatomiques (intégrales coulombiennes et d'échange) sont déterminés de façon cohérente par la théorie de McWeeny [30]. La variation des intégrales d'échange β_{ij} avec la longueur des liaisons est introduite dans les calculs à l'aide d'une méthode itérative. Une nouvelle fonction d'itération est décrite pour le lien $C=C$ aromatique et une méthode générale d'obtention de fonctions similaires pour diverses liaisons hétéroatomiques est donnée. Un programme pour calculatrice électronique permettant l'obtention de diverses propriétés moléculaires est décrit.

I. Introduction

Since the earliest quantum-mechanical calculations, it rapidly became apparent that aromatic systems constituted a very interesting field for the application of theoretical considerations. The possibility of treating the π-electrons independently of a σ-electron framework considerably simplified the computational work involved.

The best known and most widely used amongst the proposed quantum-mechanical treatments is the LCAO-method in various approximations. The simplest of these, the Hückel-theory [23, 39], has been applied with success to the interpretation and understanding of various physico-chemical properties of conju-

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gated molecules [9, 42, 48]. With the recent development of large electronic computers, this method has provided a most powerful tool to the organic chemist for discussing properties and reactivities of large unsaturated molecules commonly encountered in his field. The Hückel-method however sufers some limitations when applied to heterocyclic or substituted aromatic systems, due to the use of empirical coulomb- and exchange parameters characterising the heteroatom introduced.

The aim of this paper is to present an improvement on the original Hückel-method and to describe a computer program for the calculation of various properties of aromatic systems.

II. Parameters

The heteroatom introduced in a conjugated molecule may be characterised by the number of π-electrons it contributes to the π-system of the molecule and by the electronegativity of its $2p_z(\pi)$-orbital. Theoretically, the problem consists in determining the values of the coulomb integral α_{X} characterising the heteroatom X and of the resonance integral β_{CX} representing the C–X bond. According to Pauling and Wheland [39], this is done very conveniently by putting:

$$\alpha_{\mathrm{X}} = \alpha_{\mathrm{C}} + h_{\mathrm{X}} \cdot \beta_{\mathrm{CC'}} \tag{1a}$$

and

$$\beta_{\mathrm{CX}} = k_{\mathrm{CX}} \cdot \beta_{\mathrm{CC'}}\,, \tag{1b}$$

where α_{C} and $\beta_{\mathrm{CC'}}$ are, respectivily, the carbon coulomb integral and the carbon-carbon exchange integral between nearest neighbours in the benzene molecule; h_{X} and k_{CX} are called coulomb- and exchange parameters.

Diagonal elements H_{ii} of the hamiltonian matrix and Hückel-coulomb parameters h_i are calculated, according to McWeeny [30], by the formulas:

$$H_{ii} = -\,W_i^p + \tfrac{1}{2} \cdot Z_{ii} \cdot J_{ii} \tag{2}$$

$$h_i = \frac{H_{ii} - H_{\mathrm{CC}}}{\beta_{\mathrm{CC'}} - \frac{2}{3} \cdot J_{\mathrm{CC'}}}\,, \tag{3}$$

where W_i^p is the ionisation potential of the $2p_z$ orbital of atom i when only one electron is contributed to the π-electron system, or of its positive ion (with complete σ-configuration) if atom i contributs two electrons to the π-system*, in the appropriate valence-state;

Z_{ii} the number of electrons contributed by atom i to the π-electron system;

J_{ii} the monocentric coulomb repulsion integral [41];

$\beta_{\mathrm{CC'}}$ Pariser and Parr's empirical value for the benzene exchange-integral ($\beta_{\mathrm{CC'}} = -\,2.39$ eV) [38];

$J_{\mathrm{CC'}}$ the two-center coulomb repulsion integral for nearest neighbours in the benzene molecule ($J_{\mathrm{CC'}} = +\,8.872$ eV) [18];

H_{CC} the diagonal element of the hamiltonian matrix for the benzenic carbon atom, calculated according to formula (2).

In our calculations, the J_{ii}'s were set equal to the difference of ionisation potential and electron-affinity (E_i^p) of the π-orbital of atom i (or its positive ion) [8]; both

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* For oxygen and nitrogen atoms in "methoxy"- and "amino"-groups respectively, if one assumes a trigonal hybridization, the adequate atomic configurations of the ions are $\mathrm{O}^{\oplus}$ ($tr^2\, tr^1\, tr^1\, \pi^1$) and $\mathrm{N}^{\oplus}$($tr^1\, tr^1\, tr^1\, \pi^1$).

values were taken from Hinze and Jaffe's tables [21, 22]. Following Streitwieser's suggestion [49], an "inductive" coulomb parameter was taken into account for the carbon atom adjacent to the heteroatom X:

$$h_{C(X)} = 0.1 \cdot h_X . \tag{4}$$

Hückel-exchange parameters were calculated using a modified Wolfsberg-Helmholz approximation [34, 52]:

$$k_{ij} = 0.5 \cdot \frac{H_{ii} + H_{jj}}{H_{cc}} \cdot \frac{S_{ij}/(1+S_{ij})}{S_{cc'}/(1+S_{cc'})} , \tag{5}$$

where S_{ij} is the overlap integral for the π-orbitals on atoms i and j, $S_{CC'}$ being the carbon-carbon $2p\pi$ overlap-integral for nearest neighbours in the benzene molecule, both being calculated according to Mulliken's tables [35]. The difficulty in the calculation now appears when it is realised that the overlap integral S_{ij} is a function of the bond length R_{ij} and that molecular geometry is often unknown for the compounds studied. However, appropriate values of k_{ij} may be obtained by assuming the following bond lengths [43]:

$R_{C=C}$: 1.40 Å ;	R_{C-O}: 1.34 Å ;	R_{C-N}: 1.39 Å [24];*
$R_{C\equiv C}$: 1.20 Å ;	$R_{C=O}$: 1.23 Å [8] ;	$R_{C=N}$: 1.35 Å [19];
		$R_{C\equiv N}$: 1.15 Å .

Tab. 1 summarises the HMO-parameters thus obtained; the nitro-group, whose parameters could not be calculated by the method outlined above (owing to strong σ-polarisation), and halogens, where d-orbital conjugation is to be included, are not treated in this work.

Table 1. *Non-empirical parameters for* HMO-*calculations*

Element	Coulomb Parameter	Resonance Parameter
Carbon	$h_C = 0$	$k_{C=C} = 1$ $k_{C\equiv C} = 1.28$
Nitrogen	$h_{\dot{N}} = 0.44$ $h_{\ddot{N}} = 1.19$	$k_{C=N} = 1.06$ $k_{C\equiv N} = 1.42$ $k_{C-\ddot{N}} = 1.29$
Oxygen	$h_{\dot{O}} = 0.84$ $h_{\ddot{O}} = 1.81$	$k_{C=O} = 1.23$ $k_{C-\ddot{O}} = 1.36$

III. Iterative Procedure

In order to introduce the variation of the exchange integral β_{ij} with bond length in the calculations, several authors have used an iterative procedure based on a function of the type [2, 5, 18, 25, 27, 36, 37]:

$$\beta_{ij}(N) = f(p_{ij}(N-1)) , \tag{6}$$

where $\beta_{ij}(N)$ is the non-diagonal ij-element of the secular determinant at iteration N, and $p_{ij}(N-1)$ the bond order between atoms i and j obtained after iteration $N-1$.

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* Evaluated in comparison with the r_{C-N} distance.

This relation which, in principle, should be different for each kind of bond (e.g. C=C, C=O, C=N, etc. ...), can be constructed from the combination of two other, independent, relations:

$$\beta_{ij} = f_1(r_{ij}) \tag{7}$$

and

$$r_{ij} = f_2(p_{ij}) , \tag{8}$$

which describe, respectivily, the variation of exchange integral with bond length and the dependence of bond-length on bond-order. The calculations may then be made self-consistent by the iterative use of Eq. (6).

Unfortunately, this "self-consistent β"-procedure has been very rarely applied to the study of the electronic structure of heteroatomic systems, and in many cases the same iteration function was used for any kind of bond [12]. We here wish to report a new iteration function for the aromatic C=C link and a general method to obtain similar relations for several heteroatomic bonds.

A. The Dependence of the Exchange Integrals on Bond Lengths

Combination of Eqs. (1b) and (5) of the preceeding section enables us to account for the variation of the exchange integral β_{ij} with distance r_{ij}, by the intervention of the overlap integrals S_{ij}; the influence of the nature of the atoms forming the bond is represented by the quantities H_{ii} and H_{jj}, which depend on the ionisation potentials and electron-affinities of the π-orbitals of these atoms.

The relations $\beta_{ij} = f(r_{ij})$ so obtained, are straight lines within the limits of the bond lengths of chemical interest:

$$\beta_{ij} = \beta^0_{ij} + \theta_{ij} \cdot r_{ij} . \tag{9}$$

Fig. 1 shows these functions calculated for the acetylenic C≡C, the aromatic C=C and the carbonyl C=O bonds. Tab. 2 summarises the values of the slopes θ_{ij} and intercepts β^0_{ij} determined by the method of least squares for some bonds commonly encountered in the field of aromatic derivatives.

A similar function has been used recently [13] in the LCAO-theory describing the variation of the integrated intensity of the $\nu_{C\equiv N}$ vibration with molecular structure for a series of polycyclic aromatic nitriles.

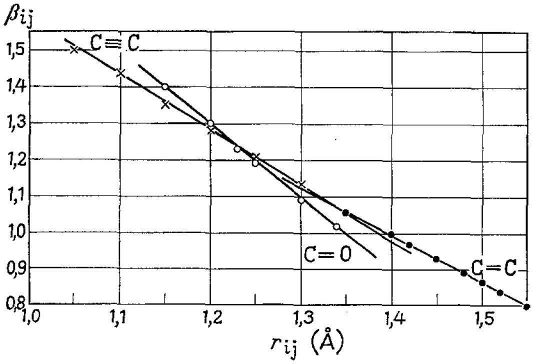

Fig. 1. The dependence of the exchange integrals on bond lengths

Table 2. *Characteristics of the straight lines describing the dependence of exchange integrals on bond lengths* (slope: θ_{ij}; intercept: β_{ij}^0)

Bond	β_{ij}^0	θ_{ij}	Limits of use (Å)
C=C	2.7898	−1.2797	1.30 – 1.55
C≡C	3.0860	−1.5029	1.10 – 1.35
C–N̈	4.1380	−2.0475	1.32 – 1.47
C=N	3.2133	−1.5952	1.32 – 1.47
C≡N	3.4531	−1.7741	1.10 – 1.35
C–Ö	4.3699	−2.2415	1.30 – 1.50
C=O	3.6819	−1.9904	1.20 – 1.34

B. The Dependence of Bond Length on Bond Order

Although various empirical relations have been put forward by several authors [2, 5, 10, 18, 25, 27, 37] in the case of the aromatic C=C bond, no systematic theory has been described to obtain similar semi-empirical relations for heteronuclear bonds.

a) Aromatic C=C *bond:*

Our aim being the study of aromatic compounds, the bond length/bond-order relationship has been calculated using the well-known Lennard-Jones theory [7, 26], with benzene as the reference molecule. This choice has the advantage of introducing only a small approximation by neglecting the anharmonic terms (order higher than two) in the development of the potential energy with respect to the bond length [see e.g. Eq. (10)]. Let us consider a benzene molecule with a bond length equal to r; if we ignore interactions between different bonds and changes in energy due to angular distortions, then the energy $E_{B(r)}$ of each of these bonds is given by:

$$E_{B(r)} = E_B^0 + \tfrac{1}{2}\cdot\delta\cdot(r - 1.397)^2\,, \tag{10}$$

where E_B^0 is the energy of a normal benzenic carbon-carbon bond with a length of 1.397 Å [47], and δ the force constant of such a bond. If we now consider a σ-bond of length r between sp^2-hybridised carbon atoms, then its energy $E_{s(r)}$ may be written as:

$$E_{s(r)} = E_s^0 + \tfrac{1}{2}\cdot\varepsilon\cdot(r - s)^2\,, \tag{11}$$

where s is the "natural" length of that bond, ε the force constant and E_s^0 the energy of the $C_{sp^2} - C_{sp^2}$ σ-bond of length s.

Thus, the π-energy of a partially double bond of length r is, to a first approximation:

$$E_{\pi(r)} = E_B^0 - E_s^0 + \tfrac{1}{2}\cdot\delta\cdot(r - 1.397)^2 - \tfrac{1}{2}\cdot\varepsilon\cdot(r - s)^2\,, \tag{12}$$

so that the total π-energy of our fictitious benzene molecule may be written as:

$$E_{\pi\,\text{total}} = 6\,(E_B^0 - E_s^0) + 3\cdot\delta\cdot(r - 1.397)^2 - 3\cdot\varepsilon\cdot(r - s)^2\,. \tag{13}$$

However, according to simple Hückel-LCAO theory,

$$E_{\pi\,\text{total}} = 6\,\alpha_C + 8\cdot\beta_{CC'}(r)\,, \tag{14}$$

and we easily obtain:

$$\beta_{CC'}(r) = \tfrac{3}{4}\,(E_B^0 - E_s^0 - \alpha_C) + \tfrac{3}{8}\cdot\delta\cdot(r - 1.397)^2 - \tfrac{3}{8}\cdot\varepsilon\cdot(r - s)^2\,. \tag{15}$$

The total potential energy of a benzene molecule of bond length r as compared to the same molecule but with bond lengths equal to single $C_{sp^2}-C_{sp^2}$ σ-bonds, may be written as:

$$F = V + E\,, \tag{16}$$

where E is the total energy of the π-electrons and V the energy of compression of the σ-bonds; according to Lennard-Jones:

$$V = \sum_{ij} \tfrac{1}{2}\cdot\varepsilon\cdot(r_{ij}-s)^2\,. \tag{17}$$

But in the equilibrium state of the molecule,

$$\frac{\partial F}{\partial r_{ij}} = \frac{\partial V}{\partial r_{ij}} + \frac{\partial E}{\partial \beta_{ij}}\cdot\frac{\partial \beta_{ij}}{\partial r_{ij}} = 0, \tag{18}$$

so that, introducing (15) and (17) into the above equation and remembering that $\frac{\partial E}{\partial \beta_{ij}} = 2\cdot p_{ij}$, we have:

$$\varepsilon\cdot(r_{ij}-s) + [\tfrac{3}{4}\cdot\delta\cdot(r_{ij}-1.397) - \tfrac{3}{4}\cdot\varepsilon\cdot(r_{ij}-s)]\cdot 2p_{ij} = 0\,. \tag{19}$$

Experimental values of ε, δ and s are: $\varepsilon = 5.6\cdot 10^{-5}$ dynes/cm [51]; $\delta = 7.6\cdot 10^{-5}$ dynes/cm [28] and $s = 1.517$ Å [1]; substituting these values in (19), the final relation between bond-order and bond-length is:

$$r_{ij} = \frac{8.495 + 3.183\cdot p_{ij}}{5.6 + 3.0\cdot p_{ij}}\,. \tag{20}$$

b) Hetero-atomic bonds:

The bond-length/bond-order relations for hetero-atomic "double" bonds are obtained by Coulson and Longuet-Higgins' theory [7]; the general equation may be written as:

$$r_{ij} = \frac{\varepsilon\cdot s + p_{ij}/p^0_{ij}\cdot(d\cdot\gamma - s\cdot\varepsilon)}{\varepsilon + p_{ij}/p^0_{ij}\cdot(\gamma-\varepsilon)}\,, \tag{21}$$

where s, d and ε, γ are the bond lengths and force constants of the pure single and double bonds respectivily, and p^0_{ij} the π-bond-order of the pure double bond ij; its value was obtained by solving the secular equations for a diatomic molecule of pure double bond length, using the appropriate coulomb and inductive parameters.

In the case of the $C—\ddot{O}$ (e.g. methoxy group) and $C—\ddot{N}$ (e.g. amino group)-bonds, the same values for the single and double bond lengths as for the corresponding $C=O$ and $C=N$ bonds were assumed. The force constants γ, however, and the values of p^0_{ij} are those calculated for the molecules

$$[{>}C—\ddot{O}]^{\oplus} \quad \text{and} \quad [{>}C—\ddot{N}{<}]^{\oplus}\,,$$

where maximum "delocalisation" of the π-lone pair of the heteroatom may be suspected, and treating them formally as a carbonyl- and iminogroup respectivily*.

Eq. (21) may also be used as the iteration function for a triple bond (e.g. $C\equiv N$, $C\equiv C$), but by assuming that, as a result of conjugation, the observed bond length and force constant will be intermediate between those of a pure double and a pure triple bond. In this case, p^0_{ij} is the "pure" bond order of the π-orbitals conjugating

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* sp^2-hybridisation of the oxygen and nitrogen atoms in these molecules is assumed.

with the rest of the aromatic part of the molecule, variations of bond order of the perpendicular π'-system being neglected.

The experimental parameters used in this work are give in Tab. 3, and Fig. 2 shows some typical curves calculated according to Eq. (21).

Table 3*. *Experimental values of single (s), double (d) and triple (t) bond lengths, corresponding force constants (ε, γ and η respectively) and reference mobile π-bond order (p^0_{ij}), for various kinds of bonds*

Bond *ij*	$\varepsilon \cdot 10^{-5}$ dynes/cm	$\gamma \cdot 10^{-5}$ dynes/cm	s(Å)	d(Å)	p^0_{ij}
C=N (aza-aromatic)	5.25 [51]	10.5 [51]	1.44 [8]	1.28 [8]	0.9861
C=O (carbonyl)	5.0 [51]	10.7 [51]	1.40 [8]	1.22 [8]	0.9574
Bond *ij*	$\gamma \cdot 10^{-5}$ dynes/cm	$\eta \cdot 10^{-5}$ dynes/cm	d(Å)	t(Å)	p^0_{ij}
C≡C (acethylenic)	9.560 [46]	15.799 [11]	1.309 [46]	1.205 [3]	1.000
C≡N (nitrile)	10.5 [51]	18.69 [33]	1.25 [8]	1.154 [33]	0.9902

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* Where necessary, a shortening of experimental bond lengths of 0.03 Å by *sp* or sp^2 hybridisation was taken into account [19, 40].

C. Construction of the Iteration Function

The final iteration functions for different kinds of bonds can now be constructed by substituting in Eq. (9) r_{ij} by the appropriate function describing the dependence of bondlength on bond order, e.g. Eqs. (20) or (21). The relations so obtained have the general form:

$$\beta_{ij}(N) = \frac{a + b \cdot [p_{ij}(N-1)]}{c + d \cdot [p_{ij}(N-1)]} \,. \tag{22}$$

The values of the coefficients *a*, *b*, *c* and *d* for the more commonly encountered bonds are given in Tab. 4.

Some iteration functions so obtained are shown in Fig. 3. Obviously, the use of a single iteration function for all the bonds present in a heteroatomic molecule is a rather crude approximation. Recently, Koutecky [25] has shown that it is essential to take into account the molecular geometry by the introduction of a $\beta = f(p)$ function in order to understand the physico-chemical properties of aromatic or chain hydrocarbons; it is therefore believed that the use of the proper

Table 4. *Iteration parameters for several kinds of bonds* [see Eq. (22)]

Bond	*a*	*b*	*c*	*d*
C=C (aromatic)	4.7518	4.2961	5.6	3.0
C≡C (acetylenic)	10.6949	9.4489	9.56	6.239
C−$\ddot{\text{N}}$ (amino)	6.2454	9.8470	5.25	5.2888
C=N (aza-aromatic)	4.8101	7.5956	5.25	5.324
C≡N (nitrile)	12.9725	13.433	10.5	8.271
C−$\ddot{\text{O}}$ (methoxy)	6.159	11.869	5.0	5.8856
C=O (carbonyl)	4.477	9.337	5.0	5.954

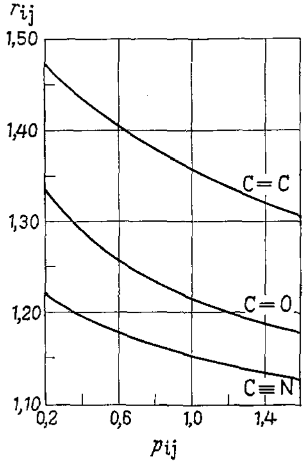

Fig. 2

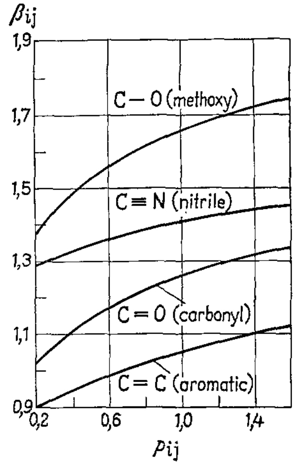

Fig. 3

Fig. 2. The dependence of bond length on bond order

Fig. 3. Calculated iteration functions for some kinds of bonds

iteration functions for substituted derivatives will give a better description of the structure and behaviour of these compounds.

The iteration function here obtained has been successfully used in the calculation of the proton chemical shifts in a series of polycyclic aromatic hydrocarbons [14] and various physico-chemical properties of their substituted derivatives: charge transfer spectra of nitriles, aldehydes and ethyl esters with TCNE [15], sensibility of aldehydes to solvent effects* in infra-red spectroscopy [16] and their half-wave reduction potential [50] in an anhydrous medium (DMF). Other work is in progress.

IV. Computer Program

A Fortran IV computer program, called LCAO-BETA, based on the iterative method described in the previous sections has been written and compiled for an IBM 7040 16 K computer**.

Computed quantities are: dipole moment, transition moment of selected UV-bands [44], π-electron polarisability of the molecule [4], integrated intensity of the stretching vibration of a localised vibrator being part of the π-electron-system [13], stretching force constants and coupling constants [7], bond lengths [see Eqs. (20) and (21)], ring-currents [32], spin densities for ESR-spectra [29] and finally the various theoretical polarizabilities: atom-atom, atom-bond and bond-bond [6]. As supplied, the program will handle molecular π-systems up to 55 orbitals, which is the maximum dimension of the secular equation that can be accomodated in the storage available.

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* The coulomb- and exchange-parameters proposed by Rasch [45] have been used in this work.

** Fortran listings and instructions for the computer program can be obtained from the authors.

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