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Charge Influence in Semi-Empirical Calculations of Heteroatomic Ionic and Neutral Molecules*

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Iterative extended Hückel calculations for all valence electrons and iterative PPP calculations in the variable electronegativity formalism for π-electrons were performed on benzene, pyridine, fluorobenzene, and the pyrylium ion. The charge distributions for all compounds were found more uniform and plausible with the iteration procedures than without. Polarization effects from the σ-electrons were found to be of importance for the π-electrons. The lone-pair picture of the highest occupied MO in pyridine is preserved in the iterative extended Hückel method, and two σ lone-pairs were obtained on the fluorine atom of fluorobenzene. The results indicate that this atom is not hybridized.

Benzol, Pyridin, Fluorbenzol und Pyriliumion wurden mit einer iterativen EH-Methode und einer iterativen PPP-VE-Methode berechnet. Es zeigte sich, daß Ladungsverteilungen bei Benutzung des Iterationsverfahrens besser beschrieben werden. Polarisationseffekte der σ-Elektronen auf die π-Elektronen stellen sich als wichtig heraus. Auch in der IEH-Methode bleibt das oberste besetzte MO des Pyridins ein einsames Elektronenpaar. Am Fluoratom im Fluorbenzol werden zwei einsame σ-Elektronenpaare erhalten. Die Resultate führen zu der Annahme, daß dieses Atom nicht hybridisiert ist.

Des calculs par les méthodes itératives de Hückel étendu pour tous les électrons de valence et de PPP avec électronégativité variable pour les électrons π ont été effectués pour le benzène, la pyridine, le fluorobenzène et l'ion pyrylium. Les distributions de charge pour tous ces composés sont plus uniformes et plus plausibles avec les procédés itératifs que sans. Les électrons σ ont un effet de polarisation important sur les électrons π. La plus haute orbitale occupée dans la pyridine reste identifiable comme la paire libre dans la méthode de Hückel étendue, et l'on obtient deux paires libres σ sur l'atome de fluor du fluorobenzène. Cet atome n'est pas hybridé.

1. Introduction

The extended Hückel method [1–3] has a tendency to exaggerate [4, 5] the gross charge distribution given by Mulliken's population analysis [6] when it is applied to heteroatomic systems. The ordinary Hückel [7] and PPP [8, 9] methods are not particularly suitable for ionic and mesoionic compounds, since population analysis for such compounds often give charge distributions very different from the starting valence state charges. The same deficiency exists for these methods when they are applied to non-ionic compounds with large redistributions of charges. Often the results can be improved in these cases by iteration procedures. In the ordinary Hückel method one has used the so called ω-technique [10, 11], where the Coulomb integrals are readjusted according to the calculated charges. In the PPP method one has the Variable Electronegativity (VESCF) approach [12, 13], where the atomic integrals are varied according to

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variations in effective charges. In the *Extended Hückel Method* (EHM) iterative procedures have been applied similar to ω-technique [14–18] and VESCF [19].

In order to get suitable semi-empirical methods for ionic molecules and molecules with large redistributions of charges we have studied the charge distributions for some molecules with the Extended Hückel Method and the PPP method. In both methods iteration procedures have been used to readjust the empirical parameters according to calculated charges. From here on the methods will be called the *Iterative Extended Hückel Method* (IEHM) and the *Iterative Pariser-Parr-Pople Method* (IPPP). The reason for the last name is to stress that the idea of VESCF could be used in other SCF methods, too.

The following molecules were studied and assumed planar: benzene (C_6H_6), pyridine (C_5H_5N), fluorbenzene (C_6H_5F), and the pyrylium ion ($[C_5H_5O]^+$). The geometries are given in Table 1.

Table 1. *Geometries of* C_6H_6, C_5H_5N, $[C_5H_5O]^+$, *and* C_6H_5F [a]

Atoms[b]	Bond distance (Å) and angle (°)[c]			
	C_6H_6	C_5H_5N	$[C_5H_5O]^+$	C_6H_5F
C_1–C_2	1.39	1.34	1.39	1.39
C_2–C_3	1.39	1.39	1.39	1.39
C_1–X_6	1.39	1.40	1.39	1.39
C_6–F_6				1.33
C–H	1.09	1.09	1.09	1.09
X_6–C_1–C_2	120	124.0	120	120
C_1–C_2–C_3	120	118.6	120	120
C_2–C_3–C_4	120	118.1	120	120
C_5–X_6–C_1	120	116.7	120	120
C_5–C_6–F_6				120

[a] Cf. Ref. [44].

[b] The heteroatoms N and O and the substituent F are placed in Position 6.

[c] Every angle between a hydrogen atom and the ring was assumed to be half the exterior angle.

2. Methods

General

We want to solve the molecular Schrödinger equation

$$H\Psi = E\Psi\,, \tag{1}$$

where in the MO-LCAO approximation Ψ is represented by an antisymmetrized product of orthonormal one-electron molecular spin-orbitals ψ_i, which are expressed as linear combinations of atomic orbitals χ_a:

$$\psi_i = \sum_{a=1}^{m} \chi_a c_{ai} \left\{ \begin{matrix} \alpha \\ \beta \end{matrix} \right. . \tag{2}$$

In this work we will consider only atomic valence orbitals χ_a in Eq. (2).

Assuming doubly occupied molecular spin-orbitals ψ_i we obtain from the variation principle the molecular Hartree-Fock equations [20, 21] for n electrons:

$$\boldsymbol{F}\boldsymbol{c}_i = E_i \boldsymbol{S}\boldsymbol{c}_i, \qquad i = 1, 2, \ldots, n, \tag{3}$$

where $\boldsymbol{F}$ is the Fock matrix, whose elements for a closed shell structure are given by

$$\begin{aligned} F_{ab} = \langle \chi_a | f_1 | \chi_b \rangle + \sum_{i=1}^{n/2} \Bigg\{ \sum_{c=1}^{m} \sum_{d=1}^{m} [2 \langle \chi_a(1) \chi_c(2) | 1/r_{12} | \chi_b(1) \chi_d(2) \rangle \\ - \langle \chi_b(1) \chi_c(2) | 1/r_{12} | \chi_d(1) \chi_a(2) \rangle] \, c_{ci}^{*} c_{di} \Bigg\}, \qquad a, b = 1, 2, \ldots, m, \end{aligned} \tag{4}$$

where f_1 is the operator of the one-electron part of the Hamiltonian H; $\boldsymbol{S}$ is the overlap matrix; and $\boldsymbol{c}_i$ is the column vector of the set $\{c_{ai}\}_{a=1}^{m}$.

The total electronic energy for a closed shell system is:

$$E_{\text{tot}} = \sum_{i=1}^{n/2} (E_i + \langle \psi_i | f_1 | \psi_i \rangle) . \tag{5}$$

In semi-empirical methods, one estimates $\boldsymbol{F}$ in different ways. In EHM the elements $\boldsymbol{F}_{ab}$ are directly given empirical values. In PPP one estimates the different integrals in Eq. (4).

The iterative procedures we have used are based on readjustments of $\boldsymbol{F}$ according to calculated charge distributions. Starting with Eq. (3) we calculate the matrix

$$\boldsymbol{R} = 2 \sum_{i=1}^{n/2} \boldsymbol{S}\boldsymbol{c}_i \boldsymbol{c}_i^{+} . \tag{6}$$

The diagonal elements of $\boldsymbol{R}$ are interpreted as the number of electrons in the atomic orbitals and are used to determine a new matrix

$$\boldsymbol{F}' = \boldsymbol{F} + \boldsymbol{G}', \tag{7}$$

where $\boldsymbol{G}'$ could be considered as a perturbation. In the nth step we will consider

$$\boldsymbol{F}^{(n-1)} = \boldsymbol{F} + \sum_{i=1}^{n-1} \boldsymbol{G}^{(i)}, \tag{8}$$

where $\sum_{i=1}^{n-1} \boldsymbol{G}^{(i)}$ is considered as a perturbation now.

The Iterative Extended Hückel Method

The Coulomb integrals $\alpha_a = F_{aa}$ were estimated by putting them equal to the negative of the ionization potentials I_a of an electron in the atomic orbital χ_a [22]:

$$\alpha_a = -I_a . \tag{9}$$

The resonance integrals $\beta_{ab} = F_{ab}$ were estimated from the Wolfsberg-Helmholz formula [23, 1]

$$\beta_{ab} = k S_{ab} (\alpha_a + \alpha_b)/2 . \tag{10}$$

Comparisons have been made with [24]

$$\beta_{ab} = -k' S_{ab} (\alpha_a \alpha_b)^{1/2} \tag{11}$$

and with [23, 25, 26]

$$\beta_{ab} = -k'' S_{ab} ; \tag{12}$$

S_{ab} are the overlap integrals and k, k', and k'' are positive constants. The effect of different values of these constants has been investigated.

Every I_a has been considered as a function of the valence gross charge q_a, which is obtained from Mulliken's population analysis [cf. Eq. (6)] [6]. The method is similar to that of Duke [18], but instead of fitting values of I_a to a parabola we used a straight line. Values of I_a were selected for the valence states of the neutral atom and its positive and negative ions. For hydrogen only the neutral and negative ionic valence states were used. The values of I_a were taken from the tables by Hinze and Jaffé [27] and used to determine slope k_a and intercept l_a in

$$I_a = k_a q_a + l_a . \tag{13}$$

If there were both paired and unpaired electrons in the p-orbitals, the ionization potential for a paired electron was used according to Hund's rules. In all cases I_a was chosen for the most stable valence state configuration. The straight lines fitted to the points were accurate enough for our purpose; the largest maximal deviation is 2.2 eV. Values of I_a, k_a, l_a, and maximal deviations Δ_a are given in Tables 2 and 3.

With formula (13) new values of α_a were calculated according to the calculated q_a. As found by others [15–18] the changes in q_a had to be damped to get convergence. Instead of q_a(out) given by Mulliken's population analysis, we used in the next iteration step

$$q_a(\text{in}) = q_a + \lambda [q_a(\text{out}) - q_a] , \tag{14}$$

Table 2. *Ionization potentials for the* IEHM *calculations*

Valence state[a]	No of valence electrons q	Ionization potential (eV)[b] I	Valence state[a]	No of valence electrons q	Ionization potential (eV)[b] I
$H(\underline{s}000)$	1	13.595	$C^+(s^2\underline{p}00)$	3	24.376
$H^-(\underline{s}^2 000)$	2	0.747	$C(s^2\underline{p}p0)$	4	10.931
$C^+(\underline{s}^2 p00)$	3	32.416	$C^-(s^2\underline{p}pp)$	5	0.763
$C(\underline{s}^2 pp0)$	4	19.423	$N^+(s^2\underline{p}p0)$	4	29.117
$C^-(\underline{s}^2 ppp)$	5	8.917	$N(s^2\underline{p}pp)$	5	13.941
$N^+(\underline{s}^2 pp0)$	4	40.345	$N^-(s^2\underline{p}^2 pp)$	6	0.842
$N(\underline{s}^2 ppp)$	5	25.583	$O^+(s^2\underline{p}pp)$	5	34.186
$N^-(\underline{s}^2 p^2 pp)$	6	14.052	$O(s^2\underline{p}^2 pp)$	6	14.613
$O^+(\underline{s}^2 ppp)$	5	49.143	$O^-(s^2\underline{p}^2 p^2 p)$	7	2.013
$O(\underline{s}^2 p^2 pp)$	6	32.301	$F^+(s^2\underline{p}^2 pp)$	6	36.213
$O^-(\underline{s}^2 p^2 p^2 p)$	7	18.445	$F(s^2\underline{p}^2 p^2 p)$	7	18.109
$F^+(\underline{s}^2 p^2 pp)$	6	58.563	$F^-(s^2\underline{p}^2 p^2 p^2)$	8	3.497
$F(\underline{s}^2 p^2 p^2 p)$	7	39.389			
$F^-(\underline{s}^2 p^2 p^2 p^2)$	8	24.372			

[a] Underlined electrons are the excited ones. – [b] From Ref. [27].

where q_a is the input value from the former iteration and λ is the damping parameter, which was given the value $\lambda = 0.15$. The iteration process was terminated when $|q_a(\text{in}) - q_a(\text{out})| < 0.5 \cdot 10^{-2}$.

When formulas (10) and (11) are used, the β_{ab}'s are involved in the iteration process. All overlap integrals S_{ab} were calculated with Slater orbitals and Slater's rules using the formulas given by Mulliken *et al.* [28]. Since the effect of including S_{ab} in the iteration process was very small, these integrals were calculated for the neutral atoms and not charge iterated. This means that the β_{ab}'s do not vary with the calculated charges when formula (12) is used.

Table 3. *Coefficients in the formula $I = kq + l$, values of ionization potentials I for the neutral atoms with this formula, and deviations Δ from the values in Table 2*

Valence state[a]	Coefficients		Value of I (eV) for neutral atom	Value of $\|\Delta\|$ (eV) for neutral atom	Maximal values of $\|\Delta\|$ (eV)
	k	l			
$H(\underline{s}000)$	-12.85	26.45	13.60	0.0	0.0
$C(\underline{s}^2pp0)$	-12.0	69.0	21.0	1.6	1.6
$C(s^2\underline{p}p0)$	-11.4	57.7	12.1	1.2	1.2
$N(\underline{s}^2ppp)$	-14.2	98.4	27.4	1.9	1.9
$N(s^2\underline{p}pp)$	-12.4	77.7	14.2	0.2	2.2
$O(\underline{s}^2p^2pp)$	-15.2	124.5	33.3	1.0	1.0
$O(s^2\underline{p}^2pp)$	-16.2	113.6	16.4	1.8	1.8
$F(\underline{s}^2p^2p^2p)$	-17.2	161.0	40.6	0.8	1.0
$F(s^2\underline{p}^2p^2p)$	-16.3	133.3	19.2	0.9	0.9

[a] Underlined electrons are the excited ones.

The Iterative Pariser-Parr-Pople Method

In this method we consider only the π-electrons.

To determine the Coulomb integrals F_{aa} and the resonance integrals F_{ab} we adopt the *zero differential overlap approximation* [8, 9]. Then we get for a closed shell structure:

$$F_{aa} = \alpha_a^{\text{core}} + \frac{1}{2} P_{aa}\gamma_{aa} + \sum_{b \neq a}^{N} P_{bb}\gamma_{ab}, \tag{15}$$

$$F_{ab} = \beta_{ab}^{\text{core}} - \frac{1}{2} P_{ab}\gamma_{ab}, \qquad a \neq b, \tag{16}$$

where $a, b = 1, 2, \ldots, N$ (N is the number of atoms contributing π-electrons);

$$\begin{gathered} \alpha_a^{\text{core}} = \langle \chi_a | f_1 | \chi_a \rangle, \quad \beta_{ab}^{\text{core}} = \langle \chi_a | f_1 | \chi_b \rangle, \\ \gamma_{ab} = \langle \chi_a \chi_b | 1/r_{12} | \chi_a \chi_b \rangle, \quad P_{ab} = 2 \sum_{i=1}^{\pi/2} c_{bi}^{*} c_{ai}. \end{gathered} \tag{17}$$

Adopting the usual PPP approximations – Goeppert-Mayer – Sklar potential [29], $\beta_{ab}^{\text{core}} = 0$ when $b \neq a \pm 1$, $\gamma_{aa} = I_a - E_a$ (I_a is the ionization potential and E_a

the electron affinity of a π-electron at atome a) – we get

$$F_{aa} = -I_a + \frac{1}{2} P_{aa}(I_a - E_a) + \sum_{b \neq a}^{N} \langle \chi_a | u_b | \chi_a \rangle + \sum_{b \neq a}^{N} (P_{bb} - p_b)\gamma_{ab}, \tag{18}$$

$$F_{ab} = \beta_{ab}^{\text{core}} \delta_{a,a \pm 1} - \frac{1}{2} P_{ab}\gamma_{ab}, \quad a \neq b, \tag{19}$$

where p_b is the number of π-electrons contributed by atom b and u_b is the potential due to the whole atom as it occurs in the molecule. The penetration integrals $\langle \chi_a | u_b | \chi_a \rangle$ are of small magnitude and are often neglected for neutral atoms, since that gives better agreement with experimental data in this approximation of F_{ab} [30]. However, in dealing with ionic and mesoionic molecules, where at least one of the atoms has ionic character, certain penetration integrals involve charged atoms instead of neutral ones and thus assume values that are not negligible [31]. Rewriting these predominant penetration integrals and neglecting all the neutral ones, the matrix elements F_{aa} take the form:

$$F_{aa} = -I_a + \frac{1}{2} P_{aa}(I_a - E_a) + \sum_{b \neq a}^{N} (P_{bb} - p_b - n_b)\gamma_{ab}, \tag{20}$$

where $n_b = +1$ if b is a positive ion, $n_b = -1$ if b is a negative ion, and $n_b = 0$ if b is a neutral atom.

Two approximations of the repulsion integrals γ_{ab} were used for each molecule: Mataga's and Nishimoto's approximation [32]

$$\gamma_{ab} = 14.40/(R_{ab} + r_{ab}) \tag{21}$$

and Ohno's approximation [33]

$$\gamma_{ab} = 14.40/(R_{ab}^2 + r_{ab}^2)^{1/2}, \tag{22}$$

where for both approximations

$$r_{ab} = 28.80/(I_a - E_a + I_b - E_b); \tag{23}$$

R_{ab} (the internuclear distance) and r_{ab} are given in Å and γ_{ab}, I_a, E_a, I_b, and E_b in eV. The resonance integrals β_{ab}^{core} were estimated from

$$\beta_{ab}^{\text{core}} = kS_{ab}(I_a + I_b), \tag{24}$$

where S_{ab} are the overlap integrals calculated in the same way as in IEHM. Comparisons were made with calculations where the β_{ab}^{core}'s were fixed to see the effect of including these parameters in the iteration procedure. The proportionality factor k was chosen equal to -0.431 to reproduce the first $^1B_{2u}$ excitation energy of benzene.

We have taken I_a and E_a as functions of the effective charge Z_a. The dependence is assumed to be parabolic and is obtained from the isoelectronic series [12, 13, 34]:

$$I_a = a_{2a}Z_a^2 + a_{1a}Z_a + a_{0a}, \tag{25}$$

$$E_a = b_{2a}Z_a^2 + b_{1a}Z_a + b_{0a}. \tag{26}$$

Considering, for example, the π-ionization potentials of carbon, we use the isoelectronic series consisting of B^-, C, N^+, O^{++}, and F^{+++} in the same valence states to determine Eqs. (25) and (26). These results are summarized in Table 4. The treatment should, however, correspond to an alteration of the exponent of the atomic orbital χ_a while the core-charge remains fixed. Then the ionization potentials and electron affinities should be adjusted for the other atoms of the isoelectronic series used to determine the curve [13]. Matsuoka and I'Haya [34] do not consider these revisions and do not adjust any of the energy values. This seems reasonable since the two different curves do not deviate much from each other in the region near neutral atoms that we consider. Calculations by Brown and Heffernan [13] also show that different curves give only small differences in the results. We have therefore borne all this in mind and did not make any revisions.

Table 4. *Ionization potentials and electron affinities for the* IPPP *calculations*

Valence state under consideration[a]	No of valence electrons q	Isoelectronic valence state[a]	Effective charge Z	Ionization potential (eV) I[b]	Electron affinity (eV) E[b]
$\mathrm{C}(tr\,tr\,tr\underline{\pi})$	1	$\mathrm{B}^-(tr\,tr\,tr\underline{\pi})$	2.25	1.061	
		$\mathrm{C}(tr\,tr\,tr\underline{\pi})$	3.25	11.160	0.026
		$\mathrm{N}^+(tr\,tr\,tr\underline{\pi})$	4.25	28.721	11.957
		$\mathrm{O}^{++}(tr\,tr\,tr\underline{\pi})$	5.25	53.255	31.107
		$\mathrm{F}^{++}(tr\,tr\,tr\underline{\pi})$	6.25		52.605
		$\mathrm{C}^-(tr^2\,tr\,tr\underline{\pi})$	2.90	1.280	
$\mathrm{N}(tr^2\,tr\,tr\underline{\pi})$	1	$\mathrm{N}(tr^2\,tr\,tr\underline{\pi})$	3.90	14.120	1.779
$\mathrm{O}^+(tr^2\,tr\,tr\underline{\pi})$	1	$\mathrm{O}^+(tr^2\,tr\,tr\underline{\pi})$	4.90	34.117	15.301
$\mathrm{O}(tr^2\,tr\,tr\underline{\pi}^2)$	2	$\mathrm{F}^{++}(tr^2\,tr\,tr\underline{\pi})$	5.90	60.966	36.766
		$\mathrm{Ne}^{+++}(tr^2\,tr\,tr\underline{\pi})$	6.90		65.783
$\mathrm{F}(s^2p^2p\underline{p}^2)$	2	$\mathrm{N}^-(s^2p^2p\underline{p})$	3.55	2.779	
		$\mathrm{O}(s^2p^2p\underline{p})$	4.55	17.278	2.013
		$\mathrm{F}^+(s^2p^2p\underline{p})$	5.55	39.637	18.109
		$\mathrm{Ne}^{++}(s^2p^2p\underline{p})$	6.55	69.577	41.919
		$\mathrm{Na}^{+++}(s^2p^2p\underline{p})$	7.55		72.675

[a] Underlined electrons are in the orbital under consideration. – [b] From Ref. [27].

The relation between effective charge Z_a and the number of π-electrons q_a is:

$$Z_a = k_a q_a + l_a \,. \tag{27}$$

Eqs. (25) and (26) then take the form:

$$I_a = c_{2a} q_a^2 + c_{1a} q_a + c_{0a} \,, \tag{28}$$

$$E_a = d_{2a} q_a^2 + d_{1a} q_a + d_{0a} \,. \tag{29}$$

where $q_a = P_{aa}$ are the number of π-electrons according to the charge and bond-order matrix $\boldsymbol{P}$, which is the same as $\boldsymbol{R}$ in Eq. (6) when $\boldsymbol{S} = \mathbf{1}$ (unit matrix).

Four values of the isoelectronic series were fitted to the parabola by the least square method. Values are given in Tables 4 and 5. A double iterative procedure was adopted: The Fock matrix $\boldsymbol{F}$ was made self-consistent with fixed I_a and E_a. Then I_a and E_a were adjusted and a new SCF calculation was performed starting

Table 5. *Coefficients in the formulas* $Z=kq+l$, $I=c_2q^2+c_1q+c_0$, *and* $E=d_2q^2+d_1q+d_0$

Valence state[a]	Coefficients							
	k	l	k_2	k_1	k_0	l_2	l_1	l_0
C($tr\,tr\,tr\underline{\pi}$)	−0.35	3.60	0.442	−5.717	16.512	0.293	−4.266	3.758
N($tr^2\,tr\,tr\underline{\pi}$)	−0.35	4.25	0.429	−6.598	20.333	0.474	−4.353	5.631
O($tr^2\,tr\,tr\underline{\pi}^2$)	−0.35	5.25	0.429	−9.050	42.688	0.474	−7.064	21.942
F($s^2p^2p\underline{p}^2$)	−0.35	5.90	0.473	−10.092	49.208	0.449	−7.868	25.642

[a] Underlined electrons are in the orbital under consideration.

with the last calculated values of $\boldsymbol{P}$, etc. This double iterative procedure went on until $|q_a(\text{in})-q_a(\text{out})|<0.5\cdot 10^{-4}$. I_a and E_a were taken from the tables by Hinze and Jaffé [27]. Some spectroscopic values, however, had to be taken from Moore's tables [35]. As in IEHM, S_{ab}'s were not iterated with charges, and they were calculated in the same way. Since the β_{ab}^{core}'s are functions of I_a and I_b, they, however, were included when formula (24) was used.

Arguments for the Iterative Procedures

The arguments for IEHM and IPPP are slightly different. In EHM the valence electrons are considered to move under the influence of a core that includes all other electrons. Change of the charge of an atom will then alter the ionization potentials of that atom. In PPP, on the other hand, the π-electrons are considered to move under the influence of a core that does not include the other π-electrons. In this case the ionization potential and the electron affinity will not directly be affected by change of π-charge, but the effective charge will, and it will then indirectly affect these quantities via the Slater orbital.

3. Dipole Moments

The full expression for the dipole moment μ of a molecule in the MO-LCAO approximation [Eq. (2)] with orthonormal MO's is:

$$\mu=e\left[\sum_{a=1}^{m}\sum_{\substack{b=1\\ b\neq a}}^{m}\langle\chi_a(1)|\boldsymbol{r}_a(1)|\chi_b(1)\rangle P_{ab}-\sum_{h=1}^{N}\boldsymbol{R}_h Q_h\right], \tag{30}$$

where for a closed shell structure

$$Q_h=-\sum_{a}^{\text{atom}\,h}2\sum_{i=1}^{n/2}\sum_{b=1}^{m}S_{ab}c_{ai}c_{bi}+Z_h \tag{31}$$

and

$$P_{ab}=2\sum_{i=1}^{n/2}c_{ai}c_{bi} \tag{32}$$

if we assume real orbitals; Z_h is the charge of the positive core particle h, $\boldsymbol{r}_a$ the position vector from nucleus h of a valence electron, $\boldsymbol{R}_h$ the position vector of nucleus h, $e<0$ the electronic charge, and N the number of atoms.

If all orbitals are of the same type with only one centered on each atom, then

$$\mu = -e \sum_{h=1}^{N} \boldsymbol{R}_h Q_h . \tag{33}$$

In the zero differential overlap approximation [8, 9] $S_{ab} = 0$ and then

$$Q_h = -2 \sum_{i=1}^{n/2} (c_{hi})^2 + Z_h . \tag{31'}$$

Formula (33) [with (31′)] holds in the PPP method and the ordinary Hückel method. In the extended Hückel method, on the other hand, we must keep expression (30) since we have more than one orbital on each atom and

$$\sum_{a=1}^{m} \sum_{\substack{b=1 \\ b \neq a}}^{m} \langle \chi_a | r_a | \chi_b \rangle \neq 0$$

in general. Especially those integrals where χ_a and χ_b are centered on the same atom may give contributions which are not small. Often, however, this term is neglected and (30) is approximated with (33). When there are no lone-pair orbitals involved, this is usually a good approximation [36, 37].

We have used formula (33) in both the PPP and the extended Hückel calculations well aware of the uncertainty in the last method.

4. NMR Chemical Shifts

The carbon and hydrogen atoms at the *para* position of a substituted benzene molecule have NMR chemical shifts δ_C and δ_H that are proportional to the gross π-charge Q_C at that site [38–43]:

$$\delta_C = -k_C Q_C , \tag{34}$$

$$\delta_C = -k_H Q_C , \tag{35}$$

where k_C and k_H are constants.

Corresponding simple relations cannot be found for the atoms at the *meta* and *ortho* positions since the effects of magnetic anisotropy and induced electric field originating from the substituent give contributions at these sites that are not negligible [40, 42].

The value of k_H lies in the interval 8.08–10.6 ppm/electron and $k_C = 160$ ppm/electron [42]. With these values of the constants formulas (34) and (35) have been applied to fluorobenzene.

5. Results

The Iterative Extended Hückel Method

Variations in Overlap Integrals. A calculation was made on the pyrylium ion in which the overlap matrix was varied by adjusting the orbital exponents according to the charge distribution. The results were compared with a calculation where the overlap integrals calculated with orbital exponents for neutral atoms were kept through the whole iteration procedure. No significant differences were found; charge distributions and orbital energies were nearly identical in the two calculations.

Since $[C_5H_5O]^+$ is a molecule with large redistribution of charges, we conclude that the effect of not including overlap integrals in the iteration procedure is so small that it can be neglected if the Slater exponents are properly chosen. This conclusion has been transferred to apply also to IPPP, and consequently overlap integrals have been fixed during the iterations in both IEHM and IPPP.

Table 6. *Gross charges for* $[C_5H_5O]^+$ *with different approximations for resonance integrals*

Atom	Method									
	(10)					(11)		(12)		
	$k=3.0$	$k=2.5$	$k=2.0$	$k=1.75$	$k=1.5$	$k'=2.0$	$k'=1.75$	$k''=60$ eV	$k''=43$ eV	$k''=35$ eV
C_1/C_5	+0.17	+0.17	+0.16	+0.15	+0.14	+0.16	+0.15	+0.19	+0.18	+0.16
C_2/C_4	+0.02	+0.04	+0.06	+0.06	+0.07	+0.06	+0.07	+0.03	+0.05	+0.06
C_3	+0.07	+0.07	+0.08	+0.08	+0.08	+0.08	+0.08	+0.09	+0.08	+0.08
O_6	+0.15	+0.07	−0.02	−0.07	−0.13	−0.03	−0.08	+0.18	+0.05	−0.01
H_1/H_5	+0.09	+0.10	+0.11	+0.13	+0.14	+0.12	+0.13	+0.07	+0.09	+0.12
H_2/H_4	+0.08	+0.08	+0.09	+0.10	+0.11	+0.10	+0.10	+0.06	+0.07	+0.09
H_3	+0.08	+0.08	+0.09	+0.10	+0.11	+0.10	+0.10	+0.07	+0.07	+0.08

Different Approximations for Resonance Integrals. Calculations were performed on the pyrylium ion with formulas (10), (11), and (12) as approximations for the resonance integrals β_{ab}. Different values of k, k', and k'' were also tested. The results for the gross charges are presented in Table 6, where the methods are numbered according to the used formula.

The differences in energy values between formulas (10) and (11) are very small, suggesting that it does not matter very much which of these two formulas we use. Formula (12) with $k''=35$ eV gives charges and energies comparable with those for $k=2.0$ with formula (10). We should remember that k'' must be larger than any diagonal matrix element α_a [3]. If, for example, $k''=\alpha_a$, then α_a would be a solution to the secular equation. The largest ionization potential is for the *s* valence electrons of the oxygen atom, around 33 eV throughout the whole iteration process. Thus we may not put $k''<35$ eV and cannot with method (12) approach the results obtained with formulas (10) and (11) with $k=k'=1.75$, the traditional value of these constants. In our calculations we used formula (10) with $k=1.75$.

The Iterative Pariser-Parr-Pople Method

Inclusion of Core Resonance Integrals in the Iteration Procedure. It is well known that the values of the core resonance integrals β_{ab}^{core} have rather little influence on charge distributions in the ordinary PPP method. To see if this holds also in IPPP we have made calculations for the pyrylium ion both with fixed values of β_{ab}^{core}'s and with β_{ab}^{core}'s varying according to formula (24). The overlap integrals S_{ab} were, however, fixed, and the Slater exponent for the oxygen atom was taken to be that of the neutral one. Formula (21) was used for γ_{ab}'s.

Varying β_{ab}^{core}'s with the charge distribution, it was found that the results were not significantly affected, compared with those which were obtained when these integrals were not charge-iterated. Since it does not increase the computation time considerably, however, we included this refinement.

Molecular Results

Calculations were performed on all four compounds within both IEHM and IPPP. In order to compare the π-calculations in IPPP with those in IEHM, we also separated the results we obtained from IEHM into a σ- and a π-part. Moreover, we made separate IEHM calculations that only involved σ-electrons and π-electrons resp. These two different separation methods will give the same results after the first computation in the iteration procedure since no interaction exists between the σ- and π-systems in that case. In the following computations the results will in general differ since in the first separation method the σ- and π-electron ionization potentials will depend on both σ- and π-charges, but in the second one they will only depend on the charges of the considered system. For pyridine and the pyrylium ion we have also made calculations on the σ-systems with the method proposed by Del Re [45].

To see the effect of the charge iteration procedures we give the results after the first computation in all methods. These results are usually slightly different from those obtained without any iterative procedure since the ionization potentials and electron affinities obtained from the curves in Section 2 are not necessarily equal to those from which the curves are constructed by our smoothing procedure. The excitation energies for all the PPP calculations are after configuration mixing of all singly excited states.

The following abbreviations are used for the different methods:

IEHM	Iterative Extended Hückel Method for all valence electrons.
$(\text{IEHM})_\sigma$	σ-part of IEHM.
$(\text{IEHM})_\pi$	π-part of IEHM.
σIEHM	Iterative Extended Hückel Method applied only to σ-electrons.
πIEHM	Iterative Extended Hückel Method applied only to π-electrons.
$\sigma\pi$IEHM	Values obtained when values of σIEHM and πIEHM are added.
EHM	Initial computation of IEHM.
$(\text{EHM})_\sigma$	σ-part of EHM.
$(\text{EHM})_\pi$	π-part of EHM.
σRE	Del Re's method for σ-electrons.
IPPPM	Iterative Pariser-Parr-Pople Method with Mataga-Nishimoto's approximation of γ_{ab}.
IPPPO	Iterative Pariser-Parr-Pople Method with Ohno's approximation of γ_{ab}.
PPPM	Initial computation of IPPPM.
PPPO	Initial computation of IPPPO.

Results by other authors are included in the tables.

Table 7. *Gross charges for* C_6H_6

Method	Atom	
	C	H
EHM	−0.13	+0.13
IEHM	−0.05	+0.05

Table 8. *Some energy values for* C_6H_6

Method	The three highest occupied orbital energies (eV)			First excitation energies (eV) (with CI)	
				Singlet ($^1B_{2u}$)	Triplet ($^3B_{1u}$)
EHM	−13.44 (σ)	−13.44 (σ)	−13.58 (π)		
IEHM	−12.96 (π)	−12.96 (π)	−13.09 (σ)		
PPPM	−10.36	−10.36	−13.36	4.90	2.49
PPPO	−11.29	−11.29	−14.64	4.97	3.43
Observed	− 9.25 (π)[a]	− 9.25 (π)[a]	−11.51[a]	4.89[b]	3.66[b]

[a] Ref. [47]. Clark and Frost assigns 11.51 eV as a π-electron ionization energy; there is, however, different opinions if it is a σ-[48, 49] or a π-electron ionization energy [47, 50, 51].

[b] Ref. [46].

Table 9. *Gross charges for* C_5H_5N

Method	Atom							Dipole
	C_1/C_5	C_2/C_4	C_3	N_6	H_1/H_5	H_2/H_4	H_3	moment (D)[a]
EHM	+0.29	−0.16	−0.00	−0.87	+0.12	+0.13	+0.13	4.55
IEHM	−0.01	−0.03	−0.03	−0.20	+0.07	+0.06	+0.06	1.68
$\sigma\pi$IEHM	+0.04	−0.03	−0.02	−0.31	+0.07	+0.06	+0.05	2.12
Hoffman	+0.30	−0.12	+0.04	−0.92	+0.10	+0.10	+0.10	4.77
Clementi	−0.11	−0.23	−0.20	−0.23	+0.22	+0.22	+0.22	1.99
(EHM)$_\sigma$	+0.14	−0.14	−0.12	−0.50	+0.12	+0.13	+0.13	2.34
(IEHM)$_\sigma$	+0.05	−0.05	−0.05	−0.26	+0.07	+0.06	+0.06	1.34
σIEHM	+0.01	−0.04	−0.04	−0.21	+0.07	+0.06	+0.05	1.34
σRE	+0.03	−0.02	−0.03	−0.14	+0.04	+0.03	+0.03	0.74
Clementi (σ)	−0.10	−0.22	−0.23	−0.22	+0.22	+0.22	+0.22	1.74
(EHM)$_\pi$	+0.15	−0.02	+0.12	−0.38				2.20
(IEHM)$_\pi$	−0.06	+0.02	+0.02	+0.06				0.32
πIEHM	+0.02	+0.01	+0.03	−0.10				0.78
PPPM	+0.11	−0.01	+0.05	−0.24				1.12
PPPO	+0.18	−0.07	+0.09	−0.31				1.01
IPPPM	+0.06	+0.01	+0.03	−0.15				0.89
IPPPO	+0.07	−0.00	+0.03	−0.17				0.83
Clementi (π)	−0.00	−0.00	+0.02	−0.01				0.25
Hameka-Liquori	+0.06	−0.00	+0.04	−0.16				0.87
Observed								2.2[b]

[a] Direction N_6 to C_3 in all cases. All calculated values have been computed with the method described in section 3.

[b] Ref. [55].

Table 10. *Some energy values for* C_5H_5N

Method	The three highest occupied orbital energies (eV)			First excitation energies (eV) (with CI)	
				Singlet ($^1B_1$)	Triplet ($^3B_1$)
EHM	−12.80 (σ)	−13.55 (π)	−13.71 (σ)		
IEHM	−11.44 (σ)	−13.17 (π)	−13.31 (σ)		
Clementi	−12.17 (π)	−12.48 (π)	−12.66 (σ)		
PPPM	−10.41	−10.99	−13.77	4.83	2.41
PPPO	−11.28	−12.08	−15.11	4.89	3.46
IPPPM	−10.56	−10.85	−13.72	4.84	2.33
IPPPO	−11.47	−11.85	−15.04	4.90	3.29
Clementi	−12.17 (π)	−12.48 (π)	−16.93 (π)		
Observed	− 9.28 (π)[a]	−10.54 (σ)[a]	−12.21 (π)[a]	4.93[b]	3.67[c]

[a] Ref. [56]. – [b] Ref. [57]. – [c] Ref. [58].

Benzene (Tables 7 and 8). Since this is an alternant π-system, only σ-electrons give rise to change in the charge distribution. For that reason we only list gross charges in EHM and IEHM.

Pyridine (Tables 9 and 10). For this molecule we have included the results for all valence electrons by Hoffman [52] and Clementi [53] and for π-electrons

Table 11. *Gross charges and chemical shifts at* C_3 *and* H_3 *for* C_6H_5F

Method	Atom								Dipole
	C_1/C_5	C_2/C_4	C_3	C_6	F_6	H_1/H_5	H_2/H_4	H_3	moment (D)[a]
EHM	−0.18	−0.12	−0.16	+0.74	−0.65	+0.14	+0.13	+0.13	+4.36
IEHM	−0.01	−0.02	−0.03	+0.11	−0.35	+0.07	+0.06	+0.06	+4.09
σπIEHM	−0.01	−0.04	−0.05	+0.18	−0.36	+0.08	+0.06	+0.06	+3.37
Davies	−0.05	+0.03	−0.01	+0.23	−0.20	+0.02	0.00	−0.00	+1.68
$(EHM)_\sigma$	−0.14	−0.12	−0.13	+0.67	−0.68	+0.14	+0.13	+0.13	+5.12
$(IEHM)_\sigma$	−0.02	−0.04	−0.05	+0.28	−0.45	+0.07	+0.06	+0.06	+4.01
σIEHM	−0.00	−0.03	−0.04	+0.16	−0.38	+0.08	+0.06	+0.06	+3.88
Davies (σ)	−0.00	+0.01	+0.01	+0.20	−0.25	+0.02	0.00	−0.00	+1.90
						Chemical shifts (ppm) (relative C_6H_6)			
						C_3	H_3		
$(EHM)_\pi$	−0.04	+0.00	−0.03	+0.07	+0.03	4.46	0.23 —	0.30	−0.76
$(IEHM)_\pi$	+0.01	+0.02	+0.02	−0.18	+0.10	−3.57	−0.18 —	−0.24	+0.08
πIEHM	−0.01	−0.01	−0.01	+0.02	+0.03	1.60	0.08 —	0.11	−0.51
PPPM	−0.05	+0.00	−0.03	+0.03	+0.10	4.80	0.24 —	0.32	−1.33
PPPO	−0.09	+0.03	−0.05	+0.04	+0.13	8.35	0.42 —	0.55	−1.45
IPPPM	−0.04	−0.01	−0.02	+0.01	+0.09	3.16	0.16 —	0.21	−1.23
IPPPO	−0.05	+0.00	−0.02	+0.01	+0.11	3.80	0.19 —	0.25	−1.33
Davies (π)	−0.05	+0.02	−0.02	+0.03	+0.05	4.00	0.20 —	0.27	−0.52
Observed						4.4[b]	0.22[b]		+1.5[c]

[a] Positive sign indicates direction F_6 to C_3; minus sign the opposite direction. All calculated values have been obtained with the method described in Section 3.

[b] Ref. [42]. – [c] Ref. [55].

Table 12. *Some energy values for* C_6H_5F

Method	The four highest occupied orbital energies (eV)				First excitation energies (eV) (with CI)	
					Singlet ($^1B_1$)	Triplet($^3B_1$)
EHM	−13.31 (σ)	−13.40 (π)	−13.60 (π)	−13.95 (σ)		
IEHM	−12.93 (π)	−13.06 (σ)	−13.40 (π)	−13.71 (σ)		
PPPM	− 9.45	−10.21	−12.49	−14.62	4.76	2.40
PPPO	−10.03	−11.08	−13.31	−15.51	4.79	3.16
IPPPM	− 9.47	−10.11	−12.53	−14.89	4.76	2.37
IPPPO	−10.13	−10.98	−13.44	−15.69	4.79	3.15
Observed	− 9.21 (π)[a]	− 9.87 (π)[a]	−11.83 (σ)[a]	−12.98 (σ)[a]	4.70[b]	

[a] Ref. [47]. – [b] Ref. [60].

Table 13. *Gross charges for* $[C_5H_5O]^+$

Method	Atom						
	C_1/C_5	C_2/C_4	C_3	O_6	H_1/H_5	H_2/H_4	H_3
EHM	+0.60	−0.14	+0.13	−0.69	+0.13	+0.14	+0.13
IEHM	+0.15	+0.06	+0.08	−0.07	+0.13	+0.10	+0.10
$\sigma\pi$IEHM	+0.22	+0.08	+0.14	−0.11	+0.09	+0.07	+0.06
(EHM)$_\sigma$	+0.33	−0.13	−0.11	−0.94	+0.13	+0.14	+0.13
(IEHM)$_\sigma$	+0.14	−0.04	−0.10	−0.65	+0.13	+0.10	+0.10
σIEHM	+0.04	−0.03	−0.03	−0.35	+0.09	+0.07	+0.06
σRE	+0.09	−0.02	−0.03	−0.30	+0.04	+0.03	+0.03
(EHM)$_\pi$	+0.27	−0.01	+0.24	+0.25			
(IEHM)$_\pi$	+0.01	+0.11	+0.18	+0.58			
πIEHM	+0.18	+0.11	+0.17	+0.24			
PPPM	+0.22	+0.04	+0.22	+0.26			
PPPO	+0.21	+0.01	+0.26	+0.30			
IPPPM	+0.14	+0.08	+0.15	+0.42			
IPPPO	+0.11	+0.08	+0.17	+0.45			

Table 14. *Some energy values for* $[C_5H_5O]^+$

Method	The three highest occupied orbital energies (eV)			First excitation energies (eV) (with CI)	
				Singlet ($^1B_1$)	Triplet ($^3B_1$)
EHM	−13.60 (π)	−13.61 (σ)	−14.06 (σ)		
IEHM	−14.35 (σ)	−14.96 (π)	−14.97 (σ)		
PPPM	−15.46	−16.91	−24.41	4.84	2.32
PPPO	−18.03	−19.42	−26.58	4.80	2.99
IPPPM	−16.08	−17.32	−22.14	5.06	2.68
IPPPO	−18.61	−19.72	−24.68	5.00	3.29
Observed				4.61[a]	

[a] Ref. [61].

by Hameka and Liquori [54]. Clementi's results have also been separated into a σ-part and a π-part.

Fluorobenzene (Tables 11 and 12). For this molecule we have included the results for all valence electrons by Davies [59] with the CNDO/2 method [66, 67]. They have also been separated into a σ-part and a π-part.

Pyrylium ion (Tables 13 and 14). We have assumed six valence electrons at the oxygen atom in the calculations; i.e., we have assumed ionization potential and Slater exponent for the neutral atom. When we separate into a σ-part and a π-part, we have assumed that the $+1$ value lies in the π-system.

6. Conclusions and Remarks

In all calculations on the three neutral molecules the effect of the iteration procedure is to smooth out the charge distribution. This holds also for the IEHM but not for the IPPP calculations of the pyrylium ion.

The difference in the charge distributions between PPPM and PPPO becomes noticably smaller when these two methods are charge iterated.

We have examined the Iterative Extended Hückel Method from two basicly different approaches. First we have considered all valence electrons (IEHM), then, in a similar manner, we have performed separate calculations only on the σ- and only on the π-electrons. Although the results of the separate calculations give σ and π charge distributions quite different from those of the full IEHM, the total electronic charge distribution obtained by adding the contributions of the two separate calculations is very similar to the total distribution obtained when all valence electrons were considered simultaneously. Similar effects have been observed by Pullman [62]. The charge distributions obtained from the separate σ and π Iterative Extended Hückel procedures show the best agreement with the charge distributions calculated from our PPP and Del Re computations, the calculations by Davies [59], and those by Hameka and Liquori [54]. The correspondence between the total charge distribution of IEHM and the π-electron one in π-electron methods has been noticed by Zerner and Gouterman [15]. All this strongly indicates that polarization effects from the σ-electrons are of importance for the π-electrons.

Both the calculations of dipole moments and of chemical shifts are very sensitive to charges. With regard to this the calculated values are satisfactory, except for the chemical shifts of fluorobenzene calculated with IEHM. The PPP calculations of the dipole moment of pyridine could be revised to account for the influence of the nitrogen lone-pair according to Hameka and Liquori [54]. This is done by adding 1.33 D from the σ-system. We then get: PPPM: 2.45 D, PPPO: 2.34 D, IPPPM: 2.22 D, IPPPO: 2.16 D; Observed: 2.2 D [55].

It is interesting to notice that the lone-pair of pyridine is rather well localized by the iterative extended Hückel methods, in contrast to the non-iterative procedure. In the former cases, the lone-pair orbital (highest occupied σ-orbital) has 1.48–1.51 electrons on the nitrogen atom; in the latter one, only 0.78 electrons.

Thus the iterative procedure restores the lone-pair picture[1]. A similar effect is noticed for fluorobenzene, where we find two lone-pairs on the fluorine atom; the highest occupied σ-orbital has 1.27 electrons in a p_σ-orbital and the lowest occupied orbital has 1.66 electrons in the s-orbital of the fluorine atom. Symmetry reasons do not prevent this s-orbital to mix with the second p_σ-orbital, so the assumption that the fluorine atom is not hybridized seems correct. The π-electron lone-pair orbital of this molecule has only 1.08 electrons on the fluorine atom. A similar interpretation for a lone-pair orbital is ambiguous for the pyrylium ion since in the full IEHM calculation the "lone-pair orbital" (highest occupied σ-orbital) has 0.83 electrons on the oxygen atom while in the calculations for only the σ-electrons the corresponding figure is 1.68.

Since the main purpose of our investigation was to see the effect of iterations on charge distributions, we have not made any deeper analysis of spectral values. The ionization energies for the molecules are always too high. Sometimes σ- and π-levels have reversed orders in the extended Hückel treatments with and without iterations. The orders in the iterative procedure appear to better reproduce the experimental ones. The first singlet and triplet excitation energies are about equally well reproduced in the PPP calculations with and without charge iterations. We note, however, that the excitation energies for the pyrylium ion are a little different in these two types of calculations (Table 14).

The influence of the iteration procedure on ionization energies and excitation energies is usually much smaller than could be expected compared with the influence on charges. In the ordinary PPP method charges are relatively stable against variations in β_{ab}^{core} of formula (16), and that parameter could be varied to fit spectra [cf. Eq. (24)]. The reason for this stability is that the sum of $\boldsymbol{G}^{(i)}$ in Eq. (8) can be considered as a small perturbation. We should then notice that $\boldsymbol{G}^{(i)}$ in the IPPP method origins from an ordinary PPP calculation according to Section 2. Now, it is well-known that a change of wave function, which in fact this perturbation gives birth to, often leads to small changes in energies but large changes in other physical quantities [64, 65]. This is probably the reason for the stability.

The resort to iterative procedures has its main advantage for charge distributions since the energy levels and excitation energies can be changed by varying the semi-empirical parameters and since they vary very little during the charge iteration procedure. The results for the chemical shift of fluorobenzene, indicate, however, that charges at a specific position may not be well reproduced in the iterative method. One should also remember that iterative procedures require more computational time. However, it is our belief that more realistic results can be obtained in this way justifying the extended time.

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[1] Cf. Refs. [63] and [53].

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