

The Coulomb integral (in eV) is finally obtained from these r_i values (in Å) by

$$(11|22) = 3.599 \sum_{i=1}^4 1/r_i \quad (3)$$

In the special case $\phi=0$, this is identical with Parr's formula.

The validity of eqn. (3) as a substitute for theoretical integrals, was tested in studies of 3,3'-bithienyl² and 2-fluorobiphenyl.³ The Coulomb integrals that are changed on rotation were calculated by both methods. The theoretical values were scaled by a distance-dependent factor given by the ratio between the approximate and the theoretical value of an integral over parallel p_π components.^{2,3}

For bithienyl the difference between the two methods was never larger than 0.01 eV. In Table 1 a few selected integral values are given as an illustration. The numbering of atoms is shown in Fig. 1.

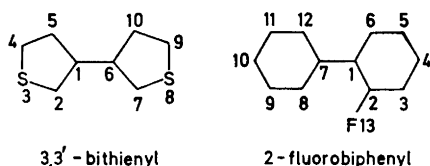


Fig. 1. Notation of atoms.

Integrals involving substituents in the *ortho* position to the R_1 - R_2 bond, are expected to show a larger difference between theoretical values and values obtained from eqn. (3). This is clearly demonstrated by the selected integral values for fluorobiphenyl, where the largest deviation is 0.1 eV.

Eqn. (3) will thus be a simple and satisfactory alternative to the laborious evaluation of theoretical integrals for use in semi-empirical MO calculations.

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The Valence Charge Distribution of Pyridine in the Iterative Extended Hückel Approach*

OLLE MÄRTENSSON

*Quantum Chemistry Group,
Uppsala University, Box 518, S-751 20
Uppsala 1, Sweden*

Pyridine is a compound of fundamental interest in the series of six-membered, aromatic heterocyclics, and its electronic structure has, therefore, been the subject of numerous calculations in various approaches. Comparatively little attention has been paid to the electron density distribution of the molecule. In connection with the valence concept the valence charge distribution is of particular interest. Visualized in the form of contour diagrams, the valence charge distribution gives insight into several features which are associated with the first order density matrix. A comparison with the corresponding diagrams of the isoelectronic pyrylium ion¹ in the same approach is also of interest. The procedure for obtaining the level diagrams has been described earlier,² and here only some additional parameter values are given. The constants for nitrogen in the second order charge iterative process are in descending order of charge

-1.616 29.302 -131.703 for 2s orbitals
-1.038 24.522 -110.591 for 2p orbitals

For hydrogen the value 1.2 has been used for the exponent of the 1s Slater orbitals in the calculation of eigenvectors as well as the density itself.³ Atomic units has been used, and the contours represent the levels 0.01, 0.03, 0.06, ..., 0.30, 0.35, ..., 0.50, 0.70. The geometry of pyridine is taken from Bak *et al.*⁴

Comments. The σ charge distribution in the molecular plane (Fig. 1) indicates a distinct lone pair at the nitrogen atom. This nitrogen contributes with 1.63 electrons to the highest occupied orbital as compared to 1.12 for the oxygen atom in the pyrylium ion (the value 1.5

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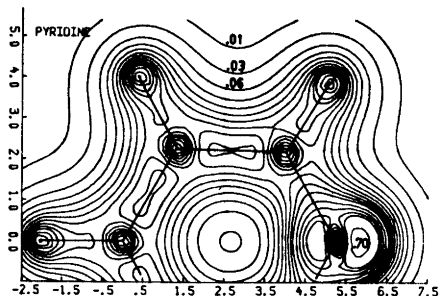


Fig. 1. σ Charge distribution of pyridine in the molecular plane.

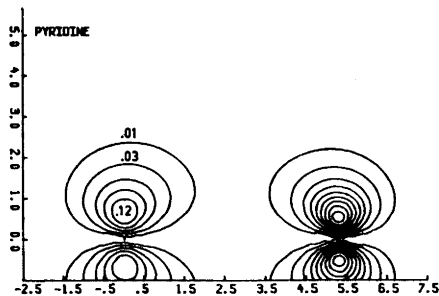


Fig. 4. π Charge distribution of pyridine in the symmetry plane perpendicular to the molecular plane.

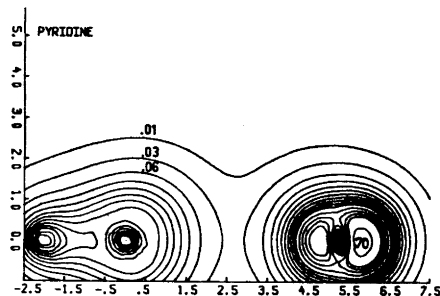


Fig. 2. Valence charge distribution of pyridine in the symmetry plane perpendicular to the molecular plane.

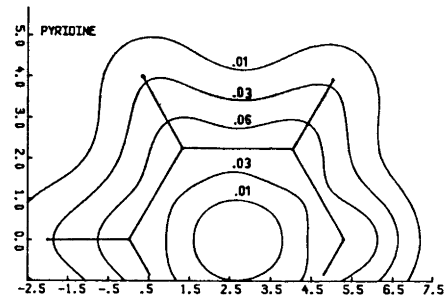


Fig. 5. Valence charge distribution of pyridine in a section 1.5 a.u. above the molecular plane.

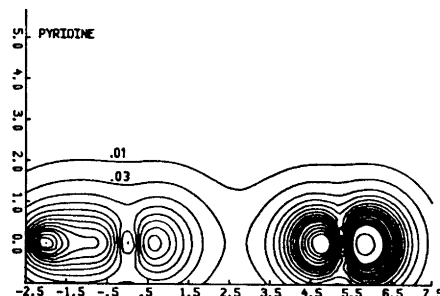


Fig. 3. σ Charge distribution of pyridine in the symmetry plane perpendicular to the molecular plane.

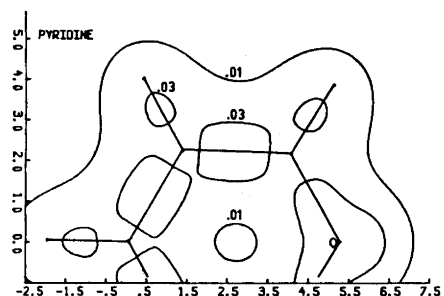


Fig. 6. σ Charge distribution of pyridine in a section 1.5 a.u. above the molecular plane.

for nitrogen given in Ref. 1 refers to a calculation with the exponent 1.0 for the hydrogen $1s$ Slater orbitals). The perturbation from the electronegative nitrogen

atom on the neighbors is not pronounced in this approach and includes mainly the C_2 atom. Basing the bond formalism on the symmetry of the valence charge distribu-

tion, we find by inspection that the C—C and C—H σ bonds are straight. How the C—N bonds ought to be considered is an open question.

The σ charge distribution can also be studied in Figs. 3 and 4. The former figure which displays the distribution in the symmetry plane perpendicular to the molecular plane shows the lone pair again and indicates a σ density maximum over the C₄—H₄ bond. The latter can also be seen in Fig. 6, which gives the σ charge distribution in a section 1.5 a.u. above the molecular plane. Here isolated maxima are seen over all C—C and C—H bonds. Over the C—N bonds we find an extensive, trigonal maximum, centered over the nitrogen atom. Comparing with pyrylium (Fig. 6 of Ref. 1) we see, that the σ charge

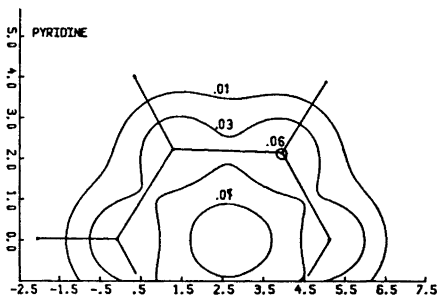


Fig. 7. π Charge distribution of pyridine in a section 1.5 a.u. above the molecular plane.

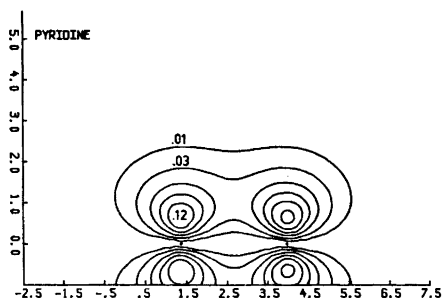


Fig. 8. π Charge distribution of pyridine in a section through the atoms C₂ and C₃ and perpendicular to the molecular plane.

at the oxygen atom is strongly concentrated towards the center of this atom, so that at 1.5 a.u. above the molecular plane it is approximately the same as for the carbon atoms. The different position of the maxima, inside the nitrogen atom in pyridine and outside the oxygen atom in pyrylium, are probably due to different lone pair occupation.

The π charge shown in the section perpendicular to the molecular plane (Fig. 4) is of rather characteristic p type with a small distortion towards the interior of the ring. As Fig. 7 indicates, the nitrogen contributes "loyally" to the formation of the π charge density. In this respect it differs strikingly from the "individualistic" oxygen atom in the isoelectronic pyrylium ion (cf. Fig. 7 of Ref. 1). The C₃—C₃ and C₃—C₄ π bonds seem to be nearly equivalent and their bond orders also do not differ much (0.51 as compared to 0.48). The higher maximum at atom C₂ is due to the fact that the IEH approach leads to a rather strong negative, net π charge at this atom (-0.06 as compared to 0.02 for the atom C₃ and C₄). The same relation between these maxima is also found in the section along the C₂—C₃ bond, perpendicular to the molecular plane, shown in Fig. 8.

The total valence charge distribution in a plane 1.5 a.u. above the molecular plane (Fig. 5) shows that the nitrogen atom even here "fits" well into the charge system and does not show the "individualistic" behaviour of the oxygen atom in pyrylium (cf. Fig. 5 of Ref. 1).

Perhaps it should be pointed out, that the valence charges of Figs. 2 and 5 are merely superpositions of the corresponding σ and π charges (of Figs. 3 and 4 and of Figs. 6 and 7, respectively).

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