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A semi-empirical LCAO calculation including σ- and π-electrons has been performed for pyridine and related heterocyclics. The diagonal matrix elements of Hamiltonian are evaluated from atomic spectroscopic data through the use of a formula derived from the SCF equations. The non-diagonal matrix elements are estimated through the Wolfsberg-Helmholz formula. All overlap integrals have been included. The results disagree with what one can expect from a π-electron treatment, mainly with respect to population analysis, but they seem strongly supported by the conclusions of “ab initio” calculations for other compounds and the trend of dipole moment in the sequence pyridine, quinoline, acridine.

It is a common assumption that, in conjugated heterocyclics like pyridine, the π-electron system can be studied from the quantum point of view without taking into account explicitly the σ-system (see for instance [18]). Such an assumption has been used in the oversimplified Hückel procedure as well as in some more sophisticated methods like the Parr-Pariser-Pople. This simplification relies on the fundamental hypothesis that the mutual interaction of the systems σ and π can be neglected. It has been noticed that this hypothesis is probably less valid for conjugated heterocyclics than for the aromatic hydrocarbons themselves (see for instance [18]). A quantum study of the whole electronic system of pyridine would be of interest in as much as it allows to have an idea of the validity of the previous hypothesis. A recent paper by HOFFMANN deals with the electronic structure of...
σ orbitals in pyridine [9], but is mainly centered on the nature of the lone pair. We have performed another study and, due to some differences in the theoretical method, our results are different from those of HOFFMANN's paper for at least one important point.

We shall report here only the main features of the theoretical method we used; some detailed accounts have been given elsewhere [3, 4]. The atomic basis orbitals are Slater orbitals 2s and 2p for the C and N atoms, 1s for the H atoms, with usual Slater exponents [25]. We used a moonelectron effective Hartree-Fock hamiltonian. The corresponding diagonal matrix element for the p orbital of atom P is given by:

\[ H_{pp} = W_p + \sum_{r \in P} q_r (J_{pr} - \frac{1}{2} K_{pr}) \]

where:

- \( W_p \) includes the kinetic term and the core interaction term (the core is made from the nucleus for the H atoms, the nucleus plus the 1s electrons for the C and N atoms);
- the summation \( \sum \) is carried over every orbital \( r \) from the P atom which is not included in the core;
- \( q_r \) is the orbital population, as defined by MULLIKEN [17], for the orbital \( r \);
- \( J_{pr} \) and \( K_{pr} \) are the atomic coulomb and exchange integrals.

This formula has been deduced from the ROOTHAAN's SCF equations [23], using in a systematic manner the MULLIKEN and RUESDENBERG approximations [24].

Using this expression, the matrix elements \( H_{pp} \) can be computed in a semi-empirical manner from the atomic valence-state energies, using the values given by PILCHER and SKINNER [21]. The details of the procedure have been given elsewhere [3]. The matrix elements \( H_{pp} \) depend explicitly on the orbital populations \( q_r \); so we can be confident of the results of the calculation only if the populations which are carried out from the calculation agree with those used for the computation of the \( H_{pp} \) elements (at least within a certain accuracy); if this condition is not fulfilled, another trial with a new set of \( q_r \) should be made. We asked for an accuracy of 0.01 electron.