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ω-Modification of Extended Hückel Theory*

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The extended Hückel theory has been applied to various organic molecules by Hoffmann [3]. However, when used to calculate the charges on NO_2 [4] and CH_3COOH [5] it failed to yield the right order. This is probably a consequence of taking matrix elements H_{ii} as a valence state ionisation potential of the neutral atom. For this reason, we varied H_{ii} as a function of charges on atoms and the populations of atomic orbitals. The method was applied to CH_2O. Overlap integrals were calculated after Mulliken et al. [6] and the variation of the H_{ii} according Basch et al. [1]. The nondiagonal elements H_{ij} were calculated with the assumption that $H_{ij} = 0.5\ K\ S_{ij}(H_{ii} + H_{jj})$ and $K = 1.75$. This value of K gave a good agreement between calculated and experimentaly determined transitions. For the first forbidden transitions $A_1 - A_2$ we obtained 4.28 eV. The calculation was made in a self consistent manner with the method of "steepest descent" [2]. The orbital populations and net charges are given in the table.

Table. *Orbital populations of* CH_2O

Atom	$2s$	$2p_x$	$2p_z$	$2p_y$	$1s$	Q
C	1.19	1.02	0.66	1.07		0.06
O	1.73	1.97	1.66	0.93		−0.29
H					0.89	0.11

(zx is the plane of the molecule with the z-axis along the C=O bond).

The most notable result concerns the population of the $2p_y(\pi)$ orbitals. The orbital population is greater on C than on O atom. This result is opposite to expectations, but is comparable to that of Peters [7] who obtained the same situation with the localisation of the SCF wave function. The described method of choosing H_{ii} and varying its value according to populations and charges constitutes a guess for the matrix elements of a Hartree-Fock Hamiltonian [3] and takes into account the correlation between electrons on the atom. The application of the method to charged species will be published shortly.

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