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MO determination from experimental X-ray structure factors of diformohydrazide

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Important papers in sixties[1] and seventies by Prof. Stewart manifested two ways for the electron density analysis. One is based on wavefunctions and the other is on electron densities. We have pursued the first way. The molecular orbitals (MO) of diformohydrazide (DFH) were determined within the Hartree-Fock approximation from X-ray structure factors starting from the theoretical MOs calculated by HONDO-8. The least-squares method incorporating the orthonormal relationships between MOs[2] is used. However, since in the Roothaan-Hartree Fock method similar atomic orbitals (AO) are combined to express a MO, parameter interaction is so severe and unpredictable that a new scheme was devised to avoid automatically the interaction, which should also give as equal chances as possible for each variable to be refined. We call it as X-ray Molecular Orbital analysis (XMO). It is an extended one of the X-ray Atomic Orbital analysis (XAO)[3], where AOs in crystal fields were determined together with the number of electrons on each AO. DFH single crystal (P21/a) was shaped into a sphere of 0.159 mm diameter. 5393 reflections were measured at 100±1 K with MoKa radiation using a four-circle diffractometer. Optimum four angles were calculated for each reflection to avoid multiple diffraction. After conventional refinement R factor reduced to 0.026. Well-tempered GTF basis sets by Huzinaga et al. contracted to (10,10,1,1,1,1/5,1,1,1,1) for C,N and O, and for H by Stewart to (2,1,1,1) were used, which does not produce a cusp on atoms. 23 MOs are expressed as a linear combination of 142 AOs. Polarization functions were not used and N-H…O intermolecular hydrogen bonds were neglected. Since the molecule is approximately planar, C2h symmetry was applied to the molecule to reduce the number of MO coefficients. Numbers of MOs of the Ag, Bu, Au and Bg states are 10, 9, 2 and 2. The atomic positions determined by the conventional method were used to define the molecule but the H positions were extended to make C-H and N-H bonds longer for theoretical calculation by HONDO-8. The 142 AOs were transferred to symmetry orbitals to simplify the relationships between the MO coefficients. The number of them is 788. When the magnitude of a correlation coefficient in the least-squares refinement is larger than 0.6, the variables were judged to correlate severely and one in each pair was fixed in the refinement. When there is no such correlation and the denominator of goodness-of-fit is reduced, the refinement was judged valid and new parameters were accepted. From larger MO coefficients to smaller ones the refinement proceeded and those with the magnitude larger than cmax=0.25 were first refined together with the crystallographic parameters. Then cmax was gradually reduced to 0.0. After a preliminary refinement R-factor becomes 0.013 and peaks on the residual density are deleted. C-H and N-H are 1.036(6) and 0.989(5) Å. Number of reflections having two-center scattering factors larger than their e.s.d.'s is 811 among 2998 reflections used in the refinement.

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