The Electronic Structure of Hydrogen Cyanide with Gaussian Orbitals

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SCHULMAN AND MOSKOWITZ[1] have recently extended the use of Gaussian orbitals in LCAO–MO–SCF calculations to a relatively large molecule, namely benzene. A small number of basis functions, in one calculation 6, and in another 7, were used by them for each carbon atom, the justification for which is obtained from the work of Moskowitz and Harrison[2] on ethylene.

In the present work the Polyatom[3] programme for Gaussian orbitals has been converted for operation on the IBM 7040 and calculations involving *s*- and *p*-type orbitals have been performed on hydrogen cyanide, using a basis set of 28 Gaussian-type functions (GTF). These consisted of two S-GTF on the hydrogen atom, seven S-GTF and two P-GTF on the carbon and on the nitrogen atom, where the notation P-GTF refers to a set consisting of one P_x, and P_y, and one P_z Gaussian-type function. These constituted a basis set not much bigger than that employed by Moskowitz and Harrison on ethylene.

For internuclear distances between the hydrogen and carbon atoms, and between the carbon and nitrogen atoms, of 2·000 and 2·187 A. U., respectively, an electronic energy of −116·133 A. U. was obtained. This corresponds to a total energy of −92·257 A. U. This may be compared with the results of McLean,[4] who used a minimal set of Slater-type functions (STF), and obtained an electronic energy of −116·424 A. U. and a total energy of −92·547 A. U. for the same internuclear distances. In more recent work McLean[5] has obtained an electronic energy of −116·8367 A. U. using a basis set of 40 STF.

A comparison of the orbital energies of HCN obtained by McLean with those found in the present work (see Table) indicates good agreement for such a small basis set. McLean obtained a dipole moment of 2·099 D, to be compared with 2·234 D found in the present work. The experimental value of the dipole moment, as given by Tyler and Sheridan,[6] is 3·00 D. Assuming Koopmans' approximation[7] to be valid, a first ionization potential of 0·4817 A. U. was calculated, to be compared

Orbital energies of hydrogen cyanide

	STF[3]	GTF (present work)
σ:	−15·7403	−15·8416
	−11·4277	−11·4047
	− 1·2522	− 1·3436
	− 0·7965	− 0·8104
	− 0·5582	− 0·5323
	+ 0·3649	+ 0·4196
	+ 1·0861	+ 0·9251
π:	− 0·5074	− 0·4817
	+ 0·2516	+ 0·2092

with an experimental value of 0·5111 A. U.[8] The results are, in general, encouraging, considering the size of basis set. It is well known that a much larger basis set of GTF than of STF is usually required. However in the present work the basis set is still small enough to permit extension to larger molecules of the same type, and at the same time the basis set of 28 GTF yields results which are not too bad even when compared with the best calculation using 40 STF. Additional work on HCN, and larger nitriles is in progress.

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