Ab-initio Crystal Orbital Study of Hydrogen Fluoride Chain. Basis Set Dependence

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The Influence of Various Basis Sets in Ab-initio Crystal Orbital Studies is Reported for Hydrogen Fluoride Chain

The ab-initio SCF method [1] seems to be a now well established method for energy band calculations of one dimensional molecular systems. In this approach two problems normally influence the results. The first one is connected with the number of neighbours that interact with the reference elementary cell. The second one is a common problem of all ab-initio calculations and is connected with the basis set dependence of the calculated quantities. The influence depends on the particular system treated. In hydrogen bonded systems one can expect that the basis set dependence is larger than the influence of neighbours. This is a consequence of the fact that the intermolecular distances in hydrogen bonded systems are larger than the intramolecular distances.

We will discuss mainly the basis set dependence of two quantities: the energy gap between valence and conduction bands and the widths of the valence bands. The results are given in Table 1 and 2. The experimentally [2] determined F—F distance (2.49 Å) and angle (120.1°) of the zig-zag chain were used and the H atoms were placed along the F···F lines at recently determined [3] distances 0.95 Å. In all calculations the number of

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Table 1. Basis set dependence of total energies, energy gaps and charges.

Basis set	Energy per HF (a.u.)	Energy gap (a.u.)	Atomic (orbital) charges
STO-2G[a]	95.63258	0.996	$q_F = 9.249$ $q_H = 0.751$
STO-3G[a]	98.60295	1.033	$q_F = 9.378$ $q_H = 0.622$
	(98.61465)[b]	(0.990)	($q_F = 9.236$; $q_H = 0.764$)
STO-3G[c]	98.62933	1.039	$q_F = 9.315$ $q_H = 0.685$ ($q_{1s} = 0.612$, $q_{2p} = 0.073$)
	(98.63193)[d]	(1.025)	
STO-3G[e]	98.63913	1.0395	$q_F = 9.291$ $q_H = 0.709$ ($q_{1s} = 0.602$, $q_{2p} = 0.107$)
STO-3G[f]	98.67882	1.078	
4-31G[g]	99.99790	1.205	
F(4s 2p)H(2s)[h]	100.18907	1.333	
F(4s 3p)H(3s)[h]	100.21418	1.336	

[a] Ref. [5], [b] Number of neighbours 8, [c] STO-3G with 2p Gaussian (exponent 1) on H, [d] Number of neighbours 7, [e] STO-3G with 2p Gaussian (exponent 0.8) on H, [f] STO-3G with 3s and 3p Gaussians (exponent from Ref. [6]) on F, [g] Ref. 7, [h] Ref. [8].

Table 2. Band widths with various basis sets (description as in Table 1).

Basis set	Band width (a.u.)				
STO-2G[a]	0.003	0.051	0.153	0.007 (π)[i]	0.0224
STO-3G[a]	0.001	0.042	0.138	0.008 (π)	0.020
	(0.001	0.049	0.144	0.008 (π)	0.023)[b]
STO-3G[c]	0.000	0.043	0.135	0.013 (π)	0.020
	(0.000	0.045	0.134	0.014 (π)	0.019)[d]
STO-3G[e]	0.000	0.043	0.134	0.016 (π)	0.021
STO-3G[f]	0.000	0.036	0.126	0.013 (π)	0.010
4-31[g]	0.002	0.055	0.118	0.011	0.021 (π)
F(4s 2p)H(2s)[h]	0.000	0.063	0.193	0.019	0.025 (π)
F(4s 3p)H(3s)[h]	0.000	0.064	0.233	0.022	0.024 (π)

[i] crystal orbital from π atomic orbitals.

neighbours is five, which means that each atom is interacting with 5 neighbour atoms. In two basis sets the number of neighbours has been increased (Table 1). Few apparent conclusions can be done. Increase of the basis set leads to an increase of the energy gap. Large basis sets can produce a reordering of the bands. It was often claimed that in hydrogen bonded systems the p orbitals on hydrogens are of special significance. As can be seen from the results this statement is incorrect. The inclusion of p orbitals lowers the energy, but this result is trivial. The populations of p orbitals are very small. These conclusions are in agreement with results obtained previously [4] on hydrogen bonded clusters. The same effect can be observed also when 3s and 3p Gaussian functions are added to fluorine. Such an inclusion produces a lowering of the total energy and is in fact more effective than the inclusion of a polarization function on hydrogen. The number of neighbours influences the results less than various basis sets. As was mentioned before this conclusion may be not valid for typical molecular crystals where the separation between the unit cells is of the same order of magnitude as the distances within cells.

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[1] G. Del Re, J. Ladik, and G. Biczo, Phys. Rev. **155**, 997 (1967).
[2] M. Atoji and W. N. Lipscomb, Acta Cryst. **7**, 173 (1954).
[3] S. P. Habuda and Yu. V. Gagarinsky, Acta Cryst. **B27**, 1677 (1971).
[4] P. A. Kollman and L. C. Allen, J. Amer. Chem. Soc. **92**, 6101 (1970).
[5] W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. **51**, 2657 (1969).
[6] N. W. Winter, W. A. Goddard, and F. W. Bobrowicz, J. Chem. Phys. **62**, 4325 (1975).
[7] R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. **54**, 724 (1971).
[8] T. H. Dunning, J. Chem. Phys. **53**, 2823 (1970).