Localized Orbitals in Hydrogen-Bonded Systems

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The localized orbitals in hydrogen bonded systems are de-
scribed. The localized orbitals of the systems are composed of the
localized orbitals of the proton donors and acceptors. The three-
-center model for the hydrogen bond is found to be inadequate.

In recent years a large number of papers appear which treat the electronic
configuration of hydrogen bonded systems using the molecular orbital
method[1]. The aim of this paper is to deduce the localized orbitals from the
molecular ones. With this approach we would like to obtain some new insight
into the phenomena of the hydrogen bonding that are more easily inferred
from the localized orbitals than from the canonical molecular ones. The studied
systems were HF, HF_2^-, HCOOH, $(HCOOH)_2$, H_2O, and $(H_2O)_2$. The canonical
orbitals were obtained with the CNDO method (parametrization from ref. 2)
for the geometries from ref. 3 and ref. 4.

The localized procedure we have used is due to Edmiston and Rueden-
berg[5]. The localized orbitals for the HF and H_2O can be compared with the
ones calculated from the *ab-initio* procedure[5]. The differences between the
coefficients corresponding to the atomic orbitals in the localized molecular
orbitals are of the order of 0.08. These small differences are the reason of
our confidence that the localized orbitals of all the treated systems are
meaningful.

i) HF, $(HF_2)^-$

The localized orbitals of HF consist of the HF bond and three lone pairs
on the F atom. For the reason to be stated later we listed in Table I (also
in Table II and III) only the changes in the coefficients between hydrogen-
bonded and unbonded system. The meaning of the term »changes« is as
follows:

The localized orbitals of the hydrogen-bonded system consist of the
atomic orbitals, with the appropriate coefficients, from the proton donor and
the acceptor. In the Tables are listed the differences between the coefficients
of the hydrogen-bonded and the unbonded donors and the coefficients of
the hydrogen-bonded acceptors. In brackets are listed some values for the
orbitals of the unbonded donors. The localized orbitals of (FHF)⁻ are two
F—H bonds and the lone pairs on F atoms. The changes on the localized
orbitals of the proton donor (HF) are of the same order of magnitude as
the values of the coefficients from the proton acceptor (F⁻).

TABLE I

Differences between the Coefficients of the Localized Orbitals of the Hydrogen Bonded and Unbonded System

Coefficients (absolute values) of the unbonded system are in brackets.

	$(1s)_{H1}$	$(2s)_{F2}$	$(2p_x)_{F2}$	$(2p_y)_{F2}$	$(2p_z)_{F2}$	$(2s)_{F3}$	$(2p_x)_{F3}$	$(2p_y)_{F3}$	$(2p_z)_{F3}$	
	—0.18255	—0.19214	0.12577	~ 0	~ 0	0.01919	0.07150	~ 0	~ 0	HF bond
	(0.54391)	(0.24681)	(0.80209)	(~ 0)	(~ 0)					
	0.1220	0.03633	—0.28542	~	~	0.00726	0.02680	~	~	lone pair

F2 —— H1 —— F3

$y \uparrow \quad \xrightarrow{\ x\ }$
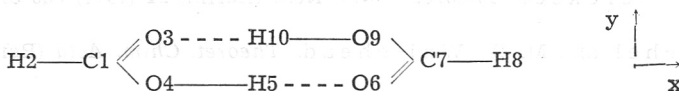
ii) HCOOH, (HCOOH)$_2$

In Table II only a few interesting changes in the localized orbitals are listed. Again, as in the previous system i), the same conclusion can be inferred from Table II. From Table II one can conclude that the changes in localized orbitals are not greater on the bonds or the lone pairs directly affected by the hydrogen bond. The changes are almost the same on the O 4 H 5 bond or O 3 lone pair as well as on the C 1O3 σ bond or C 1O3 π bond. This consequence is in accordance with the conclusion[6] that the three-center model can not adequately represent the hydrogen bond.

TABLE II

Differences ($\times$ 10^{-5}) between the Coefficients of the Localized Orbitals of the Hydrogen-Bonded and Unbonded System

Coefficients (absolute values) of the unbonded system are in brackets

$(2\,s)_{C1}$	$(2\,p_x)_{C1}$	$(2\,p_y)_{C1}$	$(2\,p_z)_{C1}$	$(1\,s)_{H2}$	$(2\,s)_{O3}$
— 2296	— 3681	4991	0	2660	1243
431	3887	3787	0	— 3312	— 274
(0.00519)	(0.069521)	(0.00897)	(0)	(0.04725)	(0.00689)
— 1361	6371	— 2414	5	6406	2334

$(2\,p_x)_{O3}$	$(2\,p_y)_{O3}$	$(2\,p_z)_{O3}$	$(2\,s)_{O4}$	$(2\,p_x)_{O4}$	$(2\,p_y)_{O4}$
— 1471	5927	~ 0	3542	2251	— 128
4504	1350	0	3704	1571	— 4022
(0.00762)	(0.02656)	(0)	(0.17907)	(0.70942)	(0.22644)
— 17	— 869	~ 0	878	— 6665	333

$(2\,p_z)_{O4}$	$(1\,s)_{H5}$	$(2\,s)_{O6}$	$(2\,p_x)_{O6}$	$(2\,p_y)_{O6}$	$(2\,p_z)_{O6}$
0	2257	195	902	517	0
6	— 2892	1009	1860	2328	404
(0)	(0.63670)				
6	1036	35	3835	775	1045

$(2\,s)_{C7}$	$(2\,p_x)_{C7}$	$(2\,p_y)_{C7}$	$(2\,p_z)_{C7}$	$(1\,s)_{H8}$	$(2\,s)_{O9}$
881	560	538	0	~ 0	860
2396	543	1563	159	1224	2471
975	4188	1607	409	4160	3073

$(2\,p_x)_{O9}$	$(2\,p_y)_{O9}$	$(2\,p_z)_{O9}$	$(1\,s)_{H10}$	
2198;	1456;	0	3461	O 3 lone pair
1982	537	8	3984	O 4 H 5 bond
356	1203	5	767	C 1 O 4 σ bond

$$\begin{array}{c} \text{O3} ---- \text{H10} ——— \text{O9} \\ \text{H2——C1} \big< \qquad\qquad\qquad \big> \text{C7——H8} \\ \text{O4} ——— \text{H5} ---- \text{O6} \end{array}$$

y →
x →

iii) H_2O, $(H_2O)_2$

The results of the calculations carried out for these systems are summarized in Table III. From the listed values similar conclusions can be drawn as for the above mentioned systems.
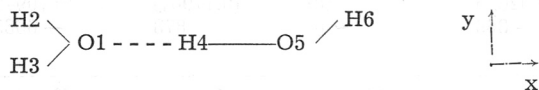
TABLE III

Differences ($\times 10^{-5}$) between the Coefficients of the Localized Orbitals of the Hydrogen-Bonded and Unbonded System

Coefficients (absolute values) of the unbonded system are in brackets

$(2s)_{O1}$	$(2p_x)_{O1}$	$(2p_y)_{O1}$	$(2p_z)_{O1}$	$(1s)_{H2}$	$(1s)_{H3}$	
102	218	11	~0	206	206	
982	2673	36	~0	2244	2283	
153	480	0	0	356	349	
0	120	116	0	0	−153	
−59	−76	83	~0	−35	127	
139	−100	134	0	112	−87	

$(1s)_{H4}$	$(2s)_{O5}$	$(2p_x)_{O5}$	$(2p_y)_{O5}$	$(2p_z)_{O5}$	$(1s)_{H6}$	
275	−381	257	−185	~0	204	O 5 H 6 bond
−89	−648	69	−99	~0	293	O 5 H 4 bond
(0.67892)	(0.14370)	(0.71783)	(0.03505)	(0)	(0.04393)	O 5 lone pair
0	274	−838	−507	~0	0	O 1 lone pair
230	424	1842	354	0	0	O 1 H 2 bond
1290	201	854	149	0	35	O 1 H 3 bond
1306	196	785	182	~0	~0	O 1 H 3 bond

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   H2                                   H6
     \                                 /
      O1 - - - - H4 ———— O5          y ↑
     /                                 |
   H3                                  | — — → x
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CONCLUSIONS

The localized orbitals of the hydrogen bonded systems can be described, to a very good approximation, as composed of the localized orbitals of the proton donors and acceptors. This includes the statement that there is not any trace of a localized bond between the two constituents. The changes of the localized orbitals on proton donor increase with the hydrogen bond strength.

The influence of the hydrogen bond spreads over the whole complex and therefore the three-center model[7] can not reproduce the changes introduced by it.

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IZVLEČEK

Lokalizirane orbitale sistemov z vodikovo vezjo

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Izračunane so lokalizirane orbitale sistemov z vodikovo vezjo. Iz velikosti sprememb lokaliziranih orbital s tvorbo vodikove vezi, lahko sklepamo, da trocentrični model ni primeren za popis teh vezi.

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