The Electronic Structure of the Hydrogen Fluoride Ion

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In order to throw light upon the hydrogen bond, the author has taken up the $[FHF]^-$ ion that is the simplest one in a theoretical treatment, and has carried out quantum-mechanical calculations for this ion.

As is well known, the hydrogen fluoride ion exists in such ionic crystals as sodium, potassium, and ammonium hydrogen fluorides and consists of the F-H-F hydrogen bond. An X-ray study[1] of potassium hydrogen fluoride has given the F···F distance of 2.26 Å. It has hitherto been a question whether the proton is at the center of two fluorine atoms or not. Peterson and Levy[2] have recently found by the neutron diffraction study that the proton occupies the central position in the linear F-H-F ion. Based on this fact, the "LCAO SCF MO method" developed by Roothan[3] was applied to the ground state of the $[FHF]^-$ ion and the nature of the F-H-F hydrogen bond was discussed.

Outline of Calculations

The calculation was carried out by taking the eleven atomic orbitals f, f', s, s', σ, σ', π_+, π_+', π_-, π_-' and h into consideration, which stand for $1s$, $2s$, $2p\sigma$*, $2p\pi_+$ and $2p\pi_-$ orbitals of two fluorine atoms and $1s$ orbital of the hydrogen atom, respectively. All the electrons were assigned to MO's extending throughout the ion and the interactions between them were explicitely included, while the $1s$ electrons of two fluorine atoms were treated as the inner-shell of the ion, because of the very small mixing with the valence electrons.

The AO's used were the analytical SCF AO's[4] for neutral fluorine, fluorine anion and hydrogen. The one-center integrals of fluorine atoms were evaluated as the arithmetic mean values of those for neutral fluorine and fluorine anion, using these SCF AO's. This procedure is based on the fact that each fluorine atom in this ion is considered as $F^{-1/2}$. The evaluations of the two-center and the three-center integral using the SCF AO's are, however, very cumbersome and it was, therefore, assumed that the use of Slater-type AO's**

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[1] L. Helmholz and M. Rogers, *J. Am. Chem. Soc.*, **61**, 2590 (1939).

[2] S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, **20**, 704 (1952).

[3] C. C. J. Roothan, *Rev. Modern Phy.*, **23**, 69 (1951).

* The $2p\sigma$ and $2p\sigma'$ orbitals are pointed towards the central atom along the molecular axis, respectively.

[4] F. W. Brown, *Phys. Rew.* **44**. 214 (1933) ; Hamano, *Bull. Tokyo Gakugei University* **6**, 9, (1955).

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$$h=(1/\pi)^{1/2}\exp(-r),$$
$$f=(z_1^3/\pi)^{1/2}\exp(-z_1 r),$$
$$s=(z_2^5/3\pi)^{1/2}\exp(-z_2 r),$$
$$\sigma=(z_2^5/\pi)^{1/2}\exp(-z_2 r)\,r\cos\theta,$$
$$\pi_\pm=(z_2^5/\pi)^{1/2}\exp(-z_2 r)\,r\sin\theta\exp(\pm\phi_i)$$
where $z_1=8.75$, $z_2=2.47$.

TABLE I

SYMMETRY ORBITALS

Symmetry species	σ_g	σ_u	π_u	π_g
Symmetry orbitals	$\sigma_1=f+f'$	$\sigma_5=f-f'$	$\sigma_8=\pi_\pm-\pi_\pm'$	$\sigma_9=\pi_\pm+\pi_\pm'$
	$\sigma_2=s+s'$	$\sigma_6=s-s'$		
	$\sigma_3=\sigma+\sigma'$	$\sigma_7=\sigma-\sigma'$		
	$\sigma_4=h$			

TABLE II

LCAO MO

$K(\sigma_g)=2^{-1/2}\sigma_1$	$K(\sigma_u)=2^{-1/2}\sigma_5$	$1\pi_u=a_{66}\sigma_8$
$1\sigma_g=a_{11}\sigma_2+a_{12}\sigma_3+a_{13}\sigma_4$	$1\sigma_u=a_{44}\sigma_6+a_{45}\sigma_7$	$1\pi_g=a_{77}\sigma_9$
$2\sigma_g=a_{21}\sigma_2+a_{22}\sigma_3+a_{23}\sigma_4$	$2\sigma_u=a_{54}\sigma_6+a_{55}\sigma_7$	
$3\sigma_g=a_{31}\sigma_2+a_{32}\sigma_3+a_{33}\sigma_4$		

instead of the SCF AO's gives satisfactory approximations to these integral values. The greater part of the two-center integrals and a few one-electron three-center integrals*** were exactly calculated. The other two-center and three-center integrals were obtained by Mulliken's approximation⁶⁾. The numerical values of these integrals are given in the appendix.

The $[FHF]^-$ ion is a linear ion belonging to the symmetry group $D_{\infty h}$. The LCAO MO's were chosen so that they belong in sets to irreducible representations of the group $D_{\infty h}$. It is convenient to introduce symmetry orbitals. These were given in Table I with the irreducible representations of the group $D_{\infty h}$.

The LCAO MO's were made up by taking linear combinations of symmetry orbitals, as shown in Table II.

Here the order of increasing number for the MO's within each symmetry species is the order of increasing energy. K refers to MO's made up of inner shell electrons only.

The ground state of this ion is to be ${}^1\Sigma^+{}_g$, resulting from configuration $(K(\sigma_g))^2$, $(K(\sigma_u))^2$, $(1\sigma_g)^2$, $(1\sigma_u)^2$, $(2\sigma_g)^2$, $(2\sigma_u)^2$, $(1\pi_u)^4$, $(1\pi_g)^4$.

The total normalized wave function is then built up as an anti-symmetrized product of these LCAO MO's. The requirement that the electronic energy should be an absolute minimum leads to the following matrix equations:

$$(\boldsymbol{H}+\boldsymbol{G})\boldsymbol{a}_i=\varepsilon_i\boldsymbol{S}\boldsymbol{a}_i \qquad (1)$$

As the definitions of these notations are given in detail by Roothan³⁾ and Mulligan⁷⁾, they will not be repeated here. The problem of finding the best LCAO MO's for the ground state thus reduces to the solution of the secular equation (1). This is attained by repeating a self-consistent field procedure.

Results and Discussion

The LCAO SCF MO's of the lowest energy state obtained by the SCF procedure are given in Table III.

TABLE III

LCAO SCF MO

LCAO SCF MO	Orbital energies (eV)
$K(\sigma_g)=2^{-1/2}(f+f')$	—
$1\sigma_g=0.768(s+s')+0.039(\sigma+\sigma')-0.199\,h$	−41.22
$2\sigma_g=-0.133(s+s/)+0.533(\sigma+\sigma')+0.464\,h$	−19.20
$3\sigma_g=0.476(s+s')+0.777(\sigma+\sigma')-1.669\,h$	—
$K(\sigma_u)=2^{-1/2}(f-f')$	—
$1\sigma_u=0.708(s-s')+0.082(\sigma-\sigma')$	−41.07
$2\sigma_u=-0.069(s-s')+0.711(\sigma-\sigma')$	−18.46
$1\pi_u=0.502(\pi_\pm-\pi_\pm')$	−16.22
$1\pi_g=0.498(\pi_\pm+\pi_\pm')$	−15.99

Except $3\sigma_g$ orbital, they are filled by two electrons with paired spins in the ground state.

The "LCAO orbital energies" obtained for these LCAO SCF MO's are also shown in Table III. These orbital energies represent good approximations to the ionization energies of the corresponding electron shells. Unfortunately, the experimental values of the ionization energies of the $[FHF]^-$ ion have not yet been obtained. The calculated minimum ionization energy in the present work is 15.99 eV. This value is somewhat lower than that of a fluorine atom (17.42 eV)⁸⁾ and that of a hydrogen

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*** These integral values were calculated by Oohata's method⁵⁾.

5) K. Oohata, *Busseiron Kenkyu*, **50**, 38 (1952).

6) R. S. Mulliken, *J. Chim. Phys.*, **46**, 500, 521 (1949).

7) J. F. Mulligan, *J. Chem. Phys.*, **19**, 347 (1951).

8) C. E. Moore, "Atomic Energy Levels", Vol. 1, Nat. Bur. Standards, Circ. 467, U. S. Department of Commerce, Washington (1949).

fluoride (19.38 eV)****. But this value seems to be too high considering that this ion is an anion. This is considered to be caused by the increasing inter-electronic repulsion compared to fluorine atom and hydrogen fluoride, because this ion is an anion.

It is convenient to adopt an equivalent orbital representation to indicate localized features of the electronic distribution in molecules or ions. The localized equivalent orbitals can be obtained by a unitary transformation of the above MO's. In the case of this ion, the localized equivalent orbitals for the σ-direction can be derived from the four occupied MO's $1\sigma_g$, $2\sigma_g$, $1\sigma_u$, and $2\sigma_u$ as linear sums of these MO's: the two $(b\sigma)$, $(b\sigma)'$ which have a bonding character, the other two $(l\sigma)$, $(l\sigma)'$ which have a lone pair character. These orbitals obtained are given in Table IV.

TABLE IV

EQUIVALENT LOCALIZED ORBITALS

$(l\sigma)=0.943s+0.353\sigma$

$(l\sigma)'=0.943s'+0.353\sigma'$

$(b\sigma)=-0.468s-0.132s'+0.809\sigma-0.139\sigma' +0.359\,h$

$(b\sigma)'=-0.468s'-0.132s+0.809\sigma'-0.139\sigma +0.359\,h$

As is seen from this result, the lone-pair orbitals have mainly s-character. On the other hand, in the bonding orbitals, only the σ-electron has a bonding property with the 1s orbital of hydrogen. This indicates that the fluorine orbitals of the F-H bonds have the almost pure p-character.

As a rough estimation of the electron distribution throughout this ion, the polarity of the $[FHF]^-$ ion has been examined. The result from the present calculation indicates that the charge densities of the $[FHF]^-$ ion may be formulated as $F^{-0.78}H^{+0.56}F^{-0.78}$. It would be expected that the polarity of the bond in this ion may be very great, because of the large difference of electronegativity between the fluorine and the hydrogen atom. The above result agrees with this expectations and it indicates that this hydrogen bond is also electrostatic. The special strength of this hydrogen bond is, therefore, considered to be based on the contributions of strong ionic character as well as covalency.

The conclusion obtained may be qualitatively correct, but should not be taken as final. The reasons are as follows: (1) The approximate atomic orbitals were used. (2) Most of the values of energy integrals were approximately evaluated. (3) A configuration interaction was neglected. (4) The MO method was applied to the large distance such as was the case for this ion. For example, the $S_{\sigma h}$ value in this work was 0.2671, while the $S_{\sigma h}$ value using the SCF AO's for fluorine and fluorine anion are 0.3525 and 0.4287, respectively.

In view of these factors, the quantum-mechanical treatment of the hydrogen bonds seems to be more troublesome than that of normal chemical bonds. It is desirable that the improvement of these points should be done in future.

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Appendix

Numerical Tables of Energy Integrals: Values for all but the overlap integrals are given in atomic units (1 atomic unit = 27.204 eV). In the Tables, the energy integrals marked by an asterisk are the approximate values. We shall list the following notations for the many types of energy integrals.

Overlap integrals:

$$S_{pq}=\int\psi_p(1)\psi_q(1)d\tau^1.$$

Kinetic energy integrals:

$$(\psi_p|-1/2\Delta|\psi_q')=\int\psi_p(1)(-1/2\Delta)\psi_q(1)d\tau^1.$$

Nuclear attraction integrals:

$$(A:\psi_p\psi_q')=\int\psi_p(1)(1/r_{a_1})\psi_q'(1)d\tau^1.$$

Coulomb integrals:

$$(pq:r't')=\int\psi_p(1)\psi_r'(2)(1/r_{12})\psi_q(1)\psi_t'(2)d\tau^{1,2}.$$

Exchange integrals:

$$(pr':qt')=\int\psi_p(1)\psi_q(2)(1/r_{12})\psi_r(1)\psi_t'(2)d\tau^{1,2}.$$

Hybrid coulomb-exchange integrals:

$$(pq:rt')=\int\psi_p(1)\psi_r(2)(1/r_{12})\psi_q(1)\psi_t'(2)d\tau^{1,2}.$$

TABLE V

ONE-CENTER INTEGRALS

$(F:ff)$	8.7500	$(ff:pp)$	1.1349
$(F:ss)$	1.3125	$(ss:ss)$	0.7755
$(F:pp)$	1.1456	$(pp:pp)$	0.8061
$\left(f\left\|-\frac{1}{2}\Delta\right\|f\right)$	38.2813	$(ss:pp)$	0.7612
$\left(s\left\|-\frac{1}{2}\Delta\right\|s\right)$	3.5945	$(p_xp_x:p_zp_z)$	0.7284
$\left(p\left\|-\frac{1}{2}\Delta\right\|p\right)$	2.7875	$(fs:fs)$	0.0955
$(ff:ff)$	5.4688	$(fp:fp)$	0.0413
$(ff:ss)$	1.1759	$(p_xp_z:p_xp_z)$	0.0388

**** This value[9] was obtained by the same method as this work. The experimental value for this molecule has not yet been obtained.

9) H. Hamano, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **77**, 985 (1956).

10) R. S. Mulliken, *J. Chem. Phys.*, **46**, 497, 675 (1949).

TABLE VI

TWO-CENTER INTEGRALS

S_{sh}	0.3772	$(sh : hh)$	0.1976
$S_{\sigma h}$	0.2671	$(\sigma h : \sigma h)$	0.0767
$(F : hh)$	0.4478	$(\sigma h : hh)$	0.1851
$(F : sh)$	0.3311	$(\pi h : \pi h)$	0.0157
$(F : \sigma h)$	0.1920	$(ss : sh)$	0.2722
$(H : sh)$	0.2506	$(ss : \sigma h)$	0.1725
$(H : \sigma h)$	0.2671	$(s\sigma : sh)$	0.0349
$(ff : hh)$	0.4474	$(s\sigma : \sigma h)$	0.0711
$(ss : hh)$	0.4338	$(s\pi : \pi h)$	0.0499
$(\sigma\sigma : hh)$	0.4574	$(\sigma\sigma : sh)$	0.2781
$(s\sigma : hh)$	0.0898	$(\sigma\sigma : \sigma h)$	0.1878
$(\pi\pi : hh)$	0.4220	$(\sigma\pi : \pi h)$	0.0068
* $(fh : fh)$	0.0023	$(\pi\pi : sh)$	0.2692
$(sh : sh)$	0.1061	$(\pi\pi : \sigma h)$	0.1648
$(sh : \sigma h)$	0.0773		
$S_{ss'}$	0.0122	$(s\sigma : \pi'\pi')$	0.0307
$S_{s\sigma'}$	0.0176	$(s\pi : s'\pi')$	0.0044
$S_{\sigma\sigma'}$	0.0249	$(s\pi : \sigma'\pi')$	0.0013
$S_{\pi\pi'}$	0.0035	$(\sigma\sigma : \sigma'\sigma')$	0.2478
$(F : ss')$	0.0062	$(\sigma\sigma : \pi'\pi')$	0.2368
$(F : s\sigma')$	0.0096	$(\sigma\pi : \sigma'\pi')$	0.0005
$(F : \sigma\sigma')$	0.0123	$(\pi_+\pi_+ : \pi_{+'}\pi_{+'})$	0.2281
$(F : \pi\pi')$	0.0016	$(\pi_+\pi_- : \pi_{-'}\pi_{+'})$	0.0003
$(F : s'\sigma)$	0.0081	* $(fs' : fs')$	0.0000
$(F : s's')$	0.2342	* $(f\sigma' : f\sigma')$	0.0000
$(F : s'\sigma')$	0.0320	* $(fs' : f\sigma')$	0.0000
$(F : \sigma'\sigma')$	0.2405	* $(f\pi' : f\pi')$	0.0000
$(F : \pi'\pi')$	0.2310	* $(ss' : ss')$	0.0001
$(H : ss)$	0.4673	* $(ss' : \sigma s')$	0.0002
$(H : s\sigma)$	0.1263	* $(ss' : \sigma\sigma')$	0.0002
$(H : \sigma\sigma)$	0.5155	* $(ss' : \pi\pi')$	0.0000
$(H : \pi\pi)$	0.4431	* $(s\sigma' : \sigma s')$	0.0002
* $(ff : f'f')$	0.2342	* $(s\sigma' : \sigma\sigma')$	0.0003
* $(ff : s's')$	0.2342	* $(s\sigma' : \pi\pi')$	0.0000
* $(ff : \sigma'\sigma')$	0.2405	* $(s\pi' : \pi s')$	0.0000
* $(ff : \pi'\pi')$	0.2310	* $(s\pi' : \pi\sigma')$	0.0000
$(ss : s's')$	0.2342	* $(\sigma s' : \sigma s')$	0.0002
$(ss : \sigma'\sigma')$	0.2405	* $(\sigma\sigma' : \sigma\sigma')$	0.0004
$(ss : s'\sigma')$	0.0320	* $(\sigma\sigma' : \pi\pi')$	0.0000
$(ss : \pi'\pi')$	0.2310	* $(\sigma\pi' : \pi\sigma')$	0.0000
$(s\sigma : s'\sigma')$	0.0088	* $(\pi s' : \pi s')$	0.0000
$(s\sigma : \sigma'\sigma')$	0.0346	* $(\pi s' : \pi\sigma')$	0.0000
* $(\pi\sigma' : \pi\sigma')$	0.0000	* $(s\sigma : ss')$	0.0002
* $(\pi_+\pi_{+'} : \pi_+\pi_{+'})$	0.0000	* $(s\sigma : \sigma s')$	0.0003
* $(s\sigma : s\sigma')$	0.0003	* $(s\sigma : \pi\pi')$	0.0001
* $(s\sigma : \sigma\sigma')$	0.0004	* $(s\pi : \pi\sigma')$	0.0000
* $(\pi_+\pi_{-'} : \pi_+\pi_{-'})$	0.0000	* $(s\pi : \sigma\pi')$	0.0000
* $(ff : ss')$	0.0089	* $(\sigma\sigma : ss')$	0.0070
* $(ff : s\sigma')$	0.0129	* $(\sigma\sigma : s\sigma')$	0.0101
* $(ff : \sigma s')$	0.0128	* $(\sigma\sigma : \sigma s')$	0.0106
* $(ff : \sigma\sigma')$	0.0183	* $(\sigma\sigma : \sigma\sigma')$	0.0151
* $(ff : \pi\pi')$	0.0026	* $(\sigma\sigma : \pi\pi')$	0.0019
* $(fs : fs')$	0.0001	* $(\sigma\pi : \pi s')$	0.0000
* $(fs : f\sigma')$	0.0000	* $(\sigma\pi : s\pi')$	0.0000
* $(f\sigma : fs')$	0.0000	* $(\sigma\pi : \pi\sigma')$	0.0000
* $(f\sigma : f\sigma')$	0.0000	* $(\sigma\pi : \sigma\pi')$	0.0000
* $(f\pi : f\pi')$	0.0000	* $(\pi\pi : s\sigma')$	0.0100
* $(ss : ss')$	0.0069	* $(\pi\pi : \sigma s')$	0.0096
* $(ss : s\sigma')$	0.0100	* $(\pi\pi : \sigma\sigma')$	0.0137
* $(ss : \sigma s')$	0.0100	* $(\pi_+\pi_+ : \pi_+\pi_{+'})$	0.0002
* $(ss : \sigma\sigma')$	0.0142	* $(\pi_+\pi_- : \pi_-\pi_{+'})$	0.0000
* $(ss : \pi\pi')$	0.0020		

TABLE VII

THREE CENTER INTEGRALS

$(F' : hs)$	0.1066	* $(sh : s\sigma')$	0.0023
$(F' : h\sigma)$	0.0954	* $(sh : \sigma s')$	0.0034
* $(H : ss')$	0.0057	* $(sh : \sigma\sigma')$	0.0048
* $(H : s\sigma')$	0.0022	* $(sh : \pi\pi')$	0.0007
* $(H : \sigma\sigma')$	0.0128	* $(sh : s'h)$	0.0614
* $(H : \pi\pi')$	0.0016	* $(sh : \sigma'h)$	0.0442
* $(f'f' : sh)$	0.1285	* $(\sigma h : ss')$	0.0016
* $(f'f' : \sigma h)$	0.0919	* $(\sigma h : s\sigma')$	0.0024
* $(f's : f'h)$	0.0000	* $(\sigma h : \sigma s')$	0.0025
* $(f'\sigma : f'h)$	0.0000	* $(\sigma h : \sigma\sigma')$	0.0354
* $(ss : s'h)$	0.1260	* $(\sigma h : \pi\pi')$	0.0005
* $(ss : \sigma'h)$	0.0900	* $(\sigma h : \sigma'h)$	0.0319
* $(s\sigma : s'h)$	0.0230	* $(\pi h : \pi s')$	0.0000
* $(s\sigma : \sigma'h)$	0.0166	* $(\pi h : \pi\sigma')$	0.0000
* $(s\pi : \pi h')$	0.0000	* $(\pi h : s\pi')$	0.0000
* $(\sigma\sigma : s'h)$	0.1316	* $(\pi h : \sigma\pi')$	0.0000
* $(\sigma\sigma : \sigma'h)$	0.0942	* $(\pi h : \pi'h)$	0.0000
* $(\sigma\pi : \pi'h)$	0.0000	* $(hh : ss')$	0.0053
* $(\pi\pi : s'h)$	0.1231	* $(hh : s\sigma')$	0.0078
* $(\pi\pi : \sigma'h)$	0.0880	* $(hh : \sigma\sigma')$	0.0114
* $(sh : ss')$	0.0023	* $(hh : \pi\pi')$	0.0015

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