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關於氟化氫分子的一個計算*

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在這篇短文裏，我們根據量子力學，計算氟化氫分子的各個構造常數。計算時採用氟離子被氫離子極化的看法，利用變分法計算；氟離子中各個電子的哈吹氏函數，用了以前布朗氏[1]所計算的結果。氟離子所有電子的總的波函數，是一個行列式的形狀，用 ψ_0 代表之。我們假定氟化氫分子中所有電子的總的波函數 ψ，是如下的簡單形狀：

$$\psi \propto (1 + as)\, \psi_0$$

式中參變數 a 將由變分法決定，而 s 代表各電子在分子軸方向的座標的總和。加入這個 $1 + as$ 因子，是想粗淺地來表示氟離子所受氫離子的極化影響。茲列表比較所得的計算結果與查到的實驗結果[2]，如下：（結合能指分解分子為兩離子而計）

	分子距離	結合能	振動波數	電偶矩
計算值	1.11 Å	10.84 *ev*	2797 cm^{-1}	2.13 *debyes*
實驗值	0.92 Å	15.66 *ev*	3962 cm^{-1}	1.91 *debyes*

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* 本文根據於作者 1950 在清華大學所交入碩士論文。

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[1] Brown, *Phys. Rev.* **44**, (1933), 223.

[2] Landolt-Börnstein, *Phys. Chem. Tabelen*, 1935, Smyth and Hannay, *J. Am. Chem. Soc.* **68**, (1946), 171.

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A QUANTUM MECHANICAL CALCULATION FOR THE MOLECULE HF*

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ABSTRACT

A quantum-mechanical variational calculation is made for the molecule HF, based on the ionic model, the fluorine negative ion being polarized on the whole by the proton. Brown's numerical results for the Hartree-Fock functions of the fluorine ion are used. The calculated results do not agree well with the experimental results, which indicates that, even for this most polar molecule, the above model serves only for a very poor representation of the motion of the electrons in the molecule.

Since we shall confine ourselves to internuclear distances large in comparison with the 1s orbit of the fluorine atoms, the two 1s electrons can be grouped together with the fluorine nucleus. We split the Hamiltonian for the remaining eight electrons of the molecule HF into the following two parts, in accordance with the ionic model:

$$H = H_o + v. \tag{1}$$

Here H_o represents the Hamiltonian for the fluorine ion, while v denotes the interaction of this ion with the proton. If we denote the distance of the j-th electron from the proton by r'_j, and denote the internuclear distance by R, we have, using atomic units throughout.

$$v = \frac{7}{R} - \sum_{j=1}^{8} \frac{1}{r'_j}. \tag{2}$$

For the free fluorine ion the Hartree-Fock functions have been obtained approximately by Brown[1], the radial functions for 1s, 2s and 2p are denoted

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[1] *Phys. Rev.* **44** (1933), 223.

by f_1, f_2 and f_3. Regarded as an eight-electron system we simply take for the wave function of the free fluorine ion the following determinant

$$\psi_o = (8!)^{-\frac{1}{2}} \, det\, [u_1, u_2, u_3, \dots u_8], \tag{3}$$

with

$$\left.\begin{aligned} u_1 &= \frac{f_2}{r} \cdot \frac{1}{2\sqrt{\pi}} \cdot \alpha, \qquad u_2 = \frac{f_2}{r} \cdot \frac{1}{2\sqrt{\pi}} \cdot \beta, \\ u_3 &= \frac{f_3}{r} \cdot \frac{\sqrt{3}}{2\sqrt{\pi}} \sin\theta \cos\varphi \cdot \alpha, \dots, u_8 = \frac{f_3}{r} \cdot \frac{\sqrt{3}}{2\sqrt{\pi}} \cos\theta \cdot \beta. \end{aligned}\right\} \tag{4}$$

Here the spin functions are denoted by α and β as usual. The various one-electron functions are normalized and are mutually orthogonal, so the wave function (3) is normalized to unity.

For the molecule HF we shall use the variational method and try to take into account the polarization of the fluorine ion by the proton by using a variational function of the following form:

$$\psi = S\psi_o, \qquad S = \frac{1 + a s}{\sqrt{1 + a^2 \overline{s^2}}}, \qquad s = \sum_j z_j = \sum_j r_j \cos\theta_j. \tag{5}$$

Here the parameter a is to be determined by minimizing the energy. The polar axis for the spherical coordinate is directed from the origin at the fluorine nucleus to the proton. The bar on the top of a letter denotes the average with the weight ψ_o^2. Hence by symmetry $\bar{s}$ vanishes, so the ψ of (5) is correctly normalized to unity.

We shall refer the energy of the molecule to that of free ions at infinite distance of separation. This is given by the minimum of the following quantity

$$\begin{aligned} \varepsilon(a) \equiv \int \psi H \psi \, d\tau - \int \psi_o H_o \psi_o \, d\tau = \int v\, S^2 \psi_o^2 \, d\tau \\ + \int \psi_o S (H_o S - S H_o) \psi_o \, d\tau + \int \psi_o S^2 H_o \psi_o \, d\tau - \int \psi_o H_o \psi_o \, d\tau. \end{aligned} \tag{6}$$

Here the last two terms will cancel each other exactly if ψ_o is an exact eigenfunction for H_o. Now ψ_o is obtained only approximately by the Hartree-Fock method, these terms will not cancel exactly, leaving a difference which we shall neglect in what follows. The integral containing the commutator between H_o and S can be transformed by means of Green's theorem, and we get

$$\int \psi_o S\,(H_o S - S H_o)\,\psi_o\,d\tau = \frac{a^2}{1 + a^2\,\overline{s^2}} \int \psi_o\, s\, \tfrac{1}{2} \sum \Big(z_j \nabla_j^2 - \nabla_j^2 z_j \Big) \psi_o\, d\tau$$

$$= -\frac{a^2}{1 + a^2\,\overline{s^2}} \int s\, \tfrac{1}{2} \sum_j \frac{\partial}{\partial z_j} (\psi_o^2)\, d\tau = \frac{4\,a^2}{1 + a^2\,\overline{s^2}} \tag{7}$$

Thus we get for (6) the simple expression

$$\varepsilon\,(a) = \overline{v} + \frac{A\,a + B\,a^2}{1 + C\,a^2}\,, \tag{8}$$

with the abbreviation

$$A = 2\,\overline{v\,s}\,, \qquad B = \overline{v\,s^2} - \overline{v}\cdot\overline{s^2} + 4\,, \qquad C = \overline{s^2}\,. \tag{9}$$

The expression (8) reaches its minimum

$$\varepsilon = \overline{v} + \tfrac{1}{2}\,A\,a = \overline{v} + \frac{B - \sqrt{B^2 + C\,A^2}}{2\,C} \tag{10}$$

at

$$a = \frac{B - \sqrt{B^2 + C\,A^2}}{C\,A}\,. \tag{11}$$

The value of this parameter is needed for the evaluation of the dipole moment of the molecule, for which we have

$$\mu = \int \psi\,(R - \sum_j z_j)\,\psi\,d\tau = R - \frac{2\,a\,C}{1 + C\,a^2}\,, \tag{12}$$

because $\overline{s}$ and $\overline{s^3}$ vanish by symmetry.

We note the following simple rules for expressing the average values of a symmetrical sum with the weight ψ_o^2 in terms of matrix elements involving the one-electron functions u_n:

$$\overline{\sum_j \alpha_j} = \sum_n (n \mid \alpha \mid n) , \tag{13}$$

$$\overline{\sum\sum_{j \neq k} \alpha_j \beta_k} = \sum_m \sum_n \Big\{ (m \mid \alpha \mid m)\,(n \mid \beta \mid n) - (n \mid \alpha \mid m)\,(m \mid \beta \mid n) \Big\} , \tag{14}$$

$$\overline{\sum\sum\sum_{i \neq j \neq k \neq i} \alpha_i \beta_j \gamma_k} = \sum_l \sum_m \sum_n \sum \pm (l' \mid \alpha \mid l)\,(m' \mid \beta \mid m)\,(n' \mid \gamma \mid n) . \tag{15}$$

The last summation in (15) includes the six permutations of l, m and n for l', m' and n', with plus or minus sign for even or odd permutation. Furthermore, for evaluating the one-electron matrix elements of $1/r'$, we use the following expansion into Legendre's polynomials

$$\frac{1}{r'} = \sum_{l=o}^{\infty} \delta_l(r,\ R)\, P_l(\cos\theta) , \qquad \delta_l(r,\ R) = \begin{cases} r^l / R^{l+1} \text{ for } r < R , \\ R^l / r^{l+1} \text{ for } r > R , \end{cases} \tag{16}$$

In this way we get, after some calculation,

$$v = \frac{7}{R} - \int_o^\infty (2 f_2^2 + 6 f_3^2)\, \delta_o\, dr , \tag{17}$$

$$C = \frac{1}{3} \int_o^\infty (2 f_2^2 + 6 f_3^2)\, r^2\, dr - \frac{4}{3} \Big\{ \int_o^\infty f_2 f_3\, r\, dr \Big\}^2 , \tag{18}$$

$$A = -\frac{2}{3} \int_o^\infty (2 f_2^2 + 6 f_3^2)\, r\, \delta_1\, dr + \frac{8}{3} \int_o^\infty f_2 f_3\, r\, dr \int_o^\infty f_2 f_3\, \delta_1\, dr , \tag{19}$$

$$\begin{aligned} B = 4 &- \frac{1}{3} \int_o^\infty (2 f_2^2 + 6 f_3^2)\, r^2 \left(\delta_o + \frac{2}{5}\delta_2\right) dr \\ &+ \frac{2}{3} \int_o^\infty f_2^2\, r^2\, dr \int_o^\infty f_3^2\, \delta_o\, dr + 2 \int_o^\infty f_3^2\, r^2\, dr \int_o^\infty f_3^2 \left(\delta_o + \frac{4}{25}\delta_2\right) dr \\ &+ \frac{8}{3} \int_o^\infty f_2 f_3\, r\, dr \int_o^\infty f_2 f_3\, r \left(\delta_o + \frac{2}{5}\delta_2\right) dr \\ &- \frac{4}{3} \Big\{ \int_o^\infty f_2 f_3\, r\, dr \Big\}^2 \int_o^\infty \Big\{ f_2^2 \delta_o + f_3^2 \left(\delta_o + \frac{2}{5}\delta_2\right) \Big\}\, dr . \end{aligned} \tag{20}$$

Here integrals of the following types occur:

$$I_l = R^{-l-1}\int_o^R (2f_2^2 + 6f_3^2)\, r^l\, dr\,, \qquad I_l' = R^{-l-1}\int_R^\infty (2f_2^2 + 6f_3^2)\, r^l\, dr\,;$$

$$J_l = R^{-l-1}\int_o^R f_2 f_3\, r^l\, dr\,, \qquad J_l' = R^{-l-1}\int_R^\infty f_2 f_3\, r^l\, dr\,;$$

$$L_l = R^{-l-1}\int_o^R f_3^2\, r^l\, dr\,, \qquad L_l' = R^{-l-1}\int_R^\infty f_3^2\, r^l\, dr\,.$$

Those which we need are calculated by numerical integration, using the numerical values for f_2 and f_3 given by Brown. The results are shown in the Table below:

TABLE 1. *Values for various integrals*

R	I_0	I_2	I_4	I'_{-1}	J_0	J_1
1.0	3.567	1.756	1.111	2.795	—.4301	—.3117
1.2	3.771	1.685	1.012	1.912	—.4653	—.3210
1.4	3.776	1.527	.8716	1.324	—.4698	—.3015
1.6	3.671	1.345	.7305	.9301	—.4575	—.2704
1.8	3.514	1.167	.6036	.6640	—.4366	—.2418
2.0	3.334	1.005	.4960	.4827	—.4123	—.2142
2.2	3.151	.8640	.4071	.3568	—.3873	—.1889
2.5	2.890	.6907	.3049	.2326	—.3521	—.1567
3.0	2.510	.4852	.1922	.1210	—.3009	—.1153
3.5	2.201	.3465	.1252	.0667	—.2607	—.0875
4.0	1.952	.2549	.0842	.0380	—.2291	—.0680

R	J_3	J'_{-2}	L_0	L_1	L'_{-1}	L'_{-3}
1.0	—.1840	—.2464	.4205	.2007	.3516	.1783
1.2	—.1708	—.1664	.4417	.1927	.2504	.1352
1.4	—.1488	—.1108	.4430	.1766	.1881	.1021
1.6	—.1252	—.0730	.4332	.1582	.1319	.0771
1.8	—.1032	—.0481	.4176	.1401	.0974	.0583
2.0	—.0842	—.0319	.3991	.1231	.0728	.0448
2.2	—.0683	—.0213	.3798	.1078	.0551	.0344
2.5	—.0501	—.0113	.3513	.0885	.0369	.0238
3.0	—.0299	—.0043	.3087	.0641	.0197	.0126
3.5	—.0182	—.0015	.2722	.0471	.0110	.0073
4.0	—.0115	—.0005	.2425	.0353	.0063	.0032

As $R \longrightarrow \infty$, we have $I_2 \longrightarrow 21\cdot 422\, R^{-3}$, $J_1 \longrightarrow -1\cdot 101\, R^{-2}$,

$J_o \longrightarrow -0\cdot 9196\, R^{-1}$, $L_2 \longrightarrow 3\cdot 110\, R^{-3}$.

From the numerical values given in Table 1 for the various integrals we get, by (17)—(20) and (10)—(12), the following results for the energy of the molecule and its dipole moment as a function of the internuclear distance *R*, as shown in Table 2:

TABLE 2. *Energy and dipole moment for the molecule HF*

R	$\bar{v}$	A	B	Aa/2	ε	μ
1.0	.638	—1.395	6.061	—.0751	.563	—.117
1.2	.150	—1.445	5.653	—.0852	.065	—.009
1.4	—.100	—1.450	5.278	—.0910	—.191	.125
1.6	—.226	—1.419	4.952	—.0923	—.318	.286
1.8	—.291	—1.346	4.708	—.0876	—.379	.485
2.0	—.317	—1.261	4.518	—.0801	—.397	.711
2.2	—.326	—1.174	4.369	—.0722	—.398	.946
2.5	—.323	—1.046	4.204	—.0603	—.383	1.313
3.0	—.298	—0.862	4.031	—.0435	—.342	1.946
3.5	—.267	—0.703	3.954	—.0300	—.297	2.595
4.0	—.240	—0.580	3.917	—.0208	—.261	3.229

C = 5.524

By interpolation from the values given in Table 2, we get the following calculated values for the molecular constants shown in Table 3, where comparison with the experimental values is also made.

TABLE 3. *Constants for the molecule HF*

	R_o	ε_o	μ_o	$\widetilde{\upsilon_e}$
Calculated values in atomic units	2.11	-.399	.843	(.2755)
Calculated values in usual units	1.11 Å	-10.84 ev	2.13 debyes	2797 cm^{-1}
Experimental values[2]	0.92 Å	-15.66 ev	1.91 debyes	3962 cm^{-1}

In Table 3, $\widetilde{\upsilon_e}$ denotes the vibrational frequency of the molecule, but the calculated value in atomic units refers to the curvature at the equilibrium distance, i.e. $(d^2\varepsilon/dR^2)$ at $R=R_O$ where $d\varepsilon/dR$ vanishes. Finally I wish to thank Professor H. W. Peng for suggesting the problem and for his guidance throughout the work.

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2. See Landolt-Bornstein, *Physikalisch-Chemische Tabelen* (1935), and Smyth and Hannay, *J. Am. Chem. Soc.* **68** (1946), 171.