

THE UNITED ATOM MODEL OF THE *HF* MOLECULE

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The united atom, which was used by the spectroscopists at the estimation of molecular values for more than two decades, is a suitable model in quantum chemistry too. The main features of the model are as follows : 1. Generally the nuclei are not moved adiabatically in one point, as they do in the united atom of spectroscopists, but hold their original equilibrium position or make little deviations from it. 2. The molecular eigenfunction is built up of one center one electron eigenfunctions according to the SLATER method. Excepting the geometrical configuration of the nuclei there is not any empirical or semiempirical parameter in this model. The calculations are extended to the treatment of the molecule *HF*. The theoretical values of the total energy, the dissociation energy and the equilibrium nuclear separation are in good agreement with the experimental ones.

Introduction

It is relatively not very difficult to calculate the energy at atoms of small atomic number by the aid of quantummechanical methods — at least — if the precision required is not too great. The problem is, however, far more complicated regarding molecules, since the orbitals of the electrons in the molecules extend to more atoms, which with the methods hitherto used results in the eigenfunctions having more centers. Thus more-center integrals occur in the calculation of the energy, and the evaluation of these are generally very cumbersome. In investigations concerning molecules, beside the natural demand of obtaining as precise values as possible, another not less important requirement is that the time necessary for the accomplishment of the calculations should not be too long. Therefore in the following such approximations will be used when calculating the eigenfunctions of the molecules, that the numerical work will be essentially no greater than in the case of atoms.

For this purpose the united atom treatment for example seems to be very suitable, which has been adapted recently by MATSEN [1] for the determination of the excited states of the H_2^+ molecule-ion. Further investigations [2] showed, that considering more configurations, the energy of the ground state of both the H_2^+ molecule-ion and the H_2 molecule can be determined well, though neither of these molecules can be taken in “good approximation” to be atomlike. Considering, that in the course of this treatment the molecule is always taken for a system having one center, i. e. for an “atom”, good

results by this approximation can be expected chiefly for such molecules, where one of the centers is of far more importance than the others, i. e. where the molecule is more atom-like. Diatomic molecules of such kind are the halogen-hydride molecules, where the perturbing effect of the proton results in distortions in the spherically symmetrical, atom-like charge distribution of the negatively charged halogen ion. The calculations were carried out for the HF molecule.

The method

The energy of the molecule will be calculated by the aid of the variational method. As is well known,

$$E = \frac{\int \Psi^* H \Psi d v}{\int \Psi^* \Psi d v},$$

where H is the Hamiltonian operator of the HF molecule and Ψ denotes its eigenfunction. The HF molecule has ten electrons. The Hamiltonian operator is thus

$$H = \sum_i H_i + \sum_{i>k} \frac{1}{r_{ik}} + \frac{Z}{R}, \quad (i, k = 1, 2, \dots, 10)$$

where H_i is the Hamiltonian operator of the i -th electron, disregarding the interaction between the electrons, that is

$$H_i = -\frac{1}{2} \Delta_i - \frac{Z}{r_i} - \frac{1}{r_{Hi}}$$

and

$$\Delta_i \equiv \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}.$$

R is the distance between the F and H nuclei; r_i is the distance of the i -th electron from the nucleus of the F-atom, r_{Hi} the distance of the i -th electron from the H nucleus, r_{ik} the distance between the i -th and k -th electron, and $Z = 9$ is the charge on the nucleus of the F-atom. Throughout these calculations atomic units will be used: thus the electric charge will be expressed in e , the distance in a_0 and the energy in e^2/a_0 units, where e is the charge of the proton and a_0 the radius of the first Bohr orbit in the hydrogen atom; these may all be found e. g. on page 10 of l. c. [3].

The trial eigenfunction of the HF molecule is built up of such one-electron eigenfunctions, that the distance r , occurring in their radial parts, is measured from the nucleus of the F-atom. The trial eigenfunction of the system is con-

structed of these and of the spin functions α and β according to the well-known procedure of SLATER [4], and it is a determinant with ten rows and columns being antisymmetrical against the exchange of the electrons. This has the results, that in this theory the exchange interaction is considered.

The orthonormalized one-electron eigenfunctions were as follows :

$$\begin{aligned} \psi_{1s} &= R_{10}(r) Y_{00}(\vartheta, \varphi) = 2 a^{3/2} e^{-ar} \frac{1}{\sqrt{4\pi}}, \\ \psi_{2s} &= R_{20}(r) Y_{00}(\vartheta, \varphi) = \left(\frac{12 b^5}{a^2 - ab + b^2} \right)^{1/2} \left[1 - \frac{1}{3} (a + b) r \right] \frac{1}{\sqrt{4\pi}}, \\ \psi_{2px} &= R_{21}(r) \frac{Y_{11}(\vartheta, \varphi) + Y_{1,-1}(\vartheta, \varphi)}{\sqrt{2}} = \left(\frac{c^5}{24} \right)^{1/2} r e^{-\frac{cr}{2}} \sqrt{\frac{3}{4\pi}} \sin \vartheta \cos \varphi, \\ \psi_{2py} &= R_{21}(r) \frac{Y_{11}(\vartheta, \varphi) - Y_{1,-1}(\vartheta, \varphi)}{i\sqrt{2}} = \left(\frac{c^5}{24} \right)^{1/2} r e^{-\frac{cr}{2}} \sqrt{\frac{3}{4\pi}} \sin \vartheta \sin \varphi, \\ \psi_{2pz} &= R_{21}(r) Y_{10}(\vartheta, \varphi) = \left(\frac{d^5}{24} \right)^{1/2} r e^{-\frac{dr}{2}} \sqrt{\frac{3}{4\pi}} \cos \vartheta. \end{aligned}$$

Here a , b , c and d are the variational parameters, which have been determined so as to satisfy the requirement to reduce the total energy to a minimum. Considering that the z -axis was taken as the axis of the molecule, the electron distribution in the ground state may be assumed to be symmetrical around the z -axis and consequently the parameters of the functions ψ_{2px} and ψ_{2py} may be chosen to be equal.

Calculating the energy, which is the mean value of the operator H , we have the following types of integrals :

$$\left. \begin{aligned} I_j &= \int \psi_j^*(i) \left(-\frac{1}{2} \Delta_i - \frac{Z}{r_i} \right) \psi_j(i) d v_i, \\ C_{jl} &= \int \psi_j^*(i) \psi_l^*(k) \frac{1}{r_{ik}} \psi_j(i) \psi_l(k) d v_i d v_k, \\ A_{jl} &= \int \psi_j^*(i) \psi_l^*(k) \frac{1}{r_{ik}} \psi_l(i) \psi_j(k) d v_i d v_k, \\ L_j &= \int \psi_j^*(i) \frac{1}{r_{Hi}} \psi_j(i) d v_i. \end{aligned} \right\} (*)$$

Here I denotes the term due to the kinetic energy of the electron and its Coulomb interaction energy with the nucleus of the F-atom; C is the Coulomb

interaction energy of the electrons, A the exchange energy and L a term resulting from the Coulomb attraction of the electron and the H nucleus. Three of the integrals I , C and A are usual types occurring also in atomic problems. Only L is a two-center integral. A detailed expression for the energy will be given in the Appendix.

Results

As a result of the variation the following values was obtained for the energy of the HF molecule in the ground state :

$$E_{HF} = -99,016$$

for the following values of the variational parameters :

$$a = 8,7; \quad b = 3,1; \quad c = 4,9; \quad d = 4,4.$$

The distance R between the nuclei naturally has been also taken for a variational parameter. (Thus there have been five parameters including R .) The value obtained for R is :

$$R = 1,57.$$

The experimental values of the energy and of the equilibrium nuclear separation are [5]: $E = -100,489$, $R = 1,73$. The agreement with the experimental data can be considered as good.

A further aim of the calculations was to determine the dissociation energy of the HF molecule. The halogen hydrids in general dissociate into atoms and so does the HF too. This implies, that it would be necessary to calculate the energy of the F atom to the same approximation as was done for the HF molecule so as to obtain the dissociation energy. Instead of this it was simpler, however, to calculate the dissociation energy by the aid of a Born cycle from the energy of the F^- and H^+ ions, taking into account the electron affinity of the F atom and the ionization energy of the H atom ; since the F^- ion is a system having ten electrons just as the HF molecule, the neglections due to the approximations in both processes are similar.

Having obtained the analytical formulas for the energy of the HF molecule, the energy of the F^- ion can be easily obtained also with the variational method. The Hamiltonian of the F^- ion differs from that of the molecule only in so far as the energy term due to the Coulomb interaction between the electrons and the H nucleus, i. e. $1/r_{Hi}$, and the Coulomb interaction energy term of the nuclei, i. e. Z/R , do not occur in it. Then we have

$$H = \sum_i \left(-\frac{1}{2} \Delta_i - \frac{Z}{r_i} \right) + \sum_{i>k} \frac{1}{r_{ik}} \quad (i, k = 1, 2, \dots, 10)$$

The approximate eigenfunction of the F^- -ion has evidently to be constructed of the same one-electron eigenfunctions as were used in the treatment of the molecule. However, the electron configuration of the F^- -ion is like that of a rare gas, i. e. $(1s)^2(2s)^2(2p)^6$, and thus the charge density is spherically symmetrical. Consequently not only the variational parameters of the functions ψ_{2px} and ψ_{2py} agree, but that of ψ_{2pz} is also the same ($c = d$) and there will be only three variational parameters. When taking the mean value of the Hamilton operator, integrals of the same type occur as before, except for the L . The detailed energy expression is also to be found in the Appendix.

As the result of the variational procedure the best parameter values obtained were

$$a = 8,7, \quad b = 3,1, \quad c = d = 4,6$$

and the energy

$$E_{F^-} = -98,468.$$

The electron affinity of the F^- -ion was determined experimentally [6] to be $0,15_0$ and consequently the dissociation energy of the HF molecule i. e. the energy, which is necessary for the dissociation of the HF molecule into an F and an H atom is easily obtained with the aid of the Born cycle as

$$D = 0,19_8.$$

The experimental value of the dissociation energy is $D = 0,23_5$ [5] and thus the deviation from it is approximately 15 per cent.

Discussion

Calculations have been made by several authors to obtain certain data of the HF molecule. CH. R. MUELLER [7] used semilocalized orbitals and his result for the binding energy is better ($0,1648$), than those obtained by the valence-bond or the molecular-orbital method. Zs. NÁRAY [8] has determined the energy of dissociation into the F^- and H^+ ions and the equilibrium nuclear separation of the molecule by the aid of a special wave-mechanical perturbation theory with an error of not more than 10–11 per cents. Calculations of similar character have been carried out also by INGA FISCHER-HJALMARS [9] concerning the dipolmoment of the HF molecule.

When the eigenfunction of the HF molecule is selected as in atomic problems with central symmetry, the calculated energy and dissociation energy of the molecule show good agreement with the experimental data. The results are comparable with those obtained by the methods with many center molecular orbitals. The eigenfunction constructed of one-electron eigenfunctions having one center of reference only gives a good approximation when calculating the energy. It is to be noted, however, that comparing for example the radial charge density of the electrons of the F^- ion with that of the HF molecule, no essential difference is obtained. The charge density of the molecule is almost spherically symmetrical. The charge density of the F^- ion is naturally obtained by the method presented here — as

it is in reality — as spherical symmetrical. The charge density of the HF molecule, however, is deformed by the presence of the proton. The united atom model in its present form, however, cannot take this effect sufficiently into account, and in this model the charge density of the electrons merely extends in the direction of the z -axis and slightly contracts perpendicular to it. The charge density of the molecule is also symmetrical with respect to the nucleus of the F^- ion and the model cannot give the great electron density near to the proton in the molecule. This short-coming plays evidently an essential role in the discrepancy between the calculated energy of the molecule and its experimental value. It follows further that the calculated value of the equilibrium nuclear separation must be less than the experimental one, is a natural consequence of the united atom model. From this it may be already suspected, that such constants of the molecule, for which the charge density of the electron itself is essential, will be obtained less precisely. So e. g. nearly the double of the experimental value is obtained for the dipolmoment of the HF molecule.

The method can be improved when the one-electron eigenfunctions ψ_{1s} , ψ_{2s} and ψ_{2p} or at least those, which are important from the point of view of the molecule formation, are constructed by the superposition of two or more functions. In the model of the molecule presented here it seemed suitable for example to use the linear combination $\psi_{2pz} + c \psi_{3dz}$ instead of ψ_{2pz} . In this way, namely, not only one spherical harmonic occurs in the one-electron eigenfunctions, and this can favorably influence the distribution of the charge density near the proton. Naturally the symmetry characteristics of the molecule have to be taken into consideration in the selection of the new eigenfunction. As our calculations have shown the results really improved, consequently, such eigenfunctions are more suitable for the description of the properties of the molecule. The calculations have naturally been considerably more complicated, since the introduction of a new term in the one-electron eigenfunction implies the introduction of two more variational parameters, which considerably increased the numerical work.

Appendix

In the energy expression of the HF molecule, integrals of the type I_j , C_{jl} , A_{jl} and L_j occur in the equation (*). Evaluating the integrals C_{jl} and A_{jl} , $1/r_{ik}$ has been as usually expanded into a series in terms of the Legendre polynomials in the following manner

$$\frac{1}{r_{ik}} = \sum_{h=0}^{\infty} \sum_{m=-h}^h \frac{(h-|m|)!}{(h+|m|)!} \frac{r_{<}^h}{r_{>}^{h+1}} P_h^{|m|}(\cos \vartheta_i) P_h^{|m|}(\cos \vartheta_k) e^{im(\varphi_i - \varphi_k)}.$$

The integral C_{jl} by this expansion becomes

$$C_{jl} = \sum_{h=0}^{\infty} a^h(l, m_l; l', m_{l'}) F^h(n, l; n', l'),$$

where

$$F^h(n, l; n', l') = \int_0^{\infty} \int_0^{\infty} R_{nl}^2(r_i) R_{n'l'}^2(r_k) \frac{r^{<h}}{r^{>h+1}} r_i^2 r_k^2 dr_i dr_k$$

and

$$a^h(l, m_l; l', m_{l'}) = \frac{(2l+1)(l-|m_l|)!}{2(l+|m_l|)!} \cdot \frac{(2l'+1)(l'-|m_{l'}|)!}{2(l'+|m_{l'}|)!} \times \\ \times \int_0^{\pi} \{P_l^{|m_l|}(\cos \vartheta_i)\}^2 P_h(\cos \vartheta_i) \sin \vartheta_i d\vartheta_i \int_0^{\pi} \{P_{l'}^{|m_{l'}|}(\cos \vartheta_k)\}^2 P_h(\cos \vartheta_k) \sin \vartheta_k d\vartheta_k.$$

Entirely in the same way is obtained

$$A_{jl} = \sum_{h=0}^{\infty} b^h(l, m_l; l', m_{l'}) G^h(n, l; n', l'),$$

where

$$G^h(n, l; n', l') = \int_0^{\infty} \int_0^{\infty} R_{nl}(r_i) R_{n'l'}(r_i) R_{nl}(r_k) R_{n'l'}(r_k) \frac{r^{<h}}{r^{>h+1}} r_i^2 r_k^2 dr_i dr_k$$

and

$$b^h(l, m_l; l', m_{l'}) = \frac{(h-|m_l-m_{l'}|)!(2l+1)(l-|m_l|)!(2l'+1)(l'-|m_{l'}|)!}{4(h+|m_l-m_{l'}|)!(l+|m_l|)!(l'+|m_{l'}|)!} \times \\ \times \int_0^{\pi} P_l^{|m_l|}(\cos \vartheta) P_{l'}^{|m_{l'}|}(\cos \vartheta) P_h^{|m_l-m_{l'}|}(\cos \vartheta) \sin \vartheta d\vartheta\}^2.$$

The value of the coefficients a and b is to be found for example in the quoted work of SLATER [4].

Among the integrals only the L -integrals do not occur in atomic problems, but only in the case of molecules. The evaluation of such integrals of the two-center type does not present any serious difficulty (see for example GOMBÁS [3]). Where it was necessary, the expansion of $1/r_{Hi}$ into a series mentioned above, was here also adapted. Otherwise the L -integrals can be easily evaluated in many cases by the introduction of elliptical coordinates.

Keeping in mind the above statements the following expressions were finally obtained for the energy of the HF molecule :

$$E = 2(I_{1s} + I_{2s} + I_{2px} + I_{2py} + I_{2pz}) + \\ + F^0(1s; 1s) + 4 F^0(1s; 2s) + 4 F^0(1s; 2p_x) + 4 F^0(1s; 2p_y) + 4 F^0(1s; 2p_z) + \\ + F^0(2s; 2s) + 4 F^0(2s; 2p_x) + 4 F^0(2s; 2p_y) + 4 F^0(2s; 2p_z) +$$

$$\begin{aligned}
& + F^0(2p_x; 2p_x) + \frac{1}{25} F^2(2p_x; 2p_x) + 4 F^0(2p_x; 2p_y) + \frac{4}{25} F^2(2p_x; 2p_y) + \\
& + F^0(2p_y; 2p_y) + \frac{1}{25} F^2(2p_y; 2p_y) + 4 F^0(2p_x; 2p_z) - \frac{8}{25} F^2(2p_x; 2p_z) + \\
& + 4 F^0(2p_y; 2p_z) - \frac{8}{25} F^2(2p_y; 2p_z) + F^0(2p_z; 2p_z) + \frac{4}{25} F^2(2p_z; 2p_z) + \\
& - 2 \left(G^0(1s; 2s) + \frac{1}{3} G^1(1s; 2p_x) + \frac{1}{3} G^1(1s; 2p_y) + \frac{1}{3} G^1(1s; 2p_z) + \right. \\
& + \frac{1}{3} G^1(2s; 2p_x) + \frac{1}{3} G^1(2s; 2p_y) + \frac{1}{3} G^1(2s; 2p_z) + \frac{6}{25} G^2(2p_x; 2p_y) + \\
& \left. + \frac{3}{25} G^2(2p_x; 2p_z) + \frac{3}{25} G^2(2p_y; 2p_z) \right) \\
& - 2(L_{1s} + L_{2s} + L_{2px} + L_{2py} + L_{2pz}) + Z/R.
\end{aligned}$$

From symmetry considerations follows that the corresponding terms containing the functions ψ_{2px} and ψ_{2py} are here identical.

The evaluation of the energy of the F^- ion can be accomplished in the same way as that one of the HF molecule, since both systems have ten electrons. The explicit form of the energy will also be the same, only the terms containing L and Z/R will not occur. Because of the spherical symmetry of the ion naturally not only the terms containing ψ_{2px} and ψ_{2py} agree, but also those containing ψ_{2pz} are the same.

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ОБЪЕДИНЕННАЯ АТОМНАЯ МОДЕЛЬ МОЛЕКУЛЫ HF

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Резюме

Объединенный атом, хорошо использованный спектроскопами для оценки положений молекулярных уровней, является и подходящей моделью для трактовки некоторых молекул. Существенные черты метода следующие: 1. Атомные ядра молекулы — в отличие от модели, использованной спектроскопами — сохраняют свои геометрические конфигурации и в процессе вариации они только мало смещаются с этого положения. 2. Собственная функция молекулы построена из одноцентровых — одноэлектронных собственных функций по методу Слетера. В методе эмпирическими или полуэмпирическими параметрами — кроме принятого геометрического расположения ядер — не пользуется. Вычисления произведены для молекулы HF. В этом случае полная энергия, энергия диссоциации и равновесное расстояние ядер хорошо соглашается с опытом.