Vibration-Rotation Interaction in the HF Molecule

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The contribution of the vibration-rotation interaction term to the potential results in the fact that each rotational level has a slightly different potential curve. These deformed curves are used to integrate the Schrödinger equation.

General Considerations

The theory of the diatomic molecules can be found in HERZBERG [1]. The wave function S representing the vibrational and rotational motions of such a molecule may be written as a product of three functions:

$$S(r,\theta,\varphi) = R(r)\,\Theta(\theta)\;\Phi(\varphi)$$

where r, θ, φ are the spherical polar coordinates of the second nucleus related to the first one taken as origin. We have

$$\Phi(\varphi) = \frac{1}{\sqrt{2\,\pi}} \exp\{i\,M\,\varphi\}$$

and

$$\Theta(\theta) = \left[\frac{(2\,J+1)\,(J-|\,M\,|)\,!}{2\,(J+|\,M\,|)\,!}\right]^{1/2} \cdot P_J{}^{|M|}\,(\cos\theta)$$

where M and J are the magnetic and rotational quantum numbers, respectively, and $P_J{}^{|M|}$ the associated Legendre polynomial.

As for the third function R, if we replace it by $\psi(r) = r\,R(r)$, ψ is solution of the radial wave equation:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}r^2} + \left\{-\frac{J\,(J+1)}{r^2} + \frac{8\,\pi^2\,\mu}{h^2}\,[E - V(r)]\right\}\cdot\psi = 0$$

where μ is the reduced mass and E the total energy of the molecule in its motion about the center of gravity, h being Planck's constant. $V(r)$ represents the potential energy, and $J(J+1)/r^2$ the interaction term, because it contains the rotational quantum number J together with the vibration-dependent internuclear distance r.

If we make a change of variable $x = r - r_{\mathrm{e}}$, where r_{e} is the equilibrium nuclear separation, and put $B = h/8\,\pi^2\,c\,\mu\,r_{\mathrm{e}}{}^2$, c being the velocity of light, the equation becomes:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{8\,\pi^2\,\mu}{h^2}\left\{E - \left[V(x) + \frac{B\,h\,c}{(1+x/r_{\mathrm{e}})^2}\cdot J(J+1)\right]\right\}\cdot\psi = 0\,.$$

By use of the term values (in m^{-1}) instead of energy values, we may write

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{8\,\pi^2\,\mu\,c}{h}\,[T - U_J(x)\,]\cdot\psi = 0 \qquad (1)$$

where $T = E_{\mathrm{vr}}/h\,c\,,$

$E_{\mathrm{vr}} = E - E_{\mathrm{el}}$ and

$V(x) = E_{\mathrm{el}} + V_1(x)\,,$

$E_{\mathrm{el}} =$ electronic energy,

$U(x) = V_1(x)/h\,c\,,$

$U_J(x) = U(x) + B\,J\,(J+1)/\,(1+x/r_{\mathrm{e}})^2.$

The expression of U_J being not simple, it is convenient to use its graphical representation for the solution of Eq. (1): Thus, we have to draw the potential curves with the help of a digital computer, and then solve this equation by an analogue method.

Plotting of the Potential Curves

The vibration term value in m^{-1} of the hydrogen fluoride molecule is [1]

$$\begin{aligned} G_v = {} & 413852\,(v+\tfrac{1}{2}) - 9006.9\,(v+\tfrac{1}{2})^2 \\ & + 98.0\,(v+\tfrac{1}{2})^3 - 2.5\,(v+\tfrac{1}{2})^4. \end{aligned} \qquad (2)$$

When the vibrational quantum number v varies from 0 to 4, the dominant contribution is given by

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[1] G. HERZBERG, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, 2nd ed., Van Nostrand, Princeton (N.J.) 1950.

the two first terms, and G_v may be reduced to the Morse term value:

$$G_v = \overline{\omega}_e (v+\tfrac{1}{2}) - \overline{\omega_e x_e} (v+\tfrac{1}{2})^2. \qquad (3)$$

A least squares method calculation shows that this is achieved with an error less than 0.04%, with

$$\overline{\omega}_e = 413497.3698\,, \quad \overline{\omega_e x_e} = 8572.2752\,.$$

We can now write the potential without interaction in the form of a Morse function:

$$U(x) = D[1 - \exp\{-\beta x\}]^2$$

where D, the dissociation energy referred to the potential minimum, and β are given by

$$D = \omega_e^2 / 4\,\overline{\omega_e x_e}\,, \quad \beta^2 = \overline{\omega_e x_e} / B r_e^2 .$$

From the values of the rotational constant B and the internuclear distance at equilibrium[1] r_e, we determine that of the potential taking into account the vibration-rotation interaction:

$$U_J(x) = 4986426.31\,[1 - \exp\{-2.20624\,x\}]^2 + \frac{1761.1215}{(0.9171+x)^2}\, J(J+1)\,.$$

U_J is calculated by means of an IBM 1620 digital computer for a number of J values varying from 0 to 12, and for $-0.70\,\text{Å} < x < 0.70\,\text{Å}$ with $\Delta x = 0.004\,\text{Å}$. The U_J curves are then plotted on a 25 cm × 40 cm sheet of graph paper, which has the dimensions of the input table belonging to the analogue computation device.

Description of the Analogue Computer

Figure 1 gives the schematic representation of the apparatus[2]. Let y'', the second derivative of a certain tension y, be the input to the first integrator $R_1 - C_1$. Its output $-y'/R_1 C_1$ is changed into $-a\,y'/R_1 C_1$ by the potentiometer P_1 set at the value a, and applied at the entry of the second integrator which furnishes a tension equal to $a\,y/R_1 C_1 R_2 C_2$. The latter is transformed by the potentiometer P_2, adjusted to r/R_0 (R_0 being the total resistance of P_2), into $a\,y\,r/R_0 R_1 C_1 R_2 C_2$. Inverter $R_3 - R_3$ changes the sign of this term and feeds the summer $R_4 - R_4 - R_4$, at the second entry of which is applied the output of the second integrator multiplied by the setting t/T_0 of potentiometer P_3, whose total resistance is T_0. The tension resulting from the summer, namely

$$a\,y\,(r/R_0 - t/T_0)/R_1 C_1 R_2 C_2\,,$$

is finally transformed into

$$a\,b\,y\,(r/R_0 - t/T_0)/R_1 C_1 R_2 C_2$$

through the potentiometer P_4 set at the value b. This term is fed back to integrator $R_1 - C_1$ and the loop is closed, performing thus the equality

$$y'' = a\,b\,y\,(r/R_0 - t/T_0)/R_1 C_1 R_2 C_2\,,$$

which can be written as

$$y'' + K\left(\frac{t}{T_0} - \frac{r}{R_0}\right) y = 0 \qquad (4)$$

with $\quad K = a\,b / R_1 C_1 R_2 C_2\,.$

Comparison of Eqs. (1) and (4) shows that the first one must be transformed into the form of the second, in order to be solved by analogue computation.

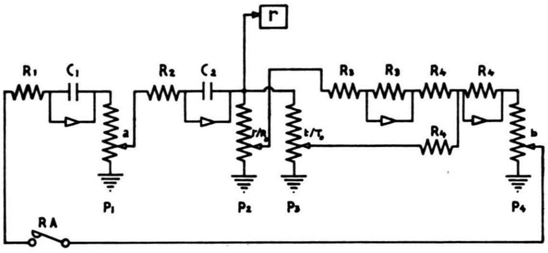

Fig. 1. Block diagram of the analogue computation device.

$R_1 - C_1$: integrator
P_1: potentiometer
$R_2 - C_2$: integrator
P_2: curve follower potentiometer
P_3: term value potentiometer
$R_3 - R_3$: inverter
$R_4 - R_4 - R_4$: summer
P_4: potentiometer
RA: relay amplifier
r: recorder

If we have a tension y proportional to the wave function ψ, Eq. (1) may be written

$$\frac{d^2 y}{dx^2} + \frac{8\,\pi^2\,\mu\,c}{h}\,[T - U_J(x)]\,y = 0\,. \qquad (5)$$

The plot of the potential curve $U_J(x)$ is mounted on an input table, before which the arm of an optical curve follower translates[2] with a constant speed parallel to the abscissae axis. We have

$$w = dx/dt = \text{const}\,,$$

$$\frac{dy}{dx} = \frac{1}{w}\frac{dy}{dt} = \frac{1}{w}\,y'\,,$$

$$\frac{d^2 y}{dx^2} = \frac{1}{w^2}\frac{d^2 y}{dt^2} = \frac{1}{w^2}\,y''\,.$$

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[2] S. FIFER, Analogue Computation, McGraw-Hill, New York 1961.

Thus Eq. (5) becomes

$$y'' + \frac{8\,\pi^2\,\mu\,c}{h}\,w^2[T - U_J(x)]\,y = 0 \tag{6}$$

and it may be solved by means of the analogue computer if *r* in Eq. (4) varies during the time proportionally to $U_J(x)$ in Equation (6). This is achieved by the optical curve follower which moves the slider arm of potentiometer P_2 in direct ratio to U_J. In this way the recorder draws curves corresponding to the output of integrator $R_2 - C_2$, that is to say $\psi(t)$, when the settings t/T_0 of P_3 are proportional to the energy levels of the HF molecule expressed in term values.

Calculation of Initial Values

To obtain a unique solution for a second-order differential equation, we must specify the values of the function and its first and second derivatives for a given value of the variable. For the above described device, this is carried out when the starting point is determined on the potential curve $U_J(x)$, and capacitors C_1 and C_2 charged under the adequate tensions[2].

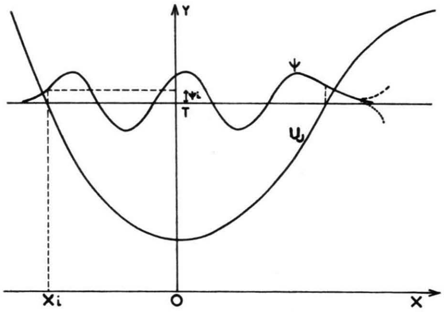

Fig. 2. Potential energy U_J and wave function ψ plotted against the change of internuclear distance. Term value $T = G_v + B\,J\,(J+1)$.

The extreme inflexion points of the wave function curve, where $d^2\psi/dx^2$ is zero, correspond to the intersections of $U_J(x)$ with the energy level T (Fig. 2) according to Eq. (1), and it is convenient to choose the left one[3]. Furthermore, ψ is equal to[4]

$$\psi = N \exp\{-z/2\}\,z^{b/2}\,L_v^b(z)$$

where N = the normalization factor,
$z = k\exp\{-a\,x\}$,
$k = \omega_e/\omega_e\,x_e$,
$b = k - 2\,v - 1$,
$a^2 = \frac{8\,\pi^2\,\mu\,c}{h}\,\omega_e\,x_e$.

The associated Laguerre polynomial of degree $v - b$ is given by

$$L_v^b(z) = \sum_{k=0}^{v} \binom{b+v}{v-r} \frac{(-z)^k}{k!}.$$

It is solution of the hypergeometric equation

$$z\frac{d^2L}{dz^2} + (b+1-z)\frac{dL}{dz} + v\,L = 0. \tag{7}$$

On the other hand, at the inflexion point, the nullity of $d^2\psi/dx^2$ leads to

$$z\frac{d^2L}{dz^2} + (b+1-z)\frac{dL}{dz} + \frac{(b-z)^2}{4\,z} - \frac{1}{2}\,L = 0. \tag{8}$$

L must satisfy Eqs. (7) and (8). The suitable solution is[5]

$$z_i = k + \sqrt{k^2 - b^2}$$

hence x_i.

By a change of variable, if we put

$$z = A + Y \quad \text{with} \quad A = b + v$$

the polynomials are transformed into the following simple forms[6]:

- for even values of v:

$$L = \frac{Y^v}{v!} + \frac{(-A)^{v/2}}{v!}\cdot C^1_{v/2} + \sum_{p=1}^{(v-2)/2}(-A)^p \sum_{j=0}^{v-2p} \frac{1}{j!\,(v-j)!}\,C^{v-2p+1-j}_{v-p-j}\,Y^i$$

- for odd values of v:

$$L = -\left\{\frac{Y^v}{v!} + \frac{(-A)^{(v-1)/2}}{v!}\,C^1_{(v-1)/2}\,v\left(Y + \frac{v-1}{3}\right) + \sum_{p=1}^{(v-3)/2}(-A)^p \sum_{j=0}^{v-2p} \frac{1}{j!\,(v-j)!}\,C^{v-2p+1-j}_{v-p-i}\,Y^i\right\}.$$

The coefficients C_i^k are found by use of the recursion relation:

$$C_i^k = (2\,i - k)\,[C_{i-1}^{k-1} + C_{i-1}^k]$$

where $C_i^i = i!$, $C_i^0 = 0$ if $i > 0$, $C_i^k = 0$ if $i < k$.

Upon taking the derivative of ψ, we obtain

$$\frac{\psi'}{\psi} = a\left(\frac{z-b}{2} - \frac{z}{L}\cdot\frac{dL}{dz}\right).$$

We need only to calculate L and dL/dz for $z = z_i$, and to apply the preceding relations in order to determine ψ_i'. This is achieved by means of an IBM 1620 computer supplied with a program in which L and dL/dz are given by the same statements.

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[3] R. Grandmontagne, Cahiers Phys. **15**, 385 [1961].
[4] P. Morse, Phys. Rev. **34**, 57 [1929].
[5] H. Kobeisse, Thesis, Lyon 1962.
[6] P. Perdigon, Thesis, Lyon 1969.

Operation Procedure

ψ_i may be arbitrary. For convenience, it is kept at a constant value; so ψ_i' is easily deduced for a given vibrational quantum number[6] v. The outputs of integrators $R_1 - C_1$ and $R_2 - C_2$ being proportional to ψ' and ψ respectively, capacitors C_1 and C_2 are charged with the help of initial condition potentiometers in order to insert tensions in direct ratio to ψ_i' and ψ_i across the integrators.

Potentiometer P_3 is then adjusted to the corresponding value of the spectral term T, and the recorder switched on. Its stylus draws a parallel to the abscissae axis, having ψ_i as ordinate. In order to plot the right branch (for $x > x_i$) of the wave function curve, the optical follower which makes use of a photocell is put on the potential curve at a point where $x < x_i$ and $U_J > T$, and allowed to start. The value of $(U_J - T)$ decreases and at the very moment when it becomes null the relay RA (Fig. 1) establishes the connection and so the integration is permitted to proceed. Therefore the recorder plots the wave function curve.

As the automatic follower moves only in one way, to draw the left branch ($x < x_i$) we must turn up the graph paper of the potential curve. In this way, the left inflexion point is always taken as origin of integration. The procedure is then the same, but the curve follower starts at a point where $U_J < T$.

Results

The wave functions relative to $v = 0$, 1, and 3, and $0 \leqq J \leqq 12$ have been determined[7]. Table 1 gives as an example the numerical values corresponding to $v = 3$ and $J = 10$, the maxima and minima having the greatest absolute values in this latter case. The absolute error is not greater than 0.02.

Theoretically, ψ vanishes for x having an infinite value. Because of the inaccuracy of the potentiometers and the errors due to the thickness of the potential energy curve, instead of an asymptotic branch we get rather a parabolic one (Fig. 2, broken line), or a curve crossing the abscissae axis (dotted line).

Table 1. Values of the wave function for $v=3$ and $J=10$.

r [Å]	ψ	r [Å]	ψ	r [Å]	ψ
0.58690	+ 0.02	0.87148	− 0.40	1.15606	− 2.37
0.59608	+ 0.04	0.88066	− 0.96	1.16524	− 2.68
0.60526	+ 0.06	0.88984	− 1.42	1.17442	− 2.88
0.61444	+ 0.08	0.89902	− 1.86	1.18360	− 3.04
0.62362	+ 0.10	0.90820	− 2.14	1.19278	− 3.11
0.63280	+ 0.13	0.91738	− 2.33	1.20196	− 3.14
0.64198	+ 0.18	0.92656	− 2.37	1.21114	− 3.14
0.65116	+ 0.21	0.93574	− 2.33	1.22032	− 3.10
0.66034	+ 0.26	0.94492	− 2.05	1.22950	− 3.00
0.66952	+ 0.35	0.95410	− 1.64	1.23868	− 2.83
0.67870	+ 0.45	0.96328	− 1.14	1.24786	− 2.69
0.68788	+ 0.57	0.97246	− 0.53	1.25704	− 2.48
0 69706	+ 0.72	0.98164	+ 0.04	1.26622	− 2.29
0.70624	+ 0.90	0.99082	+ 0.64	1.27540	− 2.10
0.71542	+ 1.10	1.00000	+ 1.19	1.28458	− 1.91
0.72460	+ 1.32	1.00918	+ 1.64	1.29376	− 1.72
0.73378	+ 1.57	1.01836	+ 2.00	1.30294	− 1.51
0.74296	+ 1.79	1.02754	+ 2.28	1.31212	− 1.36
0.75214	+ 2.02	1.03672	+ 2.44	1.32130	− 1.20
0.76132	+ 2.27	1.04590	+ 2.47	1.33048	− 1.03
0.77050	+ 2.47	1.05508	+ 2.40	1.33966	− 0.90
0.77968	+ 2.60	1.06426	+ 2.15	1.34884	− 0.77
0.78886	+ 2.65	1.07344	+ 1.80	1.35802	− 0.67
0.79804	+ 2.66	1.08262	+ 1.37	1.36720	− 0.54
0.80722	+ 2.60	1.09180	+ 0.89	1.37638	− 0.44
0.81640	+ 2.43	1.10098	+ 0.40	1.38556	− 0.36
0.82558	+ 2.10	1.11016	− 0.17	1.39474	− 0.26
0.83476	+ 1.70	1.11934	− 0.70	1.40392	− 0.19
0.84394	+ 1.23	1.12852	− 1.22	1.41310	− 0.11
0.85312	+ 0.70	1.13770	− 1.65	1.42228	− 0.05
0.86230	+ 0.13	1.14688	− 2.04		

To overcome this difficulty, we modify very slightly the setting of the initial condition potentiometer; the best convergence is thus obtained on the left branch. The adjustment of P_3 is then faintly changed in order to have the most convenient result on the right branch. It is however necessary to correct with his hand to achieve an asymptotic curve (full line).

Conclusion

By this method we obtained vibration wave functions modified by the vibration-rotation interaction. Other calculations, carried out separately on both digital and analogue computers for a slightly different problem, showed a very good agreement between the results and tested the accuracy of the analogue method.

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[7] A. H. Topouzkhanian, Thesis, Lyon 1968.