

## The Rotation-Vibration Coupling in Diatomic Molecules

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A solution of the wave equation for the nuclear motion of a diatomic molecule with a Morse potential function and the rotational term included is given. The wave functions are found to have the same form as the functions obtained when the rotational term is neglected. The constants  $D_e$  and  $\alpha_e$  in the equations

$$B_v = B_e - \alpha_e(v + \frac{1}{2}),$$

$$D_v = D_e + \beta_e(v + \frac{1}{2}),$$

are found to be given by the relations

$$D_e = -4B_e^3/\omega_e^2 \quad (1)$$

$$\alpha_e = 2x_e B_e (3[B_e/x_e \omega_e]^{\frac{1}{2}} - 3B_e/x_e \omega_e), \quad (2)$$

a result which can also be derived from Dunham's formulas. Eq. (2) differs from the corresponding relation in Kratzer's formula by the term in parenthesis. This term is fairly constant for a number of molecules and has an average value of  $0.7 \pm 0.1$  as was found empirically by Birge. The values of  $\alpha_e$  given by (2) show satisfactory agreement with experimental values for many molecules.

### INTRODUCTION

FOR the purposes of a program of study of molecular spectra in astrophysical work, we have found it necessary to examine the effect of the rotational motion on the vibrational levels of a diatomic molecule in which the internuclear potential is of the Morse form. The rotational modification of the vibrational wave functions and the resulting modification of the probabilities of transition is of special importance in astrophysical work since at the high temperatures involved the recorded band-head maximum intensities occur at high  $j$ -values.

This question is also of interest in examining to what extent the potential function for a diatomic molecule is determinable from band spectrum data<sup>1</sup> as it has been found that quite different potential functions give practically the same vibrational levels. It is only when the coupling between vibration and rotation is considered that the adequacy of a given potential function can be tested.

If we write the wave function in the usual approximate form

$$\psi = \Phi(x, r)(R(r)/r)\Theta(\theta, \varphi) \quad (1)$$

then  $R$  satisfies the equation

$$d^2R/dr^2 - j(j+1)R/r^2 + (8\pi^2\mu/h^2)[E - U(r)]R = 0, \quad (2)$$

$j$  being the rotational quantum number,  $\mu = M_1M_2/(M_1+M_2)$ . If we now assume a definite form for  $U(r)$  and solve Eq. (2) with the second term left out, we find that up to a certain vibrational quantum number, the allowed vibrational levels are of the empirical form

$$E = E_{el} + hc[\omega_e(v + \frac{1}{2}) - x_e\omega_e(v + \frac{1}{2})^2 + y_e\omega_e(v + \frac{1}{2})^3 \cdots] + hc\{B_v[(j + \frac{1}{2})^2 + \text{const.}] + D_v(j + \frac{1}{2})^4 + \cdots\} \quad (3)$$

with

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 + \cdots, \quad (4)$$

$$D_v = D_e + \beta_e(v + \frac{1}{2}) + \cdots \quad (5)$$

for a variety of functions  $U(r)$ , different functions giving, however, different values for  $B_v$ ,  $D_v$ , and especially for  $\alpha_e$  when the complete Eq. (2) is solved. It is evident then that the value of  $\alpha_e$ , though small, is of decisive importance in choosing the correct function  $U(r)$ .

<sup>1</sup> P. M. Davidson, Proc. Roy. Soc. **A135**, 459 (1932). G. Pöschl and E. Teller, Zeits. f. Physik **83**, 143 (1933). R. S. Mulliken, Rev. Mod. Phys. **4**, 77 (1932).

Morse<sup>2</sup> has shown that with his form of the potential energy

$$U(r) = E_{el} + D[1 - e^{-a(r-r_e)}]^2 \quad (6)$$

containing two disposable constants  $D$  and  $a$ , and omitting the second term in Eq. (2), one obtains

$$\alpha_e = 2B_e x_e, \quad (7)$$

$$D_e = -4B_e^3/\omega_e^2, \quad (8)$$

just as for the simple Kratzer potential function.<sup>3</sup> Of these Eq. (8) has been verified for a number of molecules<sup>4</sup> while Birge has found that the value of  $\alpha_e$  as given by Eq. (7) is, on the average, too large by a factor of about 1.4.

We shall show, however, that if one includes the second term in Eq. (2), and uses the Morse function, one obtains a modified expression for  $\alpha_e$  more in accord with the experimental values. It is to be noted that this formula can be derived readily from the general results of Dunham,<sup>5</sup> but the present analysis yields us also the modified *wave functions* which cannot be found directly by Dunham's procedure, but which are desired for later work.

We can take care of the rotational term in the following way. Substitute Eq. (6) in Eq. (2)

$$\frac{d^2R}{dr^2} - \frac{j(j+1)R}{r^2} + \frac{8\pi^2\mu}{h^2} [W - D^{-2a(r-r_e)} + 2D^{-a(r-r_e)}]R = 0, \quad (9)$$

$$W = E - E_{el} - D.$$

Following Morse, we let  $y = e^{-a(r-r_e)}$  and (9) becomes

$$\frac{d^2R}{dy^2} + \frac{1}{y} \frac{dR}{dy} + \frac{8\pi^2\mu}{a^2h^2} \left[ \frac{W}{y^2} + \frac{2D}{y} - D - \frac{Ar_e^2}{y^2r^2} \right] R = 0, \quad (10)$$

$$A = j(j+1)h^2/8\pi^2\mu r_e^2.$$

Now

$$\frac{r_e^2}{r^2} = \frac{1}{(1 - \ln y/r_e a)^2} = 1 + \frac{2}{ar_e}(y-1) + \left[ -\frac{1}{ar_e} + \frac{3}{a^2r_e^2} \right] (y-1)^2 + \left[ \frac{2}{3ar_e} - \frac{3}{a^2r_e^2} + \frac{4}{a^3r_e^3} \right] (y-1)^3 + \dots \quad (11)$$

We substitute the first three terms of (11) in (10) and leave the other terms to be treated later as a perturbation:

$$\frac{d^2R}{dy^2} + \frac{1}{y} \frac{dR}{dy} + \frac{8\pi^2\mu}{a^2h^2} \left[ \frac{W-c}{y^2} + \frac{2D-c_1}{y} - D - c_2 \right] R = 0, \quad (12)$$

$$c = A \left( 1 - \frac{3}{ar_e} + \frac{3}{a^2r_e^2} \right), \quad c_1 = A \left( \frac{4}{ar_e} - \frac{6}{a^2r_e^2} \right), \quad c_2 = A \left( -\frac{1}{ar_e} + \frac{3}{a^2r_e^2} \right). \quad (13)$$

Now assume that  $R(y) = Ne^{-z/2} z^{b/2} F(z)$ ,  $z = 2dy$ ,

$$d^2 = 8\pi^2\mu(D+c_2)/a^2h^2, \quad b^2 = -32\pi^2\mu(W-c)/a^2h^2. \quad (14)$$

Then (12) becomes:

$$d^2F/dz^2 + F(b+1-z)/z + vF/z = 0, \quad (15)$$

<sup>2</sup> P. M. Morse, Phys. Rev. **34**, 57 (1929).

<sup>3</sup> A. Kratzer, Zeits. f. Physik **3**, 289 (1920).

<sup>4</sup> Cf. W. Weizel, *Bandenspektren*, Handbuch der Experimentalphysik Ergänzungsband **1**, p. 70.

<sup>5</sup> J. L. Dunham, Phys. Rev. **41**, 721 (1932). Cf. also P. M. Davidson, reference 1. I am indebted to the referee of the Physical Review for having pointed out this fact to me.

$$v = [4\pi^2\mu(2D - c_1)]/a^2h^2d - (b+1)/2 = (k-b-1)/2; \quad b = k-1-2v. \quad (16)$$

The polynomial-condition for (15) requires  $v$  to be an integer. Substituting (16) into (14), we get

$$W = E_{el} - D = c - (D - c_1/2)^2/(D + c_2) + (D - c_1/2)ah(v + \frac{1}{2})/\pi[2\mu(D + c_2)]^{\frac{1}{2}} - a^2h^2(v + \frac{1}{2})^2/8\pi^2\mu. \quad (17)$$

Upon developing the coefficients in (17) and neglecting all powers of  $c_1/D$  beyond the second, we finally get

$$E = E_{el} + hc[\omega_e(v + \frac{1}{2}) - x_e\omega_e(v + \frac{1}{2})^2] + hc\{j(j+1)B_e[1 - (v + \frac{1}{2})][3(B_e/x_e\omega_e)^{\frac{1}{2}} - 3(B_e/x_e\omega_e)]2x_e + \dots\} \\ - hc(4B_e^3/\omega_e^2)[j(j+1)]^2 + \dots \quad (18)$$

On comparing (18) with (3), it is seen that

$$\alpha_e = 2x_eB_e[3(B_e/x_e\omega_e)^{\frac{1}{2}} - 3(B_e/x_e\omega_e)], \quad (19)$$

$$D_e = -4B_e^3/\omega_e^2. \quad (20)$$

We shall now compute by the perturbation method the contribution to the energy by the neglected part of the rotational term. Turning to Eq. (9) in the form

$$\frac{d^2R}{dr^2} + \frac{8\pi^2\mu}{h^2} \left[ W - D^{-2a(r-r_e)} + 2D^{-a(r-r_e)} - A\frac{r_e^2}{r^2} \right] R,$$

we see that the correction  $\epsilon_1$  for the energy will be given by

$$\epsilon_1 = A \int_{-\infty}^{+\infty} R^2(r) V_1(r) dr = (A/a) \int_0^{\infty} R^2(y) V_1(y) y^{-1} dy = (A/a) \int_0^{\infty} R^2(z) V_1(z) z^{-1} dz, \quad (21)$$

where  $V_1(y)$  stands for the terms after  $(y-1)^2$  in (11). We can obtain  $F(z)$  of Eq. (15) in a closed form by applying the Laplace<sup>6</sup> transformation

$$F(z) = \int e^{-zt} f(t) dt. \quad (22)$$

On substituting in (15) and integrating once partially, we obtain a linear differential equation for  $f(t)$ , which is easily integrated. We thus get

$$F(z) = (c/2\pi i) \oint e^{-zt} t^{-(1+v)} (1+t)^{(b+v)} dt, \quad (23)$$

where the path of integration is a circle—of an eventually vanishing radius—around the origin.<sup>7</sup> We have for the normalization condition,

$$\int_{-\infty}^{+\infty} R(r)^2 dr = 1 = (N^2/a) \int_0^{\infty} R^2(z) z^{-1} dz \\ = (1/2\pi i)^2 (N^2/a) \oint t^{-(1+v)} (1+t)^{v+b} dt \oint s^{-(1+v)} (1+s)^{v+b} ds \int_0^{\infty} z^{b-1} e^{-z(1+s+t)} dz \\ \int_0^{\infty} z^{b-1} e^{-z(1+s+t)} dz = (1+s+t)^{-b} \Gamma(b) = \left[ \sum_{i=0}^{\infty} \binom{-b}{i} (1+s)^{-b-i} t^i \right] \Gamma(b).$$

<sup>6</sup> R. Courant and D. Hilbert, *Methoden der Mathematischen Physik I*, Chapter 7.

<sup>7</sup> This is the correct path only when  $v$  is an integer.

$$\begin{aligned} \therefore 1 &= (1/2\pi i)^2 (N^2/a) \Gamma(b) \left[ \sum_{i=0}^{\infty} \binom{-b}{i} \oint t^{-(1+v-i)} (1+t)^{v+b} dt \oint s^{-(1+v)} (1+s)^{v-i} ds \right] \\ &= (1/2\pi i) (N^2/a) \Gamma(b) \left[ \sum_{i=0}^v \binom{-b}{i} \binom{v+b}{v-i} \oint s^{-(1+v)} (1+s)^{v-i} ds \right] = (N^2/a) \Gamma(b) \cdot \binom{v+b}{v}, \end{aligned}$$

since  $(1+s)^{v-i}$  has a power  $s^v$  only when  $i=0$ . It follows that

$$N_v = \left[ a/\Gamma(b) \cdot \binom{v+b}{v} \right]^{\frac{1}{2}}. \quad (24)$$

Similarly:

$$\begin{aligned} \int_{-\infty}^{+\infty} R^2(r) z^k dr &= (1/2\pi i)^2 \left[ \binom{b+v}{v} \cdot \Gamma(b) \right]^{-1} \\ &\quad \times \left[ \oint t^{-(1+v)} (1+t)^{v+b} dt \oint s^{-(1+v)} (1+s)^{v+b} ds \int_0^{\infty} z^{b+k-1} e^{-z(1+s+t)} dz \right] \\ &= (1/2\pi i)^2 \left[ \Gamma(b+k)/\Gamma(b) \binom{b+v}{v} \right] \left[ \sum_{i=0}^{\infty} \binom{-b-k}{i} \oint t^{-(1+v-i)} (1+t)^{v+b} dt \oint s^{-(1+v)} (1+s)^{v-k-i} ds \right] \\ &= (1/2\pi i) \left[ \Gamma(b+k)/\Gamma(b) \binom{b+v}{v} \right] \left[ \sum_{i=0}^v \binom{-b-k}{i} \binom{v+b}{v-i} \oint s^{-(1+v)} (1+s)^{v-k-i} ds \right] \\ &= (1/2\pi i) \left[ \Gamma(b+k)/\Gamma(b) \binom{b+v}{v} \right] \left[ \sum_{i=0}^v \binom{-b-k}{v-i} \binom{v+b}{i} \oint s^{-(1+v)} (1+s)^{i-k} ds \right]. \end{aligned}$$

Now  $(1+s)^{i-k}$  will have a power  $s^v$  only when  $(i-k)$  is negative so that the last sum reduces to

$$\left[ \Gamma(b+k)/\Gamma(b) \binom{b+v}{v} \right] \sum_{i=0}^{(k-1), v} \binom{-b-k}{v-i} \binom{v+b}{i} \binom{i-k}{v} = \int_{-\infty}^{+\infty} R^2(r) z^k dr, \quad (25)$$

where the summation is to be carried to the smaller one of the numbers  $(k-1)$  and  $v$ . By writing out a few terms of the series it can be easily ascertained that

$$\begin{aligned} \sum_{i=0}^{i=1, v} \binom{-b-k}{v-i} \binom{v+b}{i} \binom{i-k}{v} &= \binom{-b-k}{v} \binom{-k}{v} \left[ 1 + \frac{(b+v)v(1-k)}{(-b-k-v+1)(-k-v+1)} \right. \\ &\quad \left. + \frac{(b+v)(b+v-1)v(v-1)(1-k)(2-k)}{2!(-b-k-v+1)(-b-k-v+2)(-k-v+1)(-k-v+2)} + \dots \right] \\ &= \binom{-b-k}{v} \binom{-k}{v} \mathbf{F} \left( \begin{matrix} -b-v, -v, 1-k \\ -b-k-v+1, -k-v+1 \end{matrix}; 1 \right). \quad (26) \end{aligned}$$

The generalized hypergeometric function  $\mathbf{F}$ , although of a simple form, is not one of either of the two types which can be summed in a closed form.<sup>8</sup> However, for the application in view its summation is not laborious. The first few polynomials of  $\int R^2(r) z^k dr$  are given below:

<sup>8</sup> Hardy, Proc. Camb. Phil. Soc. 21, 492 (1923).

$$\begin{aligned}
k=0 & 1 \\
k=1 & b \\
k=2 & b^2 + 2b(v + \frac{1}{2}) \\
k=3 & b^3 + 6b^2(v + \frac{1}{2}) + 6b(v + \frac{1}{2})^2 + \frac{1}{2}b \\
k=4 & b^4 + 12b^3(v + \frac{1}{2}) + b^2[30(v + \frac{1}{2})^2 + 7/2] + 20(v + \frac{1}{2})^3 + 7(v + \frac{1}{2}). \quad (27)
\end{aligned}$$

Carrying out now the integration of  $[-\int R^2(r)(1-z/2d)^3 dr]$  and  $\int R^2(r)(1-z/2d)^4 dr$ , we find that the coefficients of  $(v + \frac{1}{2})$  are  $(-1/k^3)$  and  $(-3/k^3)$ , respectively. Since  $(1/k) \asymp x_e$ , it is clear that these terms are of a smaller order of magnitude than the terms for  $\alpha_e$  in (19).

As a check on the above calculations, we compute the perturbation of the energy due to the first three terms in (11), using Morse's solution of (9), in which the rotational term was completely neglected. We find that

$$\epsilon_1 = c_1 + c_2 + c - (2/k)(v + \frac{1}{2})(c_1 + c_2) = A[1 - 6(v + \frac{1}{2})(ar_e - 1)/ka^2 r_e^2]. \quad (28)$$

This gives an expression for  $\alpha_e$  which is identical with (19), but it does not contain the term  $[j(j+1)]^2$  of (18). Now the smallness of the perturbation term for the energy shows that  $R(z)$  is a close approximation to the wave function of a diatomic molecule whose energy equation conforms to (18).

#### COMPARISON WITH EXPERIMENTAL RESULTS

Values of  $\alpha_e$  were computed by (19) for the molecules for which the table of molecular constants in Jevons' *Report on Band Spectra of Diatomic Molecules* contains sufficient data. The ratio of these values to the observed values of  $\alpha_e$  are given in the third column of Table I. The prefix *H* in this column signifies, in the notation of Jevons, that the vibrational coefficients are derived from band-spectra data; where there is no *H*, the coefficients are derived from band-origin data. The sign to the right in this column gives the sign of  $y_e \omega_e$  when it is known. The agreement is generally good, the discrepancies being within the probable error in the data. Some of the molecules which contain a cubic term in the vibrational energy equation, and for which therefore the present theory is strictly not applicable, show considerable deviations of  $\alpha_e$  from the computed values. In most cases of large discrepancies

TABLE I. Comparison of experimental and computed values of  $\alpha_e$ . Values of  $3(B_e/x_e \omega_e)^{\frac{1}{2}} - 3B_e/x_e \omega_e (\equiv F)$ .

Molecule	State	$\frac{\alpha_e \text{ comp.}}{\alpha_e \text{ obs.}}$	<i>F</i>	Molecule	State	$\frac{\alpha_e \text{ comp.}}{\alpha_e \text{ obs.}}$	<i>F</i>	Molecule	State	$\frac{\alpha_e \text{ comp.}}{\alpha_e \text{ obs.}}$	<i>F</i>	Molecule	State	$\frac{\alpha_e \text{ comp.}}{\alpha_e \text{ obs.}}$	<i>F</i>
CuH	A	0.96	0.72	CdH	B	0.8 +	0.72	Na <sub>2</sub>	C	H 1.01 -	0.74	BO	X	0.93	0.71
	X	.89	.75		A	.74	.73		B	H 1.25	.75	AlO	B	.83	.72
AgH	A	1.11	.59		X	.85 -	.68		A	H 1.28 +	.75		X	1.01	.63
	X	0.91	.74	HgH <sup>+</sup>	A	.92 -	.73	K <sub>2</sub>	C	H 1.45	.68	CO	B	H 1.5	.48
AuH	A	1.05	.62	HgH	X	1.19 +	.53		A	H 1.41	.72		A	H 0.97	.64
	X	1.02	.73	AlH	A	0.87 +	.75	C <sub>2</sub>	d	1.38	.53	SiO	<sup>1</sup> H	H .90 +	.65
BeH <sup>+</sup>	<sup>1</sup> $\Sigma^+$	0.67 -	.63	BiH	A	.71	.75		B	1.39	.63		X	H .97 +	.68
	<sup>1</sup> $\Sigma^+$	.94 -	.75		X	.64	.72		b	0.97	.69	TiO	C	H .95	.66
BeH	<sup>2</sup> $\Pi$	.92 -	.75	OH	<sup>2</sup> $\Sigma^+$	.92	.73	CN	A	1.10	.70		X	H 1.18	.68
	<sup>2</sup> $\Sigma^+$	.96 -	.75	HF	<sup>1</sup> $\Sigma$	.47	.69		B	1.07 -	.64	PbO	D	H 1.3	.75
MgH <sup>+</sup>	<sup>1</sup> $\Sigma^+$	.96	.66	HCl	<sup>1</sup> $\Sigma$	.90	.74		A	0.97	.69		A	H 1.0	.60
	<sup>1</sup> $\Sigma^+$	1.02	.74	BeF	A	.95	.72		X	.99	.71		X	H 1.0	.61
MgH	A	1.0	.73		X	.92	.72	SiN	B	1.12 +	.49	NO	B	0.64	.72
	X	1.0	.74	Cl <sub>2</sub>		H 1.0	.43		X	0.98	.67		B	.94	.71
CaH	D	7	.60		<sup>1</sup> $\Sigma^+$	H 1.1	.56	N <sub>2</sub> <sup>+</sup>	B	.94 -	.64		A	1.2	.68
	B	1.1	.75	Br <sub>2</sub>	B	H 0.86 -	.47		X	1.0 -	.68		X	0.95	.68
	X	1.0	.75		X	H 1.2	.68	N <sub>2</sub>	B	H 0.81	.67		X	.97	.68
	A	0.95	.75	ICl	A	H 0.8	.45		A	H 1.4 -	.65	O <sub>2</sub> <sup>+</sup>	A	H 1.4	.60
ZnH <sup>+</sup>	<sup>1</sup> $\Sigma^+$	H .9	.71		X	H .54	.59		a	H 0.83 -	.68		X	H 2.	.64
	<sup>1</sup> $\Sigma^+$	H .89 -	.74	I <sub>2</sub>	B	H 1.0	.46	P <sub>2</sub>	X	H .93 -	.67	O <sub>2</sub>	B	1.1	.58
	<sup>1</sup> $\Sigma^+$	H .37	.47		X	H 1.0	.56		C	H .83	.74		A	0.94 -	.65
CdH <sup>+</sup>	<sup>1</sup> $\Sigma^+$	H 1.0 -	.73	Li <sub>2</sub>	C	H 1.05 -	.74	BeO	C	H .93	.67		X	.91	.69
	<sup>1</sup> $\Sigma^+$				B	H 1.	.73		B	H .93	.72		X	.91	.63
					A	H 1.00 -	.75		A	H 1.00	.70	SO	B	H .91	.63
													X	.93	.67

there is also considerable deviation of the factor in brackets of Eq. (19) from its mean value. This factor has for the 93 tabulated molecules a mean value of 0.67 with a mean deviation of 0.06.

We may therefore expect that the wave functions of Morse, as presently modified, give a satisfactory representation of vibration and rotation states of a diatomic molecule whose energy equation does not contain any appreciable cubic term in  $(v + \frac{1}{2})$ . With these functions it should be possible to determine the probabilities of transition between a state  $(j', v')$  of one electronic state to a state  $(j'', v'')$  of another electronic state of the molecule. We shall have occasion to return to this matter in another communication.

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