DIATOMIC MOLECULES ACCORDING TO THE WAVE MECHANICS. II. VIBRATIONAL LEVELS

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Abstract

An exact solution is obtained for the Schroedinger equation representing the motions of the nuclei in a diatomic molecule, when the potential energy function is assumed to be of a form similar to those required by Heitler and London and others. The allowed vibrational energy levels are found to be given by the formula $E(n) = E_e + h\omega_0(n+1/2) - h\omega_0 x(n+1/2)^2$, which is known to express the experimental values quite accurately. The empirical law relating the normal molecular separation r_0 and the classical vibration frequency ω_0 is shown to be $r_0^3\omega_0 = K$ to within a probable error of 4 percent, where K is the same constant for all diatomic molecules and for all electronic levels. By means of this law, and by means of the solution above, the experimental data for many of the electronic levels of various molecules are analyzed and a table of constants is obtained from which the potential energy curves can be plotted. The changes in the above mentioned vibrational levels due to molecular rotation are found to agree with the Kratzer formula to the first approximation.

Introduction

THE wave equation for the nuclear motion[1] of a diatomic mocluele of nuclear masses M_1 and M_2 and charges Z_1 and Z_2, is approximately

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}[W - (e^2 Z_1 Z_2/r) + V_e(r)]\psi = 0 \tag{1}$$

where $\mu = M_1 M_2/(M_1+M_2)$, r is the distance between the nuclei, θ and ϕ the usual orientation angles measured from the center of gravity, and $V_e(r)$ the electronic energy calculated by considering the two nuclei as fixed in space a distance r apart.

The combination of the energy of repulsion and the electronic energy can be considered as a nuclear potential energy

$$E(r) = (e^2 Z_1 Z_2/r) - V_e(r).$$

The wave function Ψ can be considered as a product of three factors $\Psi = N \cdot \Phi(\phi) \cdot \Theta(\theta) \cdot R(r)/r$, where it can be shown that

$$\Phi = e^{ig\phi}$$

$$\Theta = \sin^g \theta \cdot P_j^g(\cos\theta)$$

where g and j are integers. The normalizing factor N is adjusted so that $\int \Psi \cdot \bar{\Psi} \, dv = 1$.

When these functions have been substituted in the general equation an equation for R results,

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[1] Born and Oppenheimer, Ann. d. Physik **84**, 457 (1927).

$$\frac{d^2R}{dr^2}+\frac{j(j+1)R}{r^2}+\frac{8\pi^2\mu}{h^2}[W-E(r)]R=0.\tag{2}$$

Since we are primarily interested in vibrational levels, j is set equal to zero.

The function $E(r)$ is a complicated function of r and of the electronic quantum numbers, and is not known accurately for any molecule, so it is useless to try to substitute the actual expression for E in the equation. It is possible, however, to assume some functional form for E which gives curves of approximately the same shape as the actual curves, and whose constants can be carried through the calculations to the end and then adjusted to conform to the experimental data.

The forms for E which have been used are, among others, the two series[2] $a/r+b/r^2+c(r-r_0)^3+\cdots$, and $b'(r-r_0)^2+c'(r-r_0)^3+\cdots$. These series give a general equation for the allowed energy levels

$$W=-D+h\omega_0[(n+\tfrac{1}{2})-x(n+\tfrac{1}{2})^2+K_3(n+\tfrac{1}{2})^3+\cdots]\tag{3a}$$

where the constants ω_0, x, K, $\cdots$, are functions of a, b, c, etc., and so if W is known empirically, E can be determined.

There are several objections to such series forms for E. In the first place the effect of all the terms in $(r-r_0)$ to the power 3 or over (which terms are not always small) must be computed by perturbation methods, thus adding another approximation to a list already long. In the second place the series for E determined from the known values of ω_0, x, K_3, etc., does not converge for large values of r, and so the series is only applicable over a restricted range of r.

In the third place the experimental data show that constants $K_3 \cdots$, are very much smaller than ω_0 or x, whereas the general series for E do not show that any such peculiarities should exist. In other words these series are too general.

We must search, then, for a form for E which will satisfy the following requirements: (1), It should come asymptotically to a finite value as $r\to\infty$; (2), It should have its only minimum point at $r=r_0$; (3), It should become infinity at $r=0$ (this need not be exactly true, however, the results are practically the same if E becomes very large at $r=0$); (4), It should exactly give the allowed energy levels as the finite polynomial.

$$W(n)=-D+h\omega_0[(n+\tfrac{1}{2})-x(n+\tfrac{1}{2})^2].\tag{3}$$

The very small correction term coefficients $K_3 \cdots$, can then be determined by perturbation methods with a reasonable expectation that these methods on such small quantities will give fairly accurate results.

A form will be chosen for E which satisfies requirements 1 and 2 exactly, and 3 approximately, and the problem will then be to show that the chosen form satisfies requirement 4.

A Solution of the Problem

The function which it is proposed to use here is the simple one

$$E(r)=De^{-2a(r-r_0)}-2De^{-a(r-r_0)}.\tag{4}$$

Fues, Ann. d. Physik **80**, 367 (1926).

This function has a minimum of $-D$ at $r=r_0$, comes asymptotically to zero at $r=\infty$ and in general gives curves of a very similar form to the few potential energy curves which have been calculated theoretically.[3,4,5] The only portion where it does not fit these curves is at $r=0$, where it should be infinity. But it will be seen that for the values of D and a used to fit the data $E(r)$ is between $100D$ and $10000D$ at $r=0$, a value so large that, as far as its effect on the energy levels and wave function goes, it is as good as infinity.

The frequency of classical small vibrations about r_0 is

$$\omega_0 = (a/2\pi)(2D/\mu)^{1/2}. \tag{5}$$

If this form of E is substituted in Eq. (3), j set equal to zero, and the transformation $u=(r-r_0)$ made, then

$$\frac{d^2R}{au^2}+\frac{8\pi^2\mu}{h^2}[W-De^{-2au}+2De^{-au}]R=0. \tag{6}$$

The boundary conditions are now set that R must be finite, single valued and continuous in the range $-\infty \leqq u \leqq +\infty$. It will be found that for some allowed solutions in this case $r\Psi$ will not be zero at $r=0$. But in every case $r\Psi$ will be extremely small, and since the point $r=0$ is some distance outside the important interval where $W>E$ this discrepancy will not affect the values of the energy levels.

In other words, since we have admittedly not used the correct form for E, and since we presumably could not find the true solution for R anyway, we must content ourselves with a solution which deviates from the correct solution in a portion which has little effect on the values of the allowed energies, especially since this deviation is very small.

Make a second transformation, letting $y=e^{-au}$. Then

$$\frac{d^2R}{dy^2}+\frac{1}{y}\ \frac{dR}{dy}+\frac{8\pi^2\mu}{a^2h^2}\left[\frac{W}{y^2}+\frac{2D}{y}-D\right]R=0 \tag{7}$$

where now R must be finite, continuous and single valued over the range $\infty \geqq y \geqq 0$. Let $R=e^{-dy}\cdot(2dy)^{b/2}\cdot F(y)$. Then if

$$d=2\pi(2\mu D)^{1/2}/ah \tag{8}$$

$$W=-a^2h^2b^2/32\pi^2\mu \tag{9}$$

and if $z=2dy$, then the equation becomes

$$z(d^2F/dz^2)+(b+1-z)(dF/dz)+\left(\frac{8\pi^2\mu D}{a^2dh^2}-b/2-1/2\right)F=0. \tag{10}$$

The solution of this equation is a finite polynomial[6] if $(8\pi^2\mu D/a^2h^2d-b/2 -1/2)=n$, an integer greater than zero. That is

$$b=4\pi(2\mu D)^{1/2}/ah-1-2n=k-1-2n \tag{11}$$

[3] O. Burrau, Klg. Danske. Vid. Selskab. **7**, 14 (1927).
[4] Heitler and London, Zeits. f. Physik **44**, 455 (1927).
[5] Morse and Stueckelberg, Phys. Rev. **33**, 907 (1929).
[6] Schroedinger Ann. d. Physik **80**, 483 (1926).

where k ($=4\pi(2\mu D)^{1/2}/ah$) must be greater than unity to have a discrete energy spectrum. The positive values of b are the only ones for which R is finite over the range $0 \leqq z \leqq \infty$. This means that n can have any integral value in the range $0 \leqq 2n \leqq (k-1)$.

The solutions for F are the generalized Laguerre polynomials

$$F = L_{n+b}^{b}(z) = \frac{d^b}{dz^b}\left[e^z \cdot \frac{d^{n+b}}{dz^{n+b}}(z^{n+b}e^{-z})\right].$$

Usually both superscript and subscript-minus-superscript are taken to be integers, although the superscript need not be integral. Here b is a fraction, and fractional differentiation must be used to obtain the polynomial from the definition above. The polynomial can be obtained by the use of the recursion formula obtained directly from Eq. (10) without evoking the use of fractional differentiation, but it is felt desirable to use the general definition for the sake of uniformity. Such differentiation does not vitiate the general formulas of integration etc., which have been developed for these polynomials, as long as n is an integer.

The formulas needed for fractional differentiation are given here for convenience.

$$\frac{d^b(z^a)}{dz^b} = \frac{\Gamma(a+1)}{\Gamma(a-b+1)}z^{a-b} \;;\quad \frac{d^b(e^{-z})}{dz^b} = e^{i\pi b}\cdot e^{-z}.$$

The application of this to the definition of F results in

$$L_{n+b}^{b}(z) = e^{i\pi(k-n-1)}\frac{\Gamma(k-n)}{n!}\left[x^n-(k-n-1)nx^{n-1}\right.$$
$$\left. +\frac{(k-n-1)(k-n-2)n(n-1)x^{n-2}}{2!}\cdots\right]$$

The normalizing integral

$$\int_0^\infty z^{b-1}\cdot e^{-z}\cdot L_{n+b}^{b}(z)\cdot L_{m+b}^{b}(z)\cdot dz = N_{nm}$$

$$= \begin{cases} 0 & (\text{if } n\neq m) \\ [\Gamma(k-n)]^2 \sum_{s=0}^{n} \frac{\Gamma(k-2n+s-1)}{\Gamma(s-1)} & (\text{if } n=m) \quad (12) \end{cases}$$

so that the complete wave function R for the nuclear vibration is

$$(2da/N_{nn})^{1/2}\cdot e^{-de^{-a(r-r_0)}}\cdot\left[2de^{-a(r-r_0)}\right]^{(k-2n-1)/2}\cdot L_{k-n-1}^{k-2n-1}\left[2de^{-a(r-r_0)}\right]$$

The square of this, times the perturbing energy, is to be multiplied by dr as a "volume element" and the integral taken from zero to infinity to obtain the perturbation energy.

The allowed energy levels are obtained from Eqs. (9) and (11)

$$W(n) = -a^2h^2(k-1-2n)^2/32\pi^2\mu$$
$$= -D+\frac{ah}{2\pi}(n+1/2)(2D/\mu)^{1/2}-a^2h^2(n+1/2)^2/8\pi^2\mu \qquad (13)$$
$$= -D+h\omega_0(n+1/2)-(h^2\omega_0^2/4D)(n+1/2)^2$$

from Eq. (5). As has been noted before, n takes on all integral values from zero to $(k-1)/2$. This is the first case noted of a Schroedinger equation giving a finite number of discrete energy levels.

Equation (13) is of the form of empirical Eq. (3), and it therefore is of the form which we set out to obtain. Since this equation expresses the empirical data so well in most cases, therefore the potential energy E, as given by Eq. (4), must have the same shape as the real potential energy throughout the range where Eq. (13) is a valid representation of the actual energy levels.

Thus if the lists of spectroscopically determined molecular constants give r_0 in Angstrom units and ω_0 and $\omega_0 x$ in wave-numbers, D is found in wave-numbers by the equation

$$D = \omega_0^2/4\omega_0 x \tag{15}$$

and the coefficient a is found by the relation

$$a = (8\pi^2 c\mu\omega_0 x/h)^{1/2} = 0.2454(M\omega_0 x)^{1/2} \tag{16}$$

where $M = M_1 M_2/(M_1 + M_2)$, M_1 and M_2 being the atomic weights of the two nuclei in terms of oxygen 16.

With r_0 known and D and a determined, the potential energy curve corresponding to the data is given by Eq. (4), where E is in wave-numbers if r is in Angstrom units.

An Empirical Law for r_0

When the available lists of molecular constants were examined it was found that in many cases ω_0 and $\omega_0 x$ were known but r_0 was not known. Several writers[7] have made use of a relation $r_0^2\omega_0 = $ constant to obtain the unknown r_0's, but deviations from this relation are quite large.[8]

To find what law obtained, if any, between r_0 and ω_0, 21 cases were taken from Birge's table[9] where r_0 and ω_0 were both known. An equation, $\log \omega_0 - p \log r_0 = \log K$ was assumed, and the data were subjected to a least squares analysis. The most probable values of the constants were found to be $p = 2.95$ and $K = 2975$. If p be taken to be 3 then the equation becomes

$$r_0^3\omega_0 = 3000\text{A}^3/\text{cm} \tag{17}$$

to within a probable error of ± 120 and a maximum deviation of 420. This is about due to the probable error of the recorded values of r_0, for if these values had a probable error of 1.3 percent, then r_0^3 would be given to a probable error of 4 percent.

[7] Birge, Phys. Rev. **25**, 240 (1925). Mecke, Zeits. f. Physik **32**, 823 (1925).

[8] Since this paper has been sent to the editor, Professor Birge has kindly brought to the writer's notice the fact that the equation $r_0^2\omega_0 = C_m$, where C_m has a different value for each molecule, is a better fit for some data than Eq. (17). In other words, the slope of the curve $\log r_0$ plotted against $\log \omega_0$ is nearer two for each individual molecule, but the slope of the band representing all molecules is nearer three, as given by Eq. (17). However, at least one value of r_0 must be known for a molecule before C_m can be known. Therefore Eq. (17) presents the only means of obtaining a value for r_0 for a molecule when no empirical value of r_0 for that molecule is available; and so it is useful, even if the probable error of the value so obtained were rather larger than the above least squares analysis would indicate.

[9] Mulliken, Phys. Rev. **32**, 206 (1928) and Birge, Int. Crit. Tables, Vol. V, 411, (1929).

TABLE I.[10]

No.	Mol.	State	A wave-nos.	D wave-nos.	a	r_0 obs. A units	r_0 calc. A units	reference
1	BeO	$^1\Sigma$	41600	42300	2.12	1.33	1.27	(14)
2	BeO	$^1\Sigma$	72200	51700	1.76	1.36	1.30	(14)
3	BO	$^2\Sigma$	74200	75100	2.14	1.21	1.17	(9)
4	BO	$^2\Pi$	59800	36800	2.04	1.36	1.34	(9)
5	BO	$^2\Sigma$	82500	40000	1.99	1.31	1.33	(9)
6	AlO	—	33100	33600	2.06	1.62	1.46	(15)
7	AlO	—	70000	49800	1.51	1.66	1.52	(15)
8	C_2	$^3\Pi$	55900	56700	2.14	1.31	1.23	(9)
9	C_2	$^3\Pi$	49100	40600	2.65	1.27	1.19	(9)
10	CN	$^2\Sigma$	75600	76600	2.32	1.17	1.14	(9)
11	CN	$^2\Pi_i$	68700	55200	2.30	—	1.20	(9)
12	CN	$^2\Sigma$	78600	53900	2.88	1.15	1.12	(9)
13	CO	$^1\Sigma$	90500	91600	2.29	1.15	1.12	(9)
14	CO	$^3\Pi$	99200	51600	2.45	—	1.20	(9)
15	CO	$^3\Sigma$?	94900	38300	1.93	—	1.37	(9)
16	CO	$^1\Pi$	96700	32600	2.67	1.24	1.26	(9)
17	CO	$^1\Sigma$	108800	28800	4.55	1.12	1.12	(9)
18	CO	$^1\Pi$	145000	46300	2.86	—	1.16	(9)
19	CO^+	$^2\Sigma$	193100	79200	2.91	1.11	1.11	(9)
20	CO^+	$^2\Pi_i$	177300	42700	2.42	1.25	1.25	(9)
21	CO^+	$^2\Sigma$	189100	29600	3.17	1.17	1.21	(9)
22	F_2	$^1\Sigma$	33600	34200	2.39	1.4	1.37	(9)
23	F_2	$^1\Sigma$	24800	1420	3.21	—	2.11	(9)
24	H_2	$1^1\Sigma$	38000	40100	1.85	.76	.89	(11)
25	H_2	$2^1\Sigma$	116900	27600	.69	1.31	1.31	(16)
26	H_2	$2^3\Pi$	112000	19500	1.48	.97	1.08	(11)
27	H_2	$2^3\Sigma$	118200	24600	1.44	1.08	1.05	(11)
28	H_2	(C)	119200	21300	1.41	1.06	1.08	(11)
29	H_2	$3^3\Pi$	131500	21200	1.37	1.14	1.09	(11)
30	H_2	$3^1\Pi$	225000	114500	.61	—	1.08	(11)
31	H_2	$4^3\Pi$	136500	20400	1.38	1.14	1.10	(11)
32	H_2	$5^3\Pi$	140400	21800	1.32	1.17	1.10	(11)
33	H_2	$6^3\Pi$	143000	23000	1.28	1.17	1.11	(11)
34	H_2^+	—	143700	20600	1.36	1.06	1.11	(11)
35	I_2	—	19100	19200	1.50	2.66	2.41	(13)
36	I_2	—	20300	4770	1.80	3.01	2.86	(13)
37	N_2	$^1\Sigma$	94300	95500	2.56	—	1.09	(9)
38	N_2	$^3\Sigma$?	103200	37600	2.42	—	1.28	(9)
39	N_2	$^1\Pi$	119100	51000	2.41	—	1.21	(9)
40	N_2	$^3\Pi_n$	126000	51200	2.46	1.21	1.21	(9)
41	N_2	$^3\Pi_n$	150300	46100	3.31	1.15	1.14	(9)
42	N_2^+	$^2\Sigma$	202800	67000	2.62	1.12	1.11	(9)
43	N_2^+	$^2\Sigma$	224500	62900	3.10	1.08	1.08	(9)
44	NO	$^2\Pi_n$	61300	62200	2.55	1.15	1.16	(9)
45	NO	$^2\Sigma$	149200	106200	2.42	1.07	1.09	(9)
46	NO	$^2\Pi_n$	80300	35400	1.82	1.42	1.43	(9)
47	NO	—	102100	50000	3.49	—	1.09	(9)
48	O_2	$^3\Sigma$	53000	53800	2.34	1.21	1.24	(9)
49	O_2	$^1\Sigma$?	54500	42100	2.39	1.23	1.29	(9)
50	O_2	$^3\Sigma$	59000	10100	2.44	1.61	1.62	(9)
51	O_2^+	$^2\Pi$	164400	56100	2.82	—	1.16	(9)
52	O_2^+	$^2\Pi$	165400	14300	2.57	—	1.50	(9)
53	O_2^+	—	174800	23800	2.31	—	1.43	(9)
54	O_2^+	—	187700	19700	2.93	—	1.37	(9)
55	SiN	—	49400	50000	1.92	1.57	1.38	(12)
56	SiN	—	38200	14500	3.15	1.58	1.43	(12)

[10] It will be noticed that the molecules for which r_0 calc. differs markedly from r_0 obs. are the least symmetric molecules in the list [ie., $M_1M_2/(M_1+M_2)$ differs considerably from $(M_1+M_2)/4$]. Professor R. S. Mulliken has kindly suggested to the writer that perhaps the rule enunciated in Eq. (17) above only holds accurately for molecules where M_1 is about equal to M_2. Certainly the calculated values of r_0 for the perfectly symmetric molecules O_2, H_2 and N_2 give the most consistent check with the experimental values. To apply the rule to very unsymmetric molecules it may be necessary to introduce an "unsymmetry factor" of the type $[4M_1M_2/(M_1+M_2)^2]^{1/4}$ into the term $r_0^3\omega_0$. Curiously enough, those levels for which the above rule is not satisfactory are the ones whose vibrational levels fit Eq. (13) least satisfactorily.

Since six different neutral molecules and two different molecular ions were used in the analysis, it would appear that K is independent of molecular weight, of the electronic state, and of the net charge on the molecule. An independent check of this rule is discussed in the following paper.

RESULTS

A table is given from which the potential energy curves can be plotted by means of the equation

$$E = A + De^{-2a(r-r_0)} - 2De^{-a(r-r_0)} \tag{18}$$

r_0 is given in Angstrom units and D, ω_0 and $\omega_0 x$ are given in wave-numbers. The values of r_0 in the column marked r_0 calc. were calculated from ω_0 by means of rule (17). The striking agreement between these values and the experimental values is to be noted. A is given so that all curves of neutral molecule and ion are reckoned from the lowest vibration level of the lowest electronic state of the neutral molecule. Figure 1 shows the levels for N_2 and N_2^+ plotted from these data.
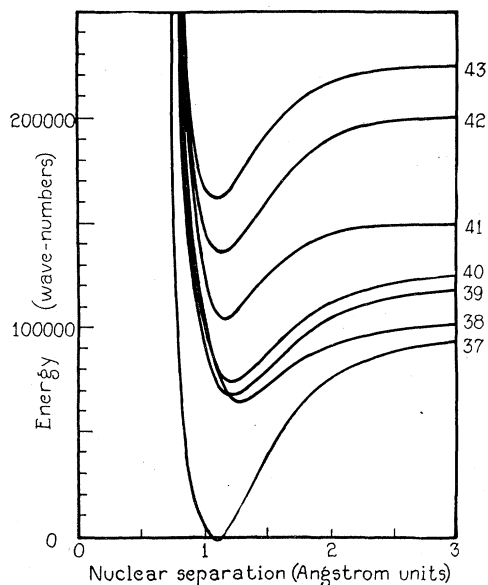

Fig. 1. Potential energy curves for nitrogen. Energy in wave-number and nuclear separation in Angstrom units. Numbers on curves refer to Table I.

ROTATIONAL LEVELS

When the rotational quantum number j is different from zero, the potential energy E in Eq. (4) is increased by an amount $E_j = j(j+1)h^2/8\pi^2\mu r_0^2$. Inasmuch as this increase only affects the wave function to an appreciable

[11] Birge, Proc. Nat. Acad. **14**, 12 (1928).
[12] Jenkins and Laszlo, Proc. Roy. Soc. **A122**, 103 (1929).
[13] Birge, Molecular Spectra in Gases, N. R. C. Bull. **57**, 230 (1927).
[14] Rosentl .1 and Jenkins, Phys. Rev. **33**, 163 (1929).
[15] Pomeroy , Phys. Rev. **29**, 57 (1927).
[16] Hyman and Birge, Nature **123**, 277 (1929).

extent in the region near $r=r_0$ (where $W>E$), it can be expanded about this point,

$$E_j = \frac{h^2 j(j+1)}{8\pi^2 \mu r_0^2}\left[1 - 2\frac{(r-r_0)}{r_0} + 3\frac{(r-r_0)^2}{r_0^2} - \cdots \right].$$

In the range where E_j has any appreciable effect, $r-r_0$ is small compared to r_0, and since $h^2 j(j+1)/8\pi^2 \mu r_0^2$, (which can be called R) is small compared to E for the usual values of j, this expansion can be added to the expansion for E, giving for the first two terms

$$E+E_j = -D+R-R^2/Da^2 r_0^2 + a^2(D-R)(r-r_0-R/r_0 a^2 D)^2$$

plus terms in higher powers of $(r-r_0)$.

These two terms can be considered as the first two terms of the expansion of

$$E+E_j = (D-R+R^2/Da^2 r_0^2)e^{-2a(r-r_0-R/r0a^2 D)}$$
$$-2(D-R+R^2/Da^2 r_0^2)e^{-a(r-r0-R/r0a^2 D)} \qquad (19)$$

indicating that to the first approximation D has decreased to $D-R+R^2/r_0^2 a^2 D$ and that r_0 has increased to $r_0+R/r_0 a^2 D$. The resultant energy levels will be, to the first approximation

$$
\begin{aligned}
W(n,j) = & -D+R+(ah/2\pi)(n+\tfrac{1}{2})\left(\frac{2D-2R}{\mu}\right)^{1/2} \\
& -a^2 h^2(n+\tfrac{1}{2})^2/8\pi^2\mu - R^2/Da^2 r_0^2 \\
= & -D+h\omega_0(n+\tfrac{1}{2})\left[1-h\omega_0(n+\tfrac{1}{2})/4D - h^2 j(j+1)/16\pi^2 D\mu r_0^2\right] \quad (20) \\
& +(h^2 j(j+1)/8\pi^2\mu r_0^2)\left[1-h^2 j(j+1)/16\pi^4\mu^2 r_0^4\omega_0^2\right].
\end{aligned}
$$

This agrees with the general Kratzer[17] formula to the first approximation. (i.e., as far as the above expansion is written).

The energy levels required by Eqs. (13) or (20) agree quite well with the experimentally determined levels for most molecules up to quite high values of n. In other words the $\Delta W(n)$ curve is a straight line for a considerable distance as n is increased. This indicates that the potential energy is effectively that given by Eq. (4) for a large range of r.

However there are some electronic states, usually the normal levels of the molecules, whose $\Delta W(n)$ curves are not straight lines, and therefore whose potential energy curves deviate somewhat from the form given by Eq. (4). This is not surprising, however, for the potential energies of initial states have usually much deeper minima than the rest, and would be expected to deviate most markedly from the standard form.

Such deviations from the straight line ΔW curve can be considered as due to an additional term in the potential energy of the form $E' = B/r + C/r^2 + \cdots$, where B and C etc., are very small compared to D. This perturbation can be dealt with in the same manner as E_j has been dealt with, and the values of B, C, $\cdots$, can be found by comparing the resulting formula for $\Delta W(n)$ with the data.

In most cases, however, the $\Delta W(n)$ curve deviates so little from the straight line that such a calculation is not necessary.

[17] Kratzer, Zeits. f. Physik **3**, 289 (1920).