liche anschauliche Interpretation der erhaltenen Wahrscheinlichkeitsdichten der Elektronen um die Atomkerne soll hier nicht eingegangen werden (vgl. Anm. [15]). Es ist beabsichtigt, in weiteren Arbeiten ausführlicher darauf einzugehen, besonders auf die Bedeutung der P_{sr} nach (8), wenn Funktionen nach (18) verwendet werden. Vorerst soll nur festgestellt werden, daß P_{ss} ein Maß dafür ist, wie wahrscheinlich von allen n Elektronen, in ihrer Verteilung im Molekül, von der Funktion χ_s nach (18) Gebrauch gemacht wird. Dies deckt sich mit der in der LCAO-Vorstellung gegebenen Interpretation der Ladungsordnung P_{ss}, wobei jetzt von Ladungsordnung im Punkt $\mathfrak{r}_s$ bei vorgegebenem η_s gesprochen werden muß. Kleine η_s (bei großem P_{ss}) weisen darauf hin, daß um $\mathfrak{r}_s$ eine weitgehende gleichmäßige Ladungsverteilung der Elektronen vorliegt. Im umgekehrten Falle darf auf eine mehr lokalisierte Dichteverteilung geschlossen werden.

Die mit (18) nach (7) erhaltenen Integrale haben die Form [10, 13]

$$[p\,q] = (\eta_p\,\eta_q)^{-3/4} A_{pq}^{3/2} \cdot \exp\{-\tfrac{1}{2} A_{pq}(\mathfrak{r}_p-\mathfrak{r}_q)^2\} = S_{pq}\,, \qquad (20\,a)$$

$$[\Delta\,|\,p\,q] = A_{pq}\{A_{pq}(\mathfrak{r}_p-\mathfrak{r}_q)^2-3\}\,S_{pq}\,, \qquad (20\,b)$$

$$[\mu^{-1}\,|\,p\,q] = C_{pq}\,K(C_{pq}\,|\,\mathfrak{r}_\mu-\mathfrak{r}_{pq}\,|)\;S_{pq}\,, \qquad (20\,c)$$

$$[p\,q\,|\,r\,s] = B_{rs}^{pq}\,K(B_{rs}^{pq}\,|\,\mathfrak{r}_{pq}-\mathfrak{r}_{rs}\,|)\;S_{pq}\,S_{rs}\,, \qquad (20\,d)$$

wobei
$$K(u) = \frac{2}{u\sqrt{\pi}}\int_0^u \exp\{-t^2\}\,dt \qquad (21)$$

und
$$A_{pq} = 2\,\eta_p\,\eta_q/(\eta_p+\eta_q)\,; \quad C_{pq} = (\eta_p+\eta_q)^{1/2};$$
$$B_{rs}^{pq} = \left[\frac{(\eta_p+\eta_q)\,(\eta_r+\eta_s)}{\eta_p+\eta_q+\eta_r+\eta_s}\right]^{1/2}; \quad \mathfrak{r}_{pq} = \frac{\eta_p\,\mathfrak{r}_p+\eta_q\,\mathfrak{r}_q}{\eta_p+\eta_q}\,. \qquad (22)$$

Das Integral $K(u)$ kann durch eine einfache Funktion $\tilde{K}(u)$ angenähert werden [13]. Die Genauigkeit beträgt

$$|K(u)-\tilde{K}(u)| < 4\cdot 10^{-6} \quad (0 \leqq u < \infty) \qquad (23)$$

und sollte in der Regel ausreichen.

Da die Integrationen sehr einfach sind, ist zu hoffen, daß die Anzahl der GAUSS-Funktionen größer gehalten werden kann. Auf diese Weise werden nicht nur einige Mängel dieser Funktionen kompensiert, sondern es besteht darüber hinaus die Hoffnung, näher an die HF-Energiewerte für Moleküle heranzukommen.

Vibrational-Rotational Levels in Diatomic Molecules

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In this paper we give an analytical formula for the energy eigenvalues of the vibrational-rotational terms of diatomic molecules on the basis of a new approximate potential function. Eigenfunctions of this problem are also discussed.

The vibrational-rotational levels of diatomic molecules are to be obtained from the radial SCHRÖDINGER equation, written in atomic units,

$$y'' + [-(\alpha\,r_e)^2 - 2\,I_e\,V(x) - J(J+1)/x^2]\,y = 0, \qquad (1)$$

in which $x = r/r_e$, $V(x)$ is the potential function and $\alpha^2 = -2\,M\,E_{vJ}$. The parameter E_{vJ} denotes the energy of the vibrational (v) and rotational (J) levels. The other symbols have the well known significance. We here use the international notation customary in the theory of diatomic molecules.

For $J = 0$ the SCHRÖDINGER equation can be solved exactly for an approximate form of the function $V(x)$ which well agrees with the experimental one. (TIETZ [1], MORSE et al. [2].)

It is the purpose of this work to give a simple potential function for which eq. (1) can be solved exactly in case of any J, provided the SUTHERLAND parameter Δ is correct.

The suggested function $V(x)$ allows to discuss the dependance of the eigenvalues of the vibrational-

[1] T. TIETZ. J. Chem. Phys. **38**, 3036 [1963].
[2] References are given in [1].

rotational levels on the rotational quantum number. This problem is physically interesting.

1. Potential Function for Diatomic Molecules

We suggest the approximate potential function

$$V(x) = [D_e r_e^{-2}] [T x^{-2} - Z r_e x^{-1} + A P r_e (1 + A x)^{-1} + A^2 Q (1 + A x)^{-2}], \quad (2)$$

where the constants allow for adaption to the correct potential energy.

In formula (2) the first term can be considered [3] as part of the centrifugal energy of the nuclei depended on the electronic states. In our calculations it decides on the nature of the singularity of the potential. The other terms denote the interaction energy of the nuclei screened by the electrons.

A similar form of the function $V(x)$ has been discussed by TIETZ [4].

The function (2) has the following properties: it reaches asymptotically a finite value as $x \to \infty$ and it becomes infinite at $x = 0$. These properties are necessary conditions for the potential energy of diatomic molecules [5].

The constants T, Z and P are determined so that the function (2) fulfils some other criteria [5]:

a) *necessary:* $V(x)$ should have a minimum at

$$x = 1 \quad (r = r_e);$$

b) *desiderable:*

$$V(\infty) - V(1) = D_e, \quad [d^2V/dx^2]_{x=1} = k_e r_e^2.$$

A simple calculation leads to

$$\begin{aligned} T &= [(1 + A)\, \Delta - A]\, r_e^2 + [A/(1 + A)]^3 Q, \\ Z r_e &= [(1 + A)(2 + A)\, \Delta - A(3 + A)]\, r_e^2 \\ &\quad + (3 + 2A)[A/(1 + A)]^3 Q, \\ P r_e &= [(1 + A)^3/A](\Delta - 1)\, r_e^2 \\ &\quad - (1 - 2A)[A/(1 + A)]\, Q. \end{aligned} \quad (3)$$

In these expression the symbol Δ denotes the SUTHERLAND parameter defined as [5]:

$$\Delta = k_e r_e^2 / 2 D_e.$$

The constants A and Q are calculated in the following chapters.

[3] L. LANDAU u. E. LIFSHITZ, Quantum Mechanics, Pergamon Press, London—Paris 1959.

[4] T. TIETZ, Acta Phys. Hung. **13**, 359 [1961].

2. Solution of the Schrödinger Equation

It is known, that the wave function fulfils the boundary conditions: a) $y(r \to 0) = r^\lambda$ (the parameter λ depends on the singularity of the equation), b) $y(r \to \infty) = e^{-\alpha r}$. For the discussed problem the quantum number v denotes the number of the zeros of the function y (except $r = 0$ and $r = \infty$).

Taking into consideration the mentioned conditions, wave functions can be determined by

$$y(r) = r^\lambda e^{-\alpha r} f(r)\, w(r),$$

where $w(r)$ is a polynomial of degree v and $f(r)$ is a limited, positive function of r.

Now, let us write the solution of eq. (1) for the potential energy function (2) (with the singularity r^{-2} at $r = 0$) in the form [6]:

$$y = x^\lambda e^{-\alpha r_e x} [1 + A x]^{-q} w(x) \quad (4)$$

where

$$\lambda = \tfrac{1}{2} + [(J + \tfrac{1}{2})^2 + 2 M D_e T]^{1/2}.$$

The parameter q is determined from the condition

$$q(q + 1) = 2 M D_e Q,$$

so that

$$q = -\tfrac{1}{2} + [\tfrac{1}{4} + 2 M D_e Q]^{1/2}.$$

Then a polynomial of degree v:

$$w(x) = \sum_{p=0}^{v} a_p x^p$$

satisfies eq. (1). The coefficients a_p follow from the recurrence formula:

$$a_{p+1} = -[d_{p,p-1} a_{p-1} + d_{pp} a_p],$$

where

$$\begin{aligned} &a_{-1} = 0; \quad a_0 = 1; \quad p = 0, 1, 2, \ldots, (v - 1), \\ &d_{p,p-1} = 2 \alpha r_e A (v - p)[(p + 1)(2\lambda + p + 2)]^{-1}, \\ &d_{p,p} = 2 \left\{ M D_e Z r_e - \alpha r_e (\lambda + p) - A q (\lambda + p) \right. \\ &\qquad \left. + A p \left(\lambda + \frac{p - 1}{2} \right) \right\} [(p + 1)(2\lambda + p + 2)]^{-1} \end{aligned}$$

and the coefficients $d_{p,p-1}$, d_{pp} fulfil the non-triviality condition:

$$\begin{vmatrix} d_{00} & 1 & 0 & \ldots & 0 \\ d_{10} & d_{11} & 1 & \ldots & 0 \\ \cdot & \cdot & \cdot & \ldots & \cdot \\ \cdot & \cdot & \cdot & \ldots & \cdot \\ 0 & 0 & \cdot & \ldots & d_{v,v-1}\ d_{vv} \end{vmatrix} = 0. \quad (5)$$

[5] Y. P. VARSHNI, Rev. Mod. Phys. **29**, 664 [1957]. — Y. P. VARSHNI u. R. CH. SHUKLA, Trans. Faraday Soc. **57**, 537 [1961].

[6] L. WOJTCZAK, Acta Phys. Polon. **23**, 205 [1963].

The eigenvalues α_{vJ} are given by the simple, exact formula:

$$\alpha_{vJ} = M D_e [Z r_e - P r_e] [(v + \lambda - q) r_e]^{-1}. \quad (6)$$

The details of the procedure described here are presented in [6].

For practical calculations condition (5) can be transformed into

$$\begin{aligned} Q &= [(1+A)^6/A] \cdot [(H^2 + \{(1+A)(\Delta - 1) + 2A(H I_A - 1)\}/\{1+A\}^2)^{1/2} - H]^2 r_e^2, \\ H &= [1 - (1 + A(1+2A) B) \Delta + \Delta^2 I_0^{-2} + AB(\{1+2A\}^2 \Delta^2 I_A^{-2} + I_A^2)]^{1/2}, \\ I_A &= [(\{1+2A\} \Delta + J(J+1)/2 M D_e r_e^2)^{1/2} + (v + \tfrac{1}{2})/(2 M D_e r_e^2)^{1/2}], \\ B &= 3(1+2A)^{1/2} [(2+A) \Delta - 1]/[4 \Delta (1+A)^2], \end{aligned} \quad (7)$$

where we assume $A = [2/3][\Delta/10]^2$ approximately.

The constant A is so chosen that the spectroscopic constants α_e and $\omega_e x_e$ would have optimal values, taking into consideration, on the other hand, the simplicity of the calculations. The parameter A can be determined in other ways also, for example by means of the variational principle for the potential energy.

It can be shown in a similar way that the SCHRÖDINGER equation has also an exact, analytical solution for the form of $V(x)$

$$V(x) = D_e r_e^{-2} \left[T x^{-2} - Z r_e x^{-1} + \sum_{i=0}^{n} (A_i P_i r_e (1 + A_i x)^{-1} + A_i^2 Q_i (1 + A_i x)^{-2}) \right]$$

with the singularity r^{-2} at $r = 0$. It may easily be verified that, analogous to (4) and (6), the eigenfunctions and the eigenvalues then have the form

$$y = x^{\lambda} e^{-\alpha r_e x} \left[\prod_{i=0}^{n} (1 + A_i x)^{-q_i} \right] w(x), \qquad \alpha_{vJ} = M D_e [\bar{Z} r_e - \bar{P} r_e] [(v + \lambda - \bar{q}) r_e]^{-1}.$$

The coefficients are to be determined here by a system of very complicated, algebraic equations and can be adapted to any spectroscopic constants and properties of the potential energy.

3. Formula for the Energy Eigenvalues

In this manner, the formula for the vibrational-rotational energy eigenvalues can be written as:

$$\begin{aligned} E_{vJ} &= -D_e [1 - (1 + A\{1+2A\} B) \Delta + \Delta^2 I_0^{-2} + AB(\{1+2A\}^2 \Delta^2 I_A^{-2} + I_A^2)], \\ I_A &= [(\{1+2A\} \Delta + J(J+1)/2 M D_e r_e^2)^{1/2} + (v + \tfrac{1}{2})/(2 M D_e r_e^2)^{1/2}] \end{aligned} \quad (8)$$

and the quantities A and B are given by (7).

The first coefficients of the power series expansion of $E_{vJ}[(v + \frac{1}{2}), J(J+1)]$ have the exact values. In the case $J = 0$ the last result agrees well with the corresponding result proposed by TIETZ [1]. The expression (8) gives the interesting dependance of the energy E_{vJ} on the rotational quantum number.

4. Examples

We present the following numerical calculations. In Table 1 we make a comparison of the spectral line frequencies for the transition:

$$J = 0 \rightarrow 1, \qquad v = 0, 1, 2$$

with the observed ones [7] for the RbCl and NaF molecules. In Tables 2 and 3 we compare our results for α_e and $\omega_e x_e$ with results obtained by MORSE [5] and TIETZ [1] and with experimental data [5].

molecule	RbCl		NaF	
	our results	exper.	our results	exper.
1	5244.4	5241.1	26092.4	26059.4
2	5223.6	5214.0	25884.4	25788.9
3	5202.8	5187.0	25676.4	25521.2

Table 1. A comparison of our results with the observed frequencies in Mc/sec of the spectral lines.

[7] J. TRISCHKA u. R. BRAUSTEIN, Phys. Rev. **96**, 968 [1954]. — R. K. BAUER u. H. LEW, Canad. J. Phys. **41**, 1461 [1963].

diatoms	experiment	our results	MORSE	TIETZ
	in atomic units			
H_2	2.993	5.003	2.222	2.993
ZnH	0.250	0.282	0.428	0.250
CdH	0.218	0.226	0.359	0.218
HgH	0.312	0.312	0.509	0.312
CH	0.534	0.543	0.523	0.534
OH	0.714	0.714	0.714	0.714
HF	0.770	0.723	0.582	0.770
HCl	0.301	0.289	0.310	0.301
HBr	0.226	0.219	0.254	0.226
HI	0.183	0.166	0.201	0.183
Li_2	0.007	0.010	0.010	0.007
Na_2	0.0008	0.012	0.001	0.0008
K_2	0.0002	0.0003	0.0004	0.0002
N_2	0.018	0.016	0.028	0.018
P_2	0.001	0.0008	0.001	0.001

Table 2. A comparison of our results for α_e with the corresponding results for the MORSE function, TIETZ function and experimental data.

diatoms	experiment	our results	MORSE	TIETZ
	in atomic units			
H_2	177.99	193.52	126.05	140.88
ZnH	55.14	44.93	84.17	66.70
CdH	46.30	44.45	82.76	65.60
HgH	83.01	82.18	129.15	101.68
CH	64.30	58.64	69.54	70.35
OH	82.81	75.52	94.38	95.02
HF	90.07	72.96	79.83	91.88
HCl	52.05	44.76	60.01	59.02
HBr	45.21	39.56	55.56	52.09
HI	39.73	34.96	51.68	48.79
Li_2	2.59	2.84	3.64	3.10
Na_2	0.72	0.72	1.06	0.84
K_2	0.35	0.30	0.51	0.40
N_2	14.45	13.00	17.42	16.72
P_2	2.80	2.08	3.71	3.26

Table 3. A comparison of our results for $\omega_e x_e$ with the corresponding results for the MORSE function, TIETZ function and experimental data.

5. Note on the Eigenfunctions of the Discussed Problem

The exact eigenfuctions y_{vJ} which belong to eigenvalues α_{vJ} are given by the formula (4).

In case of the fulfilled conditions described in chapter 2 the differential equation for $w(x)$ can be written as:

$$\frac{1+Ax}{1/\beta+x}\,x\,w''(x)+(2\lambda\beta-2A\alpha x)\,w'(x)+2\alpha A v\,w(x)=0.$$

The parameter

$$\beta=[\alpha+Aq-A\lambda]\cdot[\{1+4\alpha A\lambda(\alpha+Aq-A\lambda)^{-2}\}^{1/2}-1]/2A\lambda.$$

For practical operations it is worth to remark that

$$[1+Ax]/[1/\beta+x]\approx 1$$

for x near to the equilibrium distance ($x=1$). (For the form of the eigenfunctions the behaviour of the polynomial coefficients for very large x have no importance.) Then eq. (9) reduces to the simple, approximate form

$$x\,w''(x)+(2\lambda\beta-2A\alpha x)\,w'(x)+2\alpha A v\,w(x)=0$$

satisfied by the confluent hypergeometric series $F(-v, 2\lambda\beta, 2\alpha A x)$.

The form of the eigenfunctions is:

$$y_{vJ}=x^{\lambda}e^{-\alpha r_e x}[1+Ax]^{-q}F(-v, 2\lambda\beta, 2\alpha A x),$$

which is a good approximation helpful for many applications.

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