Potential function for diatomic molecules

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A new potential function for diatomic molecules is suggested and its Schrodinger equation has been solved by the method of Pekeris (1934). Values of anharmonicity and rotation-vibration coupling constants have been calculated by the method suggested by Varshni (1957) The results have been compared with experimental values and also with those calculated by different authors.

INTRODUCTION

Potential energy function for diatomic molecules is given by comparison with experimental data Comparative study of various potential functions was made by Varshni (1957), Manning (1935). Steele *el al* (1962) and Levine (1966), Considering some applications of the potential functions, the solution of corresponding Schrodinger equation and determination of the wave functions becomes necessary. The solution of Schrödinger equation has been possible in a few cases (Kratzer 1920, Morse 1929, Manning 1935, Eisenhart 1948, Tietz 1963, Wojtczak 1965) In some cases the solution is very complex

As suggested by Landau (1959) the potential function can be obtained by the combination of centrifugal energy and electrical interaction energy of the nuclei screened by electrons Based on this suggestion of Landau, Wojtczak (1965) proposed that the potential energy function should reach asymptotically to a finite value for $x \to \infty$, and to ∞ as $x \to 0$. He therefore suggested the following form for P.E function :

$$V(x) + D_e \left(\frac{T}{x^2} + \frac{Zf(x)}{x} + 1 \right)$$

where T and Z are arbitrary constants, $f(x)$ is screening function, variable $x = r/r_e$ and $V(x)$ is some function of x. The P.E function should also satisfy Varshni conditions.

The function having a simpler solution and comparable results of ω_e, $\omega_e x_e$ and α_e, are described here. The new function has been arrived at by giving simple values for screening function $f(x)$ and the function $V(x)$. This has been done by semiempirical logic and the following form for P.E. function has been arrived at :

$$V = D_e + \frac{A}{r} + \frac{Ar_e}{r^2} - \frac{3A}{ar_e^2} e^{-a(r-r_e)} \qquad \ldots \text{ (a)}$$

where D_e is dissociation energy, A is a constant determined to satisfy Varshni condition, r_e is equilibrium separation between nuclei, and α is a parameter the value of which determines the percentage accuracy of the results of $\omega_e x_e$ and α_e. The present discussion is divided into two parts. In the first, it is assumed that $\alpha r_e = 3/2$ and then in the second part a generalization like $\alpha r_e = \delta$ has been attempted. The Schrödinger equations for both first and second general part have been solved. From the general solution, it appears that ω_e is the same for all values of δ but $\omega_e x_e$ and α_e depend on δ. Results of $\omega_e x_e$ have been obtained and tabulated for values of δ ranging from $\delta = 1.5$ to $\delta = 2$ (table 4). The percentage errors in $\omega_e x_e$ for ZnH and HCl have been calculated at various δ's (table 5). It indicates that percentage error in the value of $\omega_e x_e$ depends on δ and for a group of molecules there exists a particular value of δ at which there is near coincidence between experimental and calculated values of $\omega_e x_e$. It appears that δ which produces near coincidence may be a function of atomic numbers of nuclei and the quantum numbers of the electrons in outermost shells.

Out of the two methods to test the validity of function, *viz.* (1) Matching of values of ω_e, $\omega_e x_e$ and α_e with the experimental values, (2) Percentage deviation of suggested potential from R.K.R. potential, (Steele *et al*) the first method is used to check the validity of suggested function.

Our function satisfies the following Varshni conditions

$$(dV/dr)_{r-r_e} = 0 \qquad \qquad \text{.. (1)}$$

$$(V)_{r=0} = \infty \qquad \qquad \text{... (2)}$$

$$(V)_{r=\infty} \equiv 0 \qquad \qquad \text{... (3)}$$

$$\left(\frac{d^2 V}{dr^2} \right)_{(r=r_-)} = k_e \qquad \qquad \text{... (4)}$$

Part I

It is assumed here that $\alpha r_e = 3/2$.

From (4) $\qquad\qquad A = \frac{2}{7} k_e r_e^3 \qquad\qquad \text{... (5)}$

According to Varshni (1957), vibration-rotation coupling constant is given by

$$\alpha_e = -\left(\frac{xr_e}{3} + 1 \right) \frac{6B_e^2}{\omega_e} \qquad \qquad \text{... (6)}$$

and $\qquad\qquad \omega_e x_e = \left(\frac{5}{3} X^2 - Y \right) \frac{2.1078 \cdot 10^{-16}}{\mu_A} \qquad \qquad \text{... (7)}$

From (a)
$$X = \left(\frac{V''}{V''} \right)_{r=r_e} = -\frac{93}{14} \frac{1}{r_e}$$

$$Y = \left(\frac{V'''}{V''} \right)_{r=r_e} = \frac{1071}{28 r_e^2}$$

Substituting these values

$$\omega_e x_e = \frac{74.47}{\mu_A r_e^2} 10^{-16} \qquad \ldots \text{(8)}$$

and
$$\alpha_e = 7.285 \, B_e^2 \qquad \ldots \text{(9)}$$

Values calculated from (8) and (9) are compared with other values given in tables 1 and 2

TABLE 1

Diatom	$\omega_e x_e$ (calculated)	$\omega_e x_e$ (experimental)	$\omega_e x_e$ (Morse)
H_2	268.6	117.99	179.00
ZnH	29.52	55.14	4.72
CdH	24.01	46.3	5.16
HgH	24.53	83.01	3.31
CH	63.84	64.3	72.55
OH	83.30	82.81	96.12
HF	92.51	90.06	122.305
HCl	46.76	52.05	56.27
HBr	37.42	45.21	42.14
HI	28.95	39.73	40.50
Li$_2$	2.973	2.59	1.425
Na$_2$	0.6837	0.726	0.092
K$_2$	0.2481	0.35	0.00389
N$_2$	8.884	14.456	14.756
P$_2$	1.341	2.8	1.895
O$_2$	6.393	12.073	11.263
SO	3.133	6.116	4.325
Cl$_2$	1.077	4.00	2.8
Br$_2$	0.3569	1.146	0.1927
I$_2$	0.1650	0.6127	0.3159
ICl	0.5041	1.465	1.054
CO	8.539	13.46	14.97
NO	7.526	13.97	12.79

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SOLUTION OF SCHRÖDINGER EQUATION [WHEN $\alpha r_e = 3/2$]

Morse (1929) solved wave equation for nuclear motion. This wave equation was originally suggested by Born and Oppenheimer (1927). By separating r, θ and ϕ dependent parts, Morse obtained the following equation for radial function $R(r)$.

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

TABLE 2

Diatom	α_e experimental	
H$_2$	2 993	6.13
ZnH	0.25	0.2022
CdH	0.21	0.1505
HgH	0 312	0.1617
CH	0 534	0.5322
OH	0.714	0 6961
HF	0.7705	0.7716
HCl	0 3019	0.2732
HBr	0 226	0.1974
HI	0 183	0.1354
Li$_2$	0.00704	0.009385
Na$_2$	0 00079	0.001095
K$_2$	0 000219	0.0002483
N$_2$	0.0187	0 01247
P$_2$	0 00142	0.0008584
O$_2$	0.015	0.009640
SO	0.00562	0.003250
Cl$_2$	0 0017	0.0007663
Br$_2$	0.000275	0 0001475
I$_2$	0.000117	0.00004749
ICl	0.00053	0 0002474
CO	0 01748	0 001251
NO	0.0178	0 01111

Changing the notation, $R = S$, $E(r) = V$ and $W = E$, the equation for radial function becomes

$$\frac{d^2S}{dr^2} - \frac{J(J+1)}{r^2} S + \frac{8\pi^2\mu}{h^2} [E - V]S = 0$$

When the value of V from equation (a) is put in the above, the following equation is obtained.

$$\frac{d^2S}{dr^2} - \frac{J(J+1)}{r^2} S + \frac{8\pi^2\mu}{h^2} \left(E - D_e - \frac{A}{r} - \frac{Ar_e}{r^2} \right.$$

$$\left. + \frac{3A}{\alpha r_e^2} e^{-\alpha(r-r_e)} \right) S = 0$$

Let $\quad B = \dfrac{h^2 J(J+1)}{8\pi^2\mu r_e^2}$, and $\quad y = e^{-\alpha(r-r_e)}$

$$\therefore \quad \frac{r_e}{r} \approx 1 + \frac{1}{\alpha r_e} \left[(y-1) - \frac{(y-1)^2}{2} \right] + \frac{1}{\alpha^2 r_e^2} (y-1)^2$$

$$\therefore \quad \left(\frac{r_e}{r} \right)^2 \approx 1 + \frac{2}{\alpha r_e} \left[(y-1) - \frac{(y-1)^2}{2} \right] + \frac{3}{\alpha^2 r_e^2} (y-1)^2$$

$$\therefore \quad y^2 \frac{d^2S}{dy^2} + y \frac{dS}{dy} + \frac{8\pi^2\mu}{\alpha^2 h^2} [C_0 + C_1 y + C_2 y^2] S = 0 \qquad (10)$$

where

$$C_0 = E - D_e - \frac{A}{r_e} \left(1 - \frac{3}{2\alpha r_e} + \frac{1}{\alpha^2 r_e^2} \right) - \frac{A}{r_e} \left(1 - \frac{3}{\alpha r_e} + \frac{3}{\alpha^2 r_e^2} \right)$$

$$- B \left(1 - \frac{3}{\alpha r_e} + \frac{3}{\alpha^2 r_e^2} \right) \qquad (11)$$

when $\quad \alpha r_e = 3/2, \quad C_0 = E - D_e - \dfrac{7}{9} \dfrac{A}{r_e} - \dfrac{B}{3}$

Similarly $\quad C_1 = -\dfrac{A}{r_e} \left(\dfrac{2}{\alpha r_e} - \dfrac{2}{\alpha^2 r_e^2} \right) - \dfrac{A}{r_e} \left(\dfrac{4}{\alpha r_e} - \dfrac{6}{\alpha^2 r_e^2} \right)$

$$+ \frac{3A}{\alpha r_e^2} - B \left(\frac{4}{\alpha r_e} - \frac{6}{\alpha^2 r_e^2} \right), \qquad (12)$$

For $\quad \alpha r_e = 3/2, \quad C_1 = \dfrac{14A}{9 r_e}$;

$$C_2 = -\frac{A}{r_e} \left(-\frac{1}{2\alpha r_e} + \frac{1}{\alpha^2 r_e^2} \right) - \frac{A}{r_e} \left(-\frac{1}{\alpha r_e} + \frac{3}{\alpha^2 r_e^2} \right) - B \left(-\frac{1}{\alpha r_e} + \frac{3}{\alpha^2 r_e^2} \right).$$

$$\dots \quad (13)$$

For $\quad \alpha r_e = 3/2, \quad C_2 = -\dfrac{7A}{9 r_e} - \dfrac{2}{3} B.$

When the following substitutions are made in (10), equation (14) is obtained.

$$S = e^{-z/2} \cdot z^{b/2} u \quad \text{where} \quad z = 2dy$$

$$d^2 = -\frac{8\pi^2 \mu C_2}{\alpha^2 h^2}$$

$$b^2 = -\frac{32\pi^2 \mu}{\alpha^2 h^2} C_0$$

$$K = \frac{8\pi^2 \mu}{\alpha^2 h^2} \frac{C_1}{2d} = -\frac{b+1}{2}$$

∴ $$\frac{d^2 u}{dz^2} + \frac{du}{dz}\left(\frac{b+1}{z} - 1\right) + \frac{k}{z} u = 0. \qquad \dots \ (14)$$

Put $\qquad\qquad u = \Sigma a_n z^n$ in (14).

This gives

$$a_{n+1} = a_n \frac{n-K}{n(n+1)+(b+1)(n+1)}$$

The series should be finite and terminate at n-th term.

∴ $\qquad\qquad\qquad n = K$

∴ $\qquad\qquad \frac{8\pi^2 \mu}{\alpha^2 h^2} \frac{C_1}{2d} - \frac{b+1}{2} = n$

∴ $\quad C_0 = \frac{C_1}{d}(n+1/2) - \frac{\alpha^2 h^2}{8\pi^2 \mu}(n+1/2)^2 - \frac{8\pi^2 \mu}{\alpha^2 h^2}(C_1/2d)^2 \qquad \dots \ (15)$

When the value of C_0 is introduced in the above, the value of E is given in the following form .

$$E = \left(\frac{14}{9}\frac{A}{r_e}\right)\frac{1}{d}(n+1/2) - \frac{\alpha^2 h^2}{8\pi^2 \mu}(n+1/2)^2 + \frac{1}{3}\frac{h^2 J(J+1)}{8\pi^2 \mu r_e{}^2} + D_e + \frac{7}{9}\frac{A}{r_e}$$

$$-\frac{8\pi^2 \mu}{\alpha^2 h^2}\frac{1}{4d^2}\left(\frac{14}{9}\frac{A}{r_e}\right)^2.$$

Substituting d and expanding the first and last terms

$$\frac{E}{ch} = \frac{\alpha}{\pi c}\sqrt{\frac{7A}{18\mu r_e}}\ (n+1/2) - \frac{3\alpha h^2 r_e}{56\pi^3 \mu r_e{}^2 Ac}\sqrt{\frac{7A}{18\mu r_e}}\ J(J+1)(n+1/2)$$

$$-\frac{\alpha^2 h}{8\pi^2 \mu c}\ (n+1/2)^2 + \frac{hJ(J+1)}{8\pi^2 \mu r_e{}^2 c} + \frac{D_e}{ch}$$

Introduce value of A from (5) in the coefficient of $(n+1/2)$ in the first term which represents ω_e of diatomic molecule so that,

$$\frac{\alpha}{\pi c} \sqrt{\frac{7A}{18\mu r_c}} = \omega_e = \frac{1}{2\pi c} \sqrt{\frac{k_e}{\mu}} \ .$$

Above formula of ω_e is the same as that obtained by other considerations. Values calculated from this are compared with experimental ones and given in table 3

TABLE 3

Diatom	ω_c calculated	ω_e experimental
H_2	4390	4395
ZnH	1603	1607.6
CdH	1429	1430
HgH	1387	1387.1
CH	2859	2861
OH	3732	3735
HF	4134	4138.5
HCl	2986	2989.7
HBr	2647	2649.7
HI	2308	2309.5
Li_2	351.1	351.43
Na_2	159 1	159.23
K_2	92.53	92 64
N_2	2357	2359.6
P_2	779 8	780.43
O_2	1579	1580 4
SO	1123	1123.7
Cl_2	563 5	564 9
Br_2	546.4	323.2
I_2	214.4	214 6
ICl	119.1	384.18
CO	2168	2170.2
NO	1902	1904

Part 11

Generalisation of α

It is assumed here that in general $\alpha r_e = \delta$.

From (a), (6) and (7)

$$x = \frac{3}{r_e} \left(\frac{-10+\delta^2}{8-3\delta} \right) \qquad \qquad \cdots \quad (16)$$

$$y = \frac{1}{r_e^2} \frac{144-3\delta^3}{8-3\delta} \qquad \qquad \cdots \quad (17)$$

$$\omega_e x_e = \left[\frac{5}{3} x^2 - y \right] \frac{2.1078 \ 10^{-16}}{\mu_A}$$

From (16) and (17) $\omega_e x_e$ assumes following form

$$\omega_e x_e = \left[\frac{348+432\delta-300\delta^2+24\delta^3+6\delta^4}{(8-3\delta)^2} \right] \frac{2.1078}{\mu_A r_e^2} 10^{-16} \qquad \cdots \quad (18)$$

The value of $\omega_e x_e$ changes with δ in the manner shown in the following table 3A.

<div align="center">

TABLE 3A

δ	$\omega_e x_e \times \mu_A r_e^2 \times 10^{16}$
1.5	74,47
1.6	83.97
1.7	96.12
1.8	111.1
1.85	120.3
1.9	131.0
2	158.1

</div>

TABLE 4. Variation of $\omega_e x_e$ with δ

$\delta =$	1.5	1.6	1.7	1.8	1.85	1.9	2	
Mol.	$\omega_e x_e$ calc.	$\omega_e x_e$ calc.	$\omega_e x_e$ calc.	$\omega_e x_e$ calc.	$\omega_e x_e$ calc.	$\omega_e x_e$ calc.	$\omega_e x_e$ calc.	$\omega_e x_e$ exptl.
H_2	268 6	302.8	346 6	400.7	433.8	472.6	570.2	117 97
ZnH	29.52	33.29	38.11	44.06	47.68	51.95	62.69	55.14
CdH	24.01	27.07	30.98	35.82	38.77	42.24	50.95	46.3
HgH	24.53	27.67	31.66	36.61	39.63	43.17	52.08	83.01
CH	63.84	71.97	82.39	95.26	103.1	112.3	135.5	64.3
OH	83.30	93.91	107.5	124 3	134.5	146.6	176.8	82.81
HF	92.51	104 3	119.4	138	149 4	162.8	196.3	90.06
HCl	46.76	52.71	60 34	69.76	75.51	82.26	99 24	52.05
HBr	37.42	42.19	48.29	55.84	60.43	65.85	79.43	45.21
HI	28.95	32.63	37.36	43.19	46.76	50.93	61.41	39.73
Li_2	2.973	3.352	3 837	4.436	4.801	5.231	6.311	2.59
Na_2	0.6837	0.7709	0.8824	1.021	1 104	1.203	1.452	0.726
K_2	0.2481	0.2799	0.3203	0.3703	0.4009	0.4367	0.5289	0.35
N_2	8.884	10.02	11.47	13.25	14.35	15 63	18.66	14.456
P_2	1.341	1.511	1.726	2.00	2.165	2.358	2.845	2.8
O_2	6.393	7.207	8.250	9.539	10.32	11.25	13.57	12.072
SO	3.133	3.533	4.043	4.676	5.060	5.513	6.651	6.116
Cl_2	1.077	1.214	1.390	1.607	1.740	1.895	2.287	4.00
Br_2	0.3569	0 4024	0.4606	0.5325	0.5763	0.6279	0.7575	1.146
I_2	0.1650	0.1860	0.2129	0.2461	0.2665	0.2902	0.3501	0.6127
ICl	0.5041	0.5683	0.6506	0.7521	0.8141	0.8869	1.070	1.465
CO	8.539	9.627	11.03	12.75	13.81	15.03	18.12	13.46
NO	7.526	8.486	9.714	11.23	12.15	13.24	15.98	13.97

General Solution of Schrödinger equation when $\alpha r_e = \delta$

From (10)

$$y^2 \frac{d^2 S}{dy^2} + y \frac{dS}{dy} + \frac{8\pi^2 \mu}{\alpha^2 h^2}[C_0 + C_1 y + C_2 y^2]S = 0$$

The values of C_0, C_1, C_2 in the present case ($\alpha r_e = \delta$), can be obtained from (11), (12) and (13).

$$C_0 = E - D_e - \frac{A}{r_e}\left(2 - \frac{9}{2\delta} + \frac{4}{\delta^2}\right) - B\left(1 - \frac{3}{\delta} + \frac{3}{\delta^2}\right) \qquad \dots \text{ (19)}$$

2

$$C_1 = -\frac{A}{r_e}\left(\frac{3}{\delta}-\frac{8}{\delta^2}\right)-B\left(\frac{4}{\delta}-\frac{6}{\delta^2}\right) \qquad \cdots \text{ (20)}$$

$$C_2 = -\frac{A}{r_e}\left(-\frac{3}{2\delta}+\frac{4}{\delta^2}\right)-B\left(-\frac{1}{\delta}+\frac{3}{\delta^2}\right) \qquad \cdots \text{ (21)}$$

Introduction of C_0, C_1, C_2 and d in (15) and corresponding expansion gives

$$\frac{E}{Ch} = \frac{\alpha}{\pi C}\left[\frac{A}{2\mu r_e}\left(\frac{-3}{2\delta}+\frac{4}{\delta^2}\right)\right]^{\tfrac{1}{2}}(n+1/2)$$

$$+\frac{h^2}{8\pi^2\mu r_e{}^2}\frac{\alpha}{\pi C}\left[\frac{A}{2\mu r_e}\left(\frac{-3}{2\delta}+\frac{4}{\delta^2}\right)\right]\frac{\left(\dfrac{3}{\delta}-\dfrac{3}{\delta^2}\right)}{\dfrac{A}{r_e}\left(\dfrac{3}{\delta}-\dfrac{8}{\delta^2}\right)}(n+1/2)J(J+1)$$

$$-\frac{\alpha^2 h}{8\pi^2\mu C}(n+1/2)^2+\frac{A}{r_e Ch}\left(2-\frac{3}{\delta}\right)+\frac{D_e}{Ch}+\frac{hJ(J+1)}{8\pi^2\mu r_e{}^2 C}$$

The coefficient of $(n+1/2)$ in first term on the right hand side is

$$\omega_e = \frac{\alpha}{\pi C}\left[\frac{A}{2\mu r_e}\left(\frac{-3}{2\delta}+\frac{4}{\delta^2}\right)\right]^{\tfrac{1}{2}} \qquad .$$

The value of force constant is given by $K_e = (8-3\delta)\, A/r_e{}^3$ in this case. When it is introduced in the above value of ω_e, usual form for ω_e is obtained, which is $\omega_e = 1/2\pi C\,.\,\sqrt{Ke/\mu}$. It suggests that ω_e is independent of δ, but $\omega_e x_e$ and α_e depend on δ.

TABLE 5.   Variation of percentage error in $\omega_e x_e$ with δ for ZnH and HCl

δ	Percentage error in $\omega_e x_e$ for	
	ZnH	HCl
1.5	−46.47	−10.16
1.6	−39.5	+ 1.3
1.7	−30 98	+16.0
1 8	−20.09	+34.1
1.85	−13.54	+45.1
1.9	− 5.79	+58.1
2	+13.7	+90.6

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