ANALYSIS OF AN EMPIRICAL INTERNUCLEAR POTENTIAL FUNCTION

M. R. Katti and M. M. Sharma

Defence Science Laboratory, Delhi

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The four parameter Tietz's potential is examined for its ability to reproduce the potential curve and the anharmoniocity constant in the case of all the electronic states of some selected diatomic molecules. It is shown, that the four parameter nature of the function gives significant improvement over the existing three-parameter functions.

Recently, Tietz[1] has proposed an analytical expression for the potential energy of diatomic molecules. It has the form $U(r) = D_e + D_e \dfrac{(a+b)\, e^{-2\beta r} - be^{-\beta r}}{1 + ce^{-\beta r}}$ (1)

where D_e is the dissociation energy and β, b, c, a are constants. Function (1) satisfies the necessary conditions that any potential energy function must satisfy and as a consequence gives the relations

$$\beta r_e = 2\triangle^{1/2} - \Gamma^{1/2}$$

$$c\,* = -\left[exp\left(\frac{2\triangle^{1/2} - \Gamma^{1/2}}{\triangle^{1/2}}\right)\right]\left[\Gamma^{1/2} - \triangle^{1/2}\right] \qquad 2$$

$$b = 2\, exp\,(2\triangle^{1/2} - \Gamma^{1/2})\,[\,2 - (\Gamma/\triangle)^{1/2}\,]$$

$$a\,* = \frac{b}{2}\,[\,-2 + (\Gamma/\triangle)^{1/2}\, exp\,(2\triangle^{1/2} - \Gamma^{1/2})]$$

and thus connects β, b, c, a with the Sutherland's parameter $\triangle = k_e\, r_e{}^2/2D_e$ and the quantity $\Gamma = [1 + \alpha_e\, \omega_e\, /6B_e{}^2\,]^2$, where all the molecular constants have their conventional meaning[2].

With these corrected relations for c and a function (1) can be put in a simple and more compact form (3) involving a single constant c.

$$U = D_e\left\{\frac{1 - e^{\beta(r_e - r)}}{1 + c\, e^{-\beta r}}\right\}^2 \qquad (3)$$

It is claimed by Tietz that this simple function adds to the list of few functions viz. Morse, Manning and Eisenhart for which one can solve exactly the Schrodinger wave equation. Considering this merit of the expression, it was thought worthwhile to investigate its applicability and workability to other problems viz. correlation of molecular constants and

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*The existence of an error in the original relations for c and a given by Tietz, viz

$$c = -[\,exp\,(2\triangle^{\frac{1}{2}} - \Gamma^{\frac{1}{2}}\,)/\triangle^{\frac{1}{2}}\,]\;\;[\Gamma^{\frac{1}{2}} - \triangle^{\frac{1}{2}}\,]$$

$$a = 2b\,[\,-2 + (\Gamma/\triangle\,)^{\frac{1}{2}}\,]\, exp\,(2\triangle^{\frac{1}{2}} - \Gamma^{\frac{1}{2}}\,)$$

was pointed out by the authors. Tietz confirmed this in a note published in *J. Chem. Phys.* August 1965.

TABLE 1

COMPARISON OF OBSERVED VALUES OF $w_e x_e$ WITH CALCULATED VALUES FOR TIETZ'S FUNCTION

Molecule	State	$w_e x_e$ (observed)	$w_e x_e$ (Tietz)
H_2	$X' \Sigma_g^+$	120·815	141·58
I_2	$X' \Sigma_g^+$	0·6127	0·7766
N_2	$X' \Sigma^+$	14·188	15·960
	$A^3 \Sigma_u^+$	13·851	16·415
	$a' \Pi_g$	13·825	14·480
	$B^3 \Pi_g$	15·198	16·758
O_2	$X^3 \Sigma_g^-$	12·073	13·920
	$B^3 \Sigma_u^-$	8·0023	11·825
	$A^3 \Sigma_u^+$	13·810	19·093
CO	$X' \Sigma^+$	13·295	13·670
	$d^3 \Delta$	7·624	8·957
	$A' \Pi$	17·2505	20·034
	$e^3 \Sigma^-$	9·578	11·725
	$a'^3 \Sigma^+$	11·0130	12·036
NO	$X^2 \Pi_{\frac{1}{2}}$	13·97	15·89
	$B^2 \Pi$	7·603	12·676
OH	$X^2 \Pi_c$	82·665	94·002
	$A^2 \Sigma^+$	113·85	113·38
HF	$X' \Sigma^+$	88·726	96·344

comparison of the $U(r)$ *vs* r dependence with curves for the different states of different molecules as determined from the RKR method. The first criterion exists for testing the validity of the function close to the equilibrium configuration and the second is a more thorough and satisfying test of the long range validity of the function.

Following Varshni's technique for the analysis of potential energy functions, expression (3) yields the following relation for the unused anharmonicity constant $\omega_e x_e$.

$$w_e x_e = \frac{-8 [\triangle^{3/2} - (\Gamma^{1/2} - \triangle^{1/2})^3] W}{(2 \triangle^{1/2} - \Gamma^{1/2}) \ \mu_A r_e^2} \tag{4}$$

where $W = 2 \cdot 1078 \times 10^{-16}$. The constant is evaluated in terms of the four known constants K_e , r_e , D_e , α_e and is then compared with the actual value. Such a test of the above expression has been made by Tietz for the ground states of 23 neutral diatomic molecules using $\triangle$ and Γ data of Varshni[3] and Varshni & Shukla[4]. He showed that the results for $w_e x_e$ come out generally better than the Morse results.

In this connection it is pertinent to make a reference to the recent work of Steele *et al*[5]., who have made a quantitative reassessment, in terms of average % deviations, for nine potential functions for the ground and excited states of some selected diatomic molecules. Molecular data has undergone considerable revision since the study carried out by Varshni[3] and Varshni & Shukla [4] and further, to make a comparative assessment of Tietz's expression (3), $w_e x_e$ has been evaluated for the molecules H_2, I_2, N_2, O_2, CO, NO, OH, HF and their excited states studied by Steele *et al.*, and using their data, Table 1 gives the results for the anharmonicity constant and Table 2 the average % errors, from the experimental values, for $w x_e$ for Tietz's function together with those quoted by Steele *et al*[5]. The Tietz's function with 18·9% is third in the decreasing order of efficiency.

TABLE 2

AVERAGE ERROR (%) FOR THE QUANTITY $w_e x_e$

	Lippincott	Linnet	Tietz	Rydberg	Rosen Morse	Frost Muslin	Poschl Teller	Morse	Varshni
$w_e x_e$	12·18	14·94	18·90	19·71	21·24	24·29	26·93	26·93	28·94

It is known that good performance of a function near the equilibrium configuration does not necessarily mean that the function accurately represents the potential at small or large internuclear distances. In what follows it may be seen that Tietz's function which has shown good performance in the predictive reliability of the constant $w_e x_e$, does equally well for its ability to reproduce the potential as determined by RKR method. The results of the potential curve calulations for all the molecules and their states are not reproduced here for the sake of conciseness. However, representative results are given in Tables 3 and 4 for the ground states of H_2 and I_2 along with the results for the other nine functions.

Table 5 gives a summary of the results showing the average % errors for the quantity $| V_{RKR} - V | / D_e$ for all states of all molecules for each function.

On the basis of the expression given by Rees[6] for the potential curve Steele *et al.*[5] in the course of their analysis, have evolved an indirect method for comparing the deviation of the

TABLE 3

RESULTS OF POTENTIAL CURVE CALCULATIONS FOR $X' \Sigma_g^+$ STATE OF H_2

r(A)°	R.K.R. (e.v.)	Tietz	Morse	Hulburt Hirsch-felder	Rydberg	Poschl Teller	Linnet	Varshni	Rosen Morse	Lippin-cott	Frost-Muslin
0·4109	4·729	4·362	3·868	4·652	3·680	4·854	6·918	5·787	3·189	4·187	4·946
0·4319	2·880	3·615	3·243	3·823	3·097	3·950	4·745	4·629	2·721	3·498	4·038
0·4597	2·935	2·769	2·533	2·913	2·435	2·982	3·920	3·421	2·172	2·716	3·054
0·5088	1·730	1·674	1·558	1·724	1·508	1·745	2·154	1·938	1·384	1·648	1·790
0·6337	0·269	0·266	0·259	0·268	0·256	0·269	0·291	0·279	0·248	0·264	0·272
0·8833	0·269	0·268	0·275	0·270	0·279	0·269	0·250	0·261	0·287	0·273	0·264
1·2186	1·730	1·655	1·734	1·724	1·790	1·687	1·450	1·608	1·869	1·757	1·608
1·5148	2·935	2·740	2·870	2·902	2·975	2·815	2·395	2·721	3·081	2·959	2·667
1·8524	3·880	3·337	3·715	3·782	3·838	3·672	3·183	3·628	3·924	3·846	3·500
2·3748	4·522	4·258	4·358	4·413	4·454	4·339	3·931	4·371	4·489	4·467	4·205
3·2835	4·729	4·644	4·679	4·690	4·712	4·676	4·491	4·712	4·714	4·711	4·626
4·2300	4·745	4·727	4·736	4·737	4·743	4·735	4·673	4·745	4·743	4·743	4·722
6·3500	4·747	4·747	4·747	4·747	4·747	4·747	4·744	4·747	4·747	4·747	4·747

TABLE 4

RESULTS OF POTENTIAL CURVE CALCULATIONS FOR $X' \Sigma_g^+$ STATE OF I_2

r(A°)	R.K.R. (e.v.)	Tietz	Morse	Hulbert-Hirsch-felder	Rydberg	Poschl-Teller	Iinnet	Varshni	Rosen Morse	Lippin-cott	Frost Muslin
2·288	(1·500 —1·556)	1·303	1·637	1·521	1·548	1·634	1·285	1·458	1·603	1·451	1·593
2·292	1·493	1·271	1·589	1·475	1·504	1·587	1·251	1·417	1·561	1·412	1·545
2·309	1·245	1·135	1·399	1·297	1·328	1·398	1·114	1·256	1·372	1·255	1·363
2·336	0·977	0·939	1·131	1·048	1·080	1·130	0·919	1·027	1·107	1·029	1·105
2·423	0·465	0·494	0·517	0·482	0·500	0·517	0·446	0·483	0·503	0·487	0·507
3·056	0·465	0·442	0·411	0·452	0·422	0·411	0·506	0·436	0·404	0·445	0·417
3·389	0·977	0·915	0·848	0·951	0·879	0·848	1·204	0·914	0·840	0·945	0·866
3·671	1·245	1·186	1·111	1·231	1·151	1·111	1·732	1·194	1·104	1·216	1·135
4·448	1·493	1·485	1·445	1·501	1·475	1·445	2·598	1·502	1·438	1·474	1·464
6·522	1·551	1·556	1·555	1·556	1·555	1·555	2·602	1·557	1·550	1·555	1·556
8·814	1·556	1·556	1·557	1·557	1·557	1·557	2·106	1·557	1·550	1·557	1·557

TABLE 5

AVERAGE ERROR % FOR THE QUANTITY $[|V_{RKR} - V| / D_e]$

	Hulburt—Hirschfelder	Lippincott	Tietz	Varshni	Rydberg	Fotst-Muslin	Poschl Teller	Morse	Rosen-Morse
$[\lvert V_{RKR} - V \rvert / D_e]^{all}_{r}$	1·51	2·17	2·20	2·28	2·94	3·41	3·48	3·68	3·71

proposed empirical functions from the experimental curve. Rees has shown that potentia energy curve can be obtained from the expressions

$$2f = (r_2 - r_1) = (B_e/w_e x_e)^{1/2} \log W \tag{5}$$

$$2g = (1/r_1 - 1/r_2) = [1/B_e (w_e x_e)^3]^{1/2} (w_e / r_e) \times [\alpha_e (4 w_e x_e V/w_e^2)^{1/2} + \left(2 \frac{w_e x_e}{w_e} B_e - \alpha\right) \log W] \tag{6}$$

$$W = (1 - 4 w_e x_e V/w_e^2)^{1/2}/[1 - (4 w_e x_e V/w_e^2)^{1/2}] \tag{7}$$

Here r_1 and r_2 are the minimum and maximum points of vibration. If w_e, $w_e x_e$ and $B_e \alpha_e$ are known, then r_1 and r_2 can be obtained for any V from (5) and

$$(r_1 + r_2)/2 = (f/g + f^2)^{1/2} \tag{8}$$

On expanding the logarithms of the numerator and denominator of W it is easy to show that

$$(4 w_e x_e V/w_e^2)^{1/2} = \tanh (w_e x_e / B_e)^{1/2} (r_2 - r_1)/ 2 r_e \tag{9}$$

and by taking B_v to be a measure of $[(r_1 + r_2)/2]^{-2}$ the relation can be written in terms of w_e, $w_e x_e$ and V to get

$$[(r_1 + r_2)/2 r_e]^2 = 1/[1 - (\alpha_e w_e / 2 B_e w_e x_e) + \{(\alpha_e w_e / 2 B_e w_e x_e)^2 - \alpha_e^2 V/B_e^2 w_e x_e\}^{1/2}] = G(V) \tag{10}$$

Therefore for a molecule whose energy levels are given by

$$G(V) = w_e (v + \tfrac{1}{2}) - w_e x_e (v + \tfrac{1}{2})^2 \tag{11}$$

plots of $(4 w_e{}^2 x_e V/w_e^2)^{\frac{1}{2}}$ vs $\tanh (w_e x_e / B_e)^{\frac{1}{2}} (r_2 - r_1)/2 r_e$

and $[(r_1 + r_2)/2r_e\ ]^2$ *vs* $G(V)$ should be straight lines with slopes of unity. Further for each function and Tietz function under study plots of the differences of

$$\tanh\ (\ w_e x_e\ /B_e\ )^{\frac{1}{2}}\ \ (r_2 - r_1)^{\frac{1}{2}}\ \ /2r_e \text{ and } [\ (r_1 + r_2)/2\ r_e\ \ ]^2$$

from the experimental values for the $X'\Sigma_g^+$ state of N_2 as a function of $(4w_e\ x_e\ V/w_e{}^2)^{\frac{1}{2}}$ and $G(V)$ are shown in Fig. 1 and 2. In general various functions show the same relative deviation from the width of the potential bowl and the midpoint of vibration as they show errors for the quantities$/V—V_{RKR}/$and $w_e\, x_e$. All of the proposed empirical functions considered predict too wide a bowl for the potential curve and they generally give too large a value for the midpoint of vibration. The exceptions to this last point are Varshni, Hulburt-Hirschfelder, Lippincott and Tietz. The H. H. potential curve gives the best predictions of bowl width and midpoint of vibration. This is in agreement with results given in Table 5.

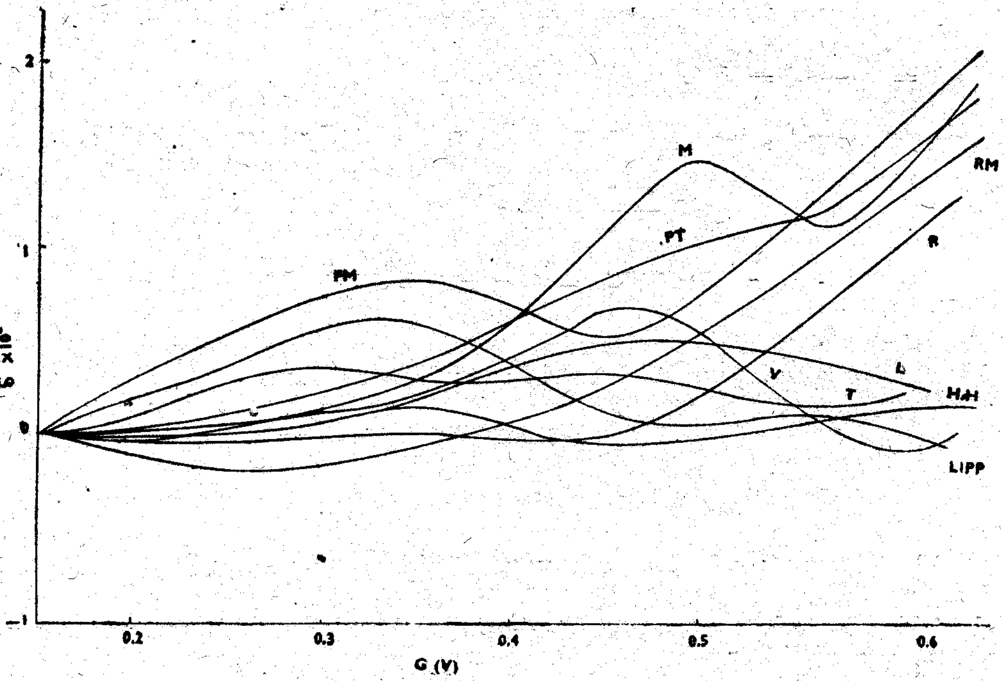

Fig. 1—Plot of$(\ \gamma—\gamma_{RKR}\ )$ *vs* $(4\ w_e\, x_e\ \ V\ /\ w_e\ {}^2)^{\frac{1}{2}}$ for the various potential functions.

where $\gamma = \tanh\ [\ (\ w_e\ \ x_e\ \ /\ \ B_e\ )^{\frac{1}{2}}\ (\ r_2—r_1)\ /\ 2\ r_e\ ]$

M—Morse	L—Linnett
FM—Frost—Muslin	HH—Hulburt—Hirschfelder
RM—Rosen—Morse	V—Varshni
PT—Poschl—Teller	Lipp—Lippincott
R—Rydberg	T—Tietz

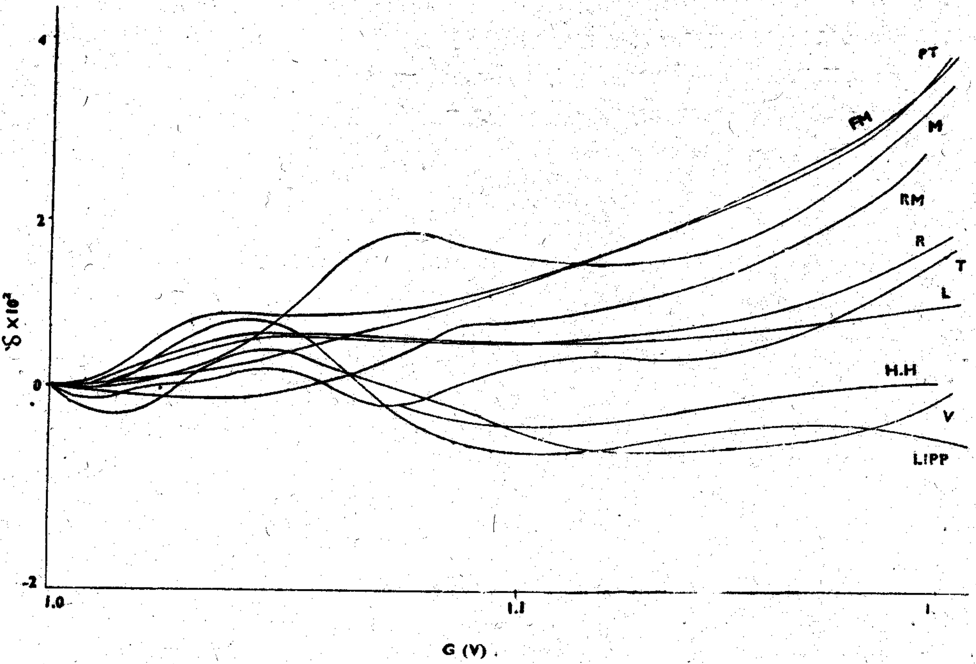

Fig. 2—Plot of $\delta = [\,(r_1 + r_2)\,/\,2r_e\,]^2 - [\,(r_1 + r_2)\,/\,2r_e\,]^2_{RKR}$ *vs* $G\,(V)$

for the various potential functions

(for symbols M, FM etc. see Fig. 1)

The uniform efficacy of Tietz's expression for the prediction of $w_e\,x_e$ and the potential curve shows its superiority over the best of the three parameter functions. Further its simple and compact form is less cumbersome for computational purposes. It appears from the above results that the performance of the potentials involving three, four and five molecular parameters for the prediction of the potential curve should show increasing efficiency.

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