

# A CASE FOR EFFICACY OF HULBURT-HIRSCHFELDER POTENTIAL FUNCTION

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**ABSTRACT** The Hulburt-Hirschfelder potential energy function has been tested for its efficacy in relation to Morse expression. Its five-parameter character has been converted to four-parameter one, with a view to derive the fifth parameter  $\alpha_e$ . The calculated data are then compared to the accurately known experimental data of a large number of diatomic molecules. The expression proves much superior to Morse's and even to some others, known to be better than Morse's.

In a recent exhaustive review, Varshni (1957) has made a critical assessment of the relative merits of various potential energy functions of diatomic molecules. The test has been confined only to the functions which do not assume, but which predict the molecular constants  $\alpha_e$  or  $\omega_e x_e$ . These latter are then compared with the actual measured values. Obviously a test of this type is not possible with functions, such as Hulburt-Hirschfelder (H-H, 1941), which employ all the known experimental constants. Hence this function does not figure in the above study. However, if this five-parameter function of H-H is converted into a four-parameter one and then the fifth parameter predicted from it, one could still carry out the test in the manner given by Varshni. This is proposed to be done in the present paper.

Varshni starts by expanding  $U(r)$  near the equilibrium value ( $r = r_e$ ). The expansion is given by

$$U(r) = \frac{1}{2!} U''(r_e)(r-r_e)^2 + \frac{1}{3!} U'''(r_e)(r-r_e)^3 + \frac{1}{4!} U^{IV}(r_e)(r-r_e)^4 + \dots \quad (1.1)$$

Here the value of the first derivative  $U'(r_e)$  does not appear as it is obviously zero. Relations first deduced by Kratzer (1920) and modified for the above form of the expansion, provide values of these derivatives in terms of the spectroscopic constants. Later Dunham (1932) has shown that

$$\alpha_e = - \left[ \frac{c_3}{c_2} r_e + 1 \right] \frac{6B_e^2}{\omega_e} \dots \quad (1.2)$$

and

$$\mu \omega_e x_e = \left[ \frac{15}{8} \left( \frac{c_3}{c_2} \right)^2 - \frac{3}{2} \left( \frac{c_4}{c_2} \right) \right] h/8\pi^2 c \dots \quad (1.3)$$

where

$$c_2 = U^{II}(r_e)/2!, \quad c_3 = U^{III}(r_e)/3! \quad \text{and} \quad c_4 = U^{IV}(r_e)/4! \quad \dots \quad (1.4)$$

After putting

$$U^{III}(r_e)/U^{II}(r_e) = X \quad \dots \quad (1.5)$$

$$U^{IV}(r_e)/U^{II}(r_e) = Y \quad \dots \quad (1.6)$$

one obtains

$$\alpha_e = - \left[ \frac{Xr_e}{3} + 1 \right] 6B_e^2/\omega_e \quad \dots \quad (1.7)$$

and

$$\omega_e x_e = \left[ \frac{5}{3} X^2 - Y \right] \frac{W}{\mu_d} \quad \dots \quad (1.8)$$

with  $W = 2.1078 \times 10^{-16}$

In the above equations (1.7) and (1.8), it is only the quantities  $\left[ \frac{Xr_e}{3} + 1 \right]$

and  $\left[ \frac{5}{3} X^2 - Y \right]$  which will be different for different functions.

Using the most generally adopted Morse's (1929) function

$$U = D_e [1 - e^{-a(r-r_e)}]^2 \quad (1.9),$$

we have the derivatives

$$U^{II}(r_e) = 2a^2 D_e \quad (2.0)$$

$$U^{III}(r_e) = -6a^3 D_e \quad (2.1)$$

and

$$U^{IV}(r_e) = 14a^4 D_e \quad (2.2)$$

From these, the values of  $X$  and  $Y$  turn out to be

$$X = -3a \quad \dots \quad (2.3)$$

$$Y = 7a^2 \quad \dots \quad (2.4)$$

Using the above in eqs. (1.7) and (1.8), Varshni has evaluated the constants  $\alpha_e$  and  $\omega_e x_e$  in the case of 23 neutral diatomic molecules for which reliable experimental data of molecular constants is available. The comparative study of the calculated and observed constants by him has revealed that the percentage dispersion between the two is of the order of  $\pm 33.1$  for  $\alpha_e$  and  $\pm 31.2$  for  $\omega_e x_e$ . In comparison to the dispersions given by Morse function, other functions give either smaller or larger departures. A function giving smaller dispersion than that of Morse is considered as more satisfactory. Thus the superiority of a function is judged in terms of the accuracy given by Morse's. As for the reproduction of  $\alpha_e$  is concerned, there are functions examined by Varshni giving percentage error as low as  $\pm 22.1$  and thus proving superior to Morse's.

Some calculational slips have been noticed in Table XIa  
reducing the percentage error in case of Morse function from  $\pm$

thus provide relatively better accuracy for it. These slips relate to OH, HF, HI, N<sub>2</sub> (two cases), SO, and ICl (cf. Table I here for corrections).

In the light of the objective outlined in para 1, the H-H function can now be viewed as a four-parameter function to predict the value of  $\alpha_e$ . Hulbert-Hirschfelder's expression is of the form

$$U = D[(1 - e^{-x})^2 + cx^2e^{-2x}(1 + bx)] \quad \dots (2.5)$$

which is the same as that of Morse, except for an additional term which acts as a correction term. Here

$$x = 2\beta\xi = \frac{\omega_e}{2(B_e D_e)^{1/2}} \cdot \frac{r - r_e}{r_e} \quad \dots (2.6)$$

and  $b$  and  $c$  are simple algebraic functions of the five spectroscopic constants  $K_e$ ,  $r_e$ ,  $D_e$ ,  $\alpha_e$  and  $\omega_e x_e$

$$c = 1 - a_1(D/a_0)^4 \quad \dots (2.7)$$

$$b = 2 - \left[ \frac{7}{12} - \frac{Da_2}{a_0} \right] / c \quad \dots (2.8)$$

where  $a_0$ ,  $a_1$ , and  $a_2$  are the Dunham coefficients

$$a_0 = \omega_e^2 / 4B_e, \quad a_1 = -1 - \alpha_e \omega_e / 6B_e^2, \quad a_2 = \frac{5}{4} a_1^2 - \frac{2\omega_e x_e}{3B_e}$$

The function (2.5) on differentiation gave

$$U^{III}(r_e) = 2a^2 D_e \quad \dots (2.9)$$

$$U^{III}(r_e) = 6a^3(c-1)D_e \quad \dots (3.0)$$

$$U^{IV}(r_e) = 2a^4 [7 + 12c(b-1)]D_e \quad \dots (3.1)$$

and

$$X = U^{III}(r_e)/U^{II}(r_e) = 3a(c-1) \quad \dots (3.2)$$

$$Y = U^{IV}(r_e)/U^{III}(r_e) = a^2[7 + 12c(b-1)] \quad \dots (3.3)$$

It may be seen from (3.2) above that it involves  $\alpha_e$  and thus assumes its value. Hence this quantity in the present form cannot be used for the prediction of  $\alpha_e$ . If we modify the expression

$$a_1 = -1 - \alpha_e \omega_e / 6B_e^2 \quad \dots (3.4)$$

by putting

$$\alpha_e = \frac{6\sqrt{\omega_e x_e B_e^3}}{\omega_e} - \frac{6B_e^2}{\omega_e} \quad \dots (3.5)$$

a relation due to Pekeris (1934), we make the quantity  $c$  independent of  $\alpha_e$ . The above substitution is justified by the fact that the Pekeris relation (3.5) is derived from the Morse function which forms an integral part of H-H's function. Thus  $c$  will be determined by

$$a_1 = -\sqrt{\frac{\omega_e x_e}{B_e}} \quad \text{and} \quad a_0 = \omega_e^2 / 4B_e \quad \dots (3.6)$$

and thus made independent of  $\alpha_e$ .

Such an operation is not possible in the case of  $Y$  in order to make it independent of  $\omega_e x_e$  and thus to predict  $\omega_e x_e$ , as too many quantities are involved. This led us to restrict ourselves to the deduction of  $\alpha_e$  only. The results of  $\alpha_e$  evaluated from Morse and H-H function used as above, are shown in the Table I. The various molecular constants employed in the present paper are uniform with those employed by Varshni.

TABLE I

Molecule	$\alpha_e$ Morse		$\alpha_e$ H.H function	
	Present calc.	% Error	Present calc.	% Error
H <sub>2</sub>	2.222	-25.8	1.084	-33.7
ZnH	0.4248	+69.9	0.3118	+24.73
CdH	0.3599	-65.1	0.2379	+9.13
HgH	0.5090	+63.1	0.3818	+22.38
CH	0.5238*	-1.9	0.4861	-8.97
OH	0.7076* (0.7141)	-9.0* (0.0)	0.6268	-12.21
HF	0.6055* (0.5822)	-8.2* (-24.4)	0.6662	-13.53
HCl	0.3109	+3.3	0.2741	-9.21
HBr	0.2540	+7.9	0.2131	-5.71
HI	0.2583* (0.2015)	+41.1* (+9.2)	0.1295	-29.23
Li <sub>2</sub>	0.0103	+46.3	0.00744	+5.68
Na <sub>2</sub>	0.00146	+84.8	0.001051	+33.04
K <sub>2</sub>	0.000412	+88.1	0.0003088	+41.02
N <sub>2</sub> (1)	0.02442* (0.02864)	+29.5* (+53.2)	0.01727	-7.65
N <sub>2</sub> (2)	0.01969* (0.01996)	+5.3* (+6.2)	"	"
P <sub>2</sub>	0.00177	+24.7	0.001443	+0.41
O <sub>2</sub>	0.00175	+10.8	0.01244	-21.21
SO	0.00719* (0.01095)	+27.9* (+94.8)	0.005197	-7.53
Cl <sub>2</sub>	0.00190	+11.8	0.001925	+13.22
Br <sub>2</sub>	0.000423	+53.8	0.0003357	+22.08
I <sub>2</sub>	0.000154	+31.6	0.0001018	-12.99
Icl	0.000670* (0.000654)	+25.0* (+22.0)	0.0005257	-1.92
CO(1)	0.01012	+9.4	0.01691	-3.26
CO(2)	0.01844	+5.5	"	"
CO(3)	0.01643	-6.0	"	"
NO(1)	0.0223	+28.1	0.01707	-4.10
NO(2)	0.0198	+11.2	"	"
Average		$\pm 31.9$ ( $\pm 33.1$ )		$\pm 15.3$

N.B. Figures with asterisk are our corrected values; bracketted are reproduced from Varshni.

It is seen from the Table I that as far as the reproduction of  $\alpha_e$  is concerned, the results obtained with H-H's function show the average percentage error to be  $\pm 15.3$ , which is much less than that given by Morse's function. Comparing this accuracy with the other three functions examined by Varshni, the H-H's function used in the manner given above, proves to be much superior to all of them. This is evident from the comparative figures of the magnitude of percentage errors recorded in Table II.

TABLE II

Comparative percentage errors in the  $\alpha_e$  estimates

Function	% Error
Morse	$\pm 31.9$
Rydberg	$+28.0$
Third	$\pm 22.9$
Empirical	$\pm 22.1$
{ Hulburt & Hirschfelder (Present paper)	$\pm 15.3$

Another feature which is apparent is that after the modifications  $\alpha_e$  becomes independent of  $D_e$ . In view of these findings the relation  $c = 1 - \left( \frac{Dx_e}{\omega_e} \right)^{\frac{1}{2}}$  becomes preferable to one originally given by H-H, viz.,  $c = 1 + a_1(D/a_0)^{\frac{1}{2}}$ . Further work on these lines is in hand.

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