A TEST FOR HULBURT-HIRSCHFELDER POTENTIAL FUNCTION

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ABSTRACT. Following up the modification recently reported of Hulburt-Hirschfelder potential function for the prediction of the molecular vibration-rotation constant a_e, it is shown that similar predictions of the anharmonicity constant $\omega_e x_e$ are possible by suitable substitutions. The comparison of the calculated data with the experimental data on $\omega_e x_e$ shows that in this case too, the H-H function works out much better than Morse's.

In a recent paper (Tawde and Katti, 1959), the efficacy of the original Hulburt–Hirschfelder (H. H, 1941) function was demonstrated by introducing in it suitable modifications. The test applied for the efficacy was the prediction of certain verifiable molecular constants. Although the original function contained all the five usual molecular constants, ω_e, $\omega_e x_e$, B_e, D_e and α_e, they were, in the ultimate analysis, reduced to four, leaving the vibration-rotation interaction constant α_e to be predicted from the knowledge of the four. Such transformation was brought about by the incorporation of Morse-Pekeris relation which made one of the constants of H-H relation independent of α_e. The modified expression proved highly successful in reproducing α_e data within $\pm 15.3\%$.

Such expressions are also possible to be tested for their capacity to predict the anharmonic constant $\omega_e x_e$. Although earlier we tried to explore this possibility in the case of H-H function in the above manner, we did not succeed. While pursuing this issue further, we could now succeed in suitably modifying the function to predict $\omega_e x_e$ in the same way as the constant α_e. This paper presents this study, as the results seemed very promising.

The development of modified H-H equation has been shown in full steps by (Tawde and Katti, 1959) for evaluation of α_e. Now for the purposes of deriving $\omega_e x_e$, we have their equations (3.2) and (3.3) as follows :

$$X = 3a(c-1)$$
$$Y = a^2[7+12c(b-1)]$$

where the Morse constant $a = 1.2177 \times 10^7 \ \omega_e(D_e/\mu_A)^{\frac{1}{2}}$ and H-H constants $c = 1+a_1(D/a_0)^{\frac{1}{2}}$, $b = 2-[7/12-Da_2/a_0]/c$ with $a_0 = \omega_e^2/4B_e$, $a_1 = -1-\alpha_e\omega_e$ $/6B_e^2$, $a_2 = 5/4a_1^2-2\omega_e x_e/3B_e$. Here X and Y need to be made independent of $\omega_e x_e$ so that by assuming the other constants ω_e, D_e, B_e and α_e, one could get

at the value of $\omega_e x_e$. The only empirical relation that we could think of was $D_e = \omega_e^2/4\omega_e x_e$. This is a quantity derived from Morse relation and since it is the basic part of H-H function, one could justify the use of this expression in the present set-up. Thus substituting $\omega_e x_e = \dfrac{\omega_e^2}{4D_e}$ in the expression for a_2 above, we get

$$a_2 = 5/4a_1{}^2 - \omega_e{}^2/6B_eD_e$$

This makes Y independent of $\omega_e x_e$ and X does not involve $\omega_e x_e$ at all.

This modified expression a_2 allows predictions to be made for $\omega_e x_e$. We have therefore calculated their values in the same set of 23 diatomic molecules,

TABLE I

Diatom	Morse % error (Varshni, 1957)	H-H % error (present paper)
H_2	+ 7.0	+24.5
ZnH	+52.9	−14 6
CdH	+78.8	+ 0 6
HgH	+55.6	−15 2
CH	+ 8.2	+12.3
OH	+13.9	+13 9
HF	−11.3	+ 6 8
HCl	+15.3	+13.0
HBr	+22.8	+11 1
HI	+30.0	+19 0
Li_2	+37.3	+ 3 3
Na_2	+44 3	−13.2
K_2	+44.6	−23.5
$N_2{}^1$	(+58.0)	(+19.9)
$N_2{}^2$	+20.5	+13.4
P_2	+32.5	+ 5 0
O_2	+23.0	+11 4
SO	+57.2	+18.4
Cl_2	− 1.7	−13 2
Br_2	+41.8	−18.5
I_2	+49.8	− 3.9
IcI	+43.4	+10 9
CO(1)	(+17 1)	(+ 7 6)
CO(2)	(+11.3)	(+ 6 5)
CO(3)	− 3 5	− 3.6
NO(1)	(+48.5)	(+14 2)
NO(2)	+21.9	+ 9.7
Average	±31 2	±12.1

which we have earlier used to prove the efficacy of the *H-H* function in terms of α_e. The calculated results when compared with observed data give errors which are recorded as percentage errors in Table I. As Morse function is the most universally used function we are giving the percentage errors (cf. Varshni, 1957) produced by Morse function too, for comparison, in order to bring out the relative merits of the present results.

It may be noted from Table I that the average percentage error ± 12.1 obtained with *H-H* function is significantly lower than that due to Morse, viz. ± 31.2. The performance of *H-H* function in relation to the other functions on the basis of percentage errors is shown in Table II. The figures for other functions are taken from Varshni. It may be noted that the only function which stands superior to *H-H* function is the empirical one. This latter has also been found to be the best among the functions examined by Varshni

TABLE II

Function	% Error
Morse	± 31.2 (a)
Rydberg	$\pm 23 \ 1$ (a)
First	± 18.2 (a)
Seventh	± 13.6 (a)
Lippincott	$+12.7$ (a)
Hulburt & Hirschfelder	± 12.1 (b)
Empirical	± 11.1 (a)

(a) Varshni,   (b) the present paper.

Further the *H-H* function which was shown to be superior in making the estimates of α_e with $\pm 15.3\%$ by (Tawde and Katti, 1959) has given a better accuracy for $\omega_e x_e$, viz. ± 12.1 on the lines of the development of *H-H* expression indicated above. This observation fits in the general conclusion arrived at by Varshni that for any function, $\omega_e x_e$ x can be estimated to a greater degree of accuracy than α_e.

REFERENCES

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