

SUPERIORITY OF HULBURT-HIRSCHFELDER FUNCTION TO SOME THREE-CONSTANT POTENTIAL ENERGY FUNCTIONS

M. R. KATTI and M. M. SHARMA

Defence Science Laboratory, Delhi

ABSTRACT

Considering the merits of the five-parameter Hulburt-Hirschfelder potential in reproducing the true potential energy curve for diatomic molecules, its predictive reliability of some molecular constants has been investigated by incorporating the modifications of H-H function suggested by Tawde and Katti. Results of α_e and $\omega_e x_e$ obtained here show that the performance of H-H function is consistent with the earlier findings of Steele *et al*¹.

INTRODUCTION

In a recent review published under the above title, Steele and associates¹ have assessed the merits of some selected potential functions for their ability to reproduce the potential curve as determined by the RKR method and for their ability to predict α_e and $\omega_e x_e$. They have shown in their analysis, that the five parameter Hulburt-Hirschfelder² (H-H) function gives the best fit of the potential with an average error of about 1.5%, among the well behaved molecular states of some common diatomic molecules. On the other hand, they found that Varshni III and Lippincott three-constant functions give reliable predictions of α_e and $\omega_e x_e$. The three-constant functions give the freedom to test their validity in two ways viz. for predicting the potential curve and the unused constants α_e and $\omega_e x_e$, while the H-H function because of its five parameter nature provides only the former test. However, Tawde and Katti³ have suggested certain modifications in the relations for H-H constants which reduce it to a four parameter function and thus enable one to predict the fifth unused constant α_e or $\omega_e x_e$. The purpose of the present communication is to report the calculated results of α_e and $\omega_e x_e$ from H-H function by incorporating the modifications due to Tawde and Katti³.

THEORY

The above modifications relate to the constants c and b involved in the term $cx^3e^{-2x}(1+bx)$ which acts as a correction term to Morse Function. α_e and $\omega_e x_e$ occurring in the Dunham coefficients

$$a_1 = -1 - \frac{\alpha_e \omega_e}{6B^2}; \quad a_2 = \frac{5}{4} a_1^2 - \frac{2\omega_e x_e}{3B_e} \quad (1)$$

RESULTS AND DISCUSSION

TABLE 1

COMPARISON OF OBSERVED VALUES OF ω_e AND $\omega_e x_e$ WITH CALCULATED VALUES FOR H-H FUNCTION

Molecule	State \bar{a}_e	Observed ω_e	Present ω_e	Observed $\omega_e x_e$	Present $\omega_e x_e$
H ₂	X ¹ Σ_g^+	3.0177	2.0512	120.817	147.0
I ₂	X ¹ Σ_g^+	.0001208	.0001218	.6127	.6768
N ₂	X ¹ Σ^+	.0171	.01496	14.188	17.961
	A ³ Σ_u^+	.01798	.01813	13.851	14.177
	a ¹ Π_g	.0183	.0178	13.825	14.560
	B ³ Π_g	.01794	.01920	15.198	15.246
O ₂	X ³ Σ_g^-	.01579	.01497	12.073	12.974
	B ³ Σ_u^-	.0110	.01221	8.0023	8.744
	A ³ Σ_u^+	.0165	.0193	13.81	13.562
CO	X ¹ Σ	.0175	.0198	13.295	12.183
	d ³ Δ	.0171	.01262	7.624	11.201
	A ¹ Π	.02229	.02367	17.2505	17.341
	b ³ Σ	0.179	.01519	9.578	11.700
	a ¹ Σ^+	.01872	.01016	11.0130	12.332
NO	X ² $\Pi_{1/2}$.01781	.01682	13.97	14.898
	B ² Π	.0116	.01165	7.603	7.866
OH	X ² $\Pi_{1/2}$.708	.626	82.665	96.718
	A ² Σ^+	.7888	.8865	118.85	104.924
HF	X ¹ Σ	.7888	.7348	88.726	85.115

TABLE 2
AVERAGE ERROR (%) FOR THE QUANTITIES α_e AND $\omega_e x_e$

	Morse	Hulburt Hirsch- felder	Rosen Morse	Rydberg	Poschl Teller	Linnet	Frost Musulin	Varshni	Lippincott
$\omega_e x_e$	26.93	11.18	21.24	19.71	26.93	14.94	24.29	28.94	12.18
α_e	19.67	12.20	22.33	17.45	18.47	15.55	23.55	15.57	13.80

which ultimately determine c and b are replaced by

$$\alpha_e = \frac{6\sqrt{\omega_e x_e B^3}}{w_e} - \frac{6B^2}{\omega_e} \quad (2)$$

$$\omega_e x_e = \frac{\omega^2}{4D_e} \quad (3)$$

The two substitutions (2) and (3) at a time make c independent of α_e and b independent of $\omega_e x_e$ allowing us to predict either α_e or $\omega_e x_e$. The above substitutions are justified by the fact that both are derived from Morse function which forms an integral part of H-H function.

The H-H function on differentiation gives

$$x = U'''(r_e)/U''(r_e) = 3a(c-1)$$

$$y = U^{iv}(r_e)/U''(r_e) = a^2[7 + 12c(b-1)]$$

Results of α_e and $\omega_e x_e$ following Varshni's⁴ technique evaluated from H-H function used as above are shown in Table I. The various molecular constants employed here are uniform with those quoted by Steele *et al*¹. Table 2 shows the percentage errors in these estimations of α_e and $\omega_e x_e$ side by side with those obtained by Steele *et al* for other three-constant functions.

It may be seen from Table 2 that the average errors (%) given by H-H function for predicting α_e or ω_e , x_e are lower than that due to Lippincott and Varshni III. It may be concluded that the H-H function when reduced to a four parameter function by introducing suitable modifications predicts the fifth one with minimum percent errors compared to other eight functions. The present performance of H-H function is consistent with the earlier findings of Steele *et al*¹.

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