MODIFIED MORSE FUNCTION FOR THE COMPUTATION OF INTERNUCLEAR DISTANCES AND CONSTRUCTION OF POTENTIAL ENERGY CURVES FOR DIATOMIC MOLECULES

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A variation in the computational procedure for the internuclear distance (r_i) and the potential energy curve for diatomic molecules was developed based on a modification of the original Morse function. This modified Morse function was also found to satisfy the Varshni criterion for "true potential". This potential was applied for species such as N_2, OH and OH^+ because of their importance in the photo-chemistry of aeronomic phenomena and the results were in close agreement with those based on existing computational methods. In addition, we showed that this simpler approach gives results which agree with those of Klein–Dunham and Vanderslice for the half width, $f = (r_2 - r_1)/2$.

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1. Introduction

An accurate knowledge of the inter-nuclear distance is of fundamental importance in molecular spectroscopy for constructing the potential energy curves of diatomic molecules. Oldenberg [1] Rydberg [2; 3] and Klein [4] were the first to set up a graphical procedure for constructing potential energy curves. However, a close scrutiny of the graphical procedures by Rees [5] revealed a few inaccuracies and inadequacies as the power series developed for the potential energy curves of diatomic molecules that showed divergence at low quantum numbers. This prompted him to put these methods in a closed form, which, however, still remained complicated. Jarmain [6] simplified his formulae in terms of vibrational quantum numbers and showed that his simplified potential energy expression is mathematically identical with that of Dunham's first approximation [7].

We, however, felt that Jarmain's formulae for the classical turning points (r_1, r_2) which involve a large number of spectroscopic constants, can be replaced by a simpler expression without an appreciable loss in accuracy. We have achieved this in Section 2

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by simply expanding the Morse function in Maclaurin's series. In Section 3, we closely examine the modified Morse approach with reference to Varshni's [8] criterion to test exactly how "true" is the modified potential. We have illustrated in Section 4 the utility of this approach for diatomic molecules such as N_2, OH and OH^+, which are of importance for our aeronomic and astrophysical investigations [9]. We, further present in Section 5 that results for half width (f-factors) converge from three approaches Sandeman [10], Davies–Vanderslice [11] and ours. Lastly, we present in the Appendix, a simplified procedure for the evaluation of C_i coefficients of Sandeman's formula [10] for classical turning points.

2. *Calculations for the internuclear distance and potential energy curves for* N_2, OH *and* OH^+

The Morse function for the potential energy of a diatomic molecule is

$$U(r) = D_e[1-\exp(-\alpha(r_i-r_e))]^2, \tag{1}$$

where D_e is the dissociation energy, r_i is the internuclear distance, r_e is the equilibrium distance and α is a parameter. This equation can be written also as:

$$-\alpha(r_i-r_e) = -\ln[1+(U/D_e)^{1/2}] \tag{2}$$

on expansion of the logarithmic function using the Maclaurin's series, one obtains:

$$-\alpha(r_i-r_e) = (U/D_e)^{1/2}-\tfrac{1}{2}(U/D_e)+\tfrac{1}{3}(U/D_e)^{3/2}+\ldots \tag{3}$$

Following Jarmain [6] we write:

$$U = \omega_e V-\omega_e X_e V^2+\omega_e Y_e V^3-\ldots, \tag{4}$$

where ω_e, $\omega_e X_e$, $\omega_e Y_e$ ... etc. are spectroscopic constants and $V = v+\frac{1}{2}$ where v is a vibrational quantum number.

For the molecules investigated viz. N_2, OH and OH^+, the cubic term is expected to be insignificant and hence substituting Eq. (4) in Eq. (3), one obtains:

$$-\alpha(r_i-r_e) = [\omega_e V-\omega_e X_e V^2/D_e]^{1/2}-\tfrac{1}{2}[\omega_e V-\omega_e X_e V^2/D_e]$$
$$+\tfrac{1}{3}[\omega_e V-\omega_e X_e V^2/D_e]^{3/2}. \tag{5}$$

This equation was used to compute the values of turning points (r_i). Eq. (5) involves only three parameters viz. ω_e, $\omega_e X_e$ and D_e. Jarmain's equation (Eq. (9) of his papers) however, is based on a few more constants viz. B_e, k and m. Some of them are functions of ω_e which lead to an extremely complicated expression for r_i. Simplicity of Eq. (5) will therefore be of considerable help in computation of spectroscopic constants. These differences primarily arise because his starting expressions were based on the extremely rigorous Rydberg–Klein formula [4], whereas we started from a semi-empirical Morse Function only.

This approach, whether it represents a true potential function or not, can be tested by applying Varshni's [8] criterion. This is shown in the next section.

3. *Criterion for the potential function*

Whether the potential energy curve of diatomic molecules can be represented satisfactorily or not by a Morse function or a modified Morse function depends on a satisfactory fit of values of experimental constants such as r_e, D_e, k_e, α_e, ω_e, $\omega_e X_e$, $\omega_e Y_e$ and r_c. For most of the molecules only a few of these constants are known. Moreover, as these constants are interdependent, usually any three are enough to determine the potential function, using the form of which other constants are determined. From these several constants, the expressions for k_e, r_e and D_e are relatively simple and are more commonly used.

The general criterion for a satisfactory representation of any potential curve given by Varshni [8] are adopted here. These are:

$$(i) \qquad U(r_e)-U(\infty) = -D_e,$$

$$(ii) \qquad (\partial U/\partial r)_{r=r_e} = 0,$$

$$(iii) \qquad (\partial^2 U/\partial r^2)_{r=r_e} = k_e. \tag{6}$$

The potential energy curve fits accurately if all the above conditions are fulfilled. We next want to show that our modified Morse function is satisfactory to show this.

Following Dunham [7], we can write α_e and $\omega_e X_e$ as:

$$\alpha_e = 6B_e^2/\omega_e \cdot F, \tag{7}$$

and

$$\omega_e X_e = W/\mu_A r_e^2 \cdot G, \tag{8}$$

where

$$F = -[1+Xr_e/3], \quad G = [5X^2/3-Y]r_e^2, \quad W = 2.1078\times 10^{-16}, \tag{9}$$

and

$$X = U'''(r_e)/U''(r_e), \tag{10}$$

$$Y = U''''(r_e)/U''(r_e). \tag{11}$$

For the Morse function, as well as for our modified Morse function, the first two criterion of Varshni are satisfied automatically. The third gives

$$k_e = 2D_e\alpha^2, \tag{12}$$

where α is the parameter defined in our Eq. (1). The Southerland parameter is then given by

$$\Delta = k_e r_e^2/2D_e = \alpha^2 r_e^2, \tag{13}$$

which is now independent of D_e. In terms of this new parameter we have

$$\alpha_e = 6B_e^2[\Delta^{1/2}-1]/\omega_e, \tag{14}$$

and

$$\omega_e X_e = 8\Delta \cdot W/r_e^2 \cdot \mu_A. \tag{15}$$

The values of α_e and $\omega_e X_e$ can be computed from these equations and compared with experimental values to test the fit of the modified Morse function.

4. *The application of* OH, OH^+ *and* N_2

4.1. Computations for α_e and $\omega_e X_e$

The validity of our approach can easily be tested by evaluating the constants, α_e, $\omega_e X_e$, as outlined in Section 2. We present in Table I, the results of our computations for α_e for OH, OH^+ and N_2 for a simultaneous comparison with the experimental results as well as those obtained based on earlier theoretical approaches. It can be seen that our values are comparable to those of others. In fact, the standard errors are smaller. In Table II, we show the results of our computations for $\omega_e X_e$. The values of $\omega_e X_e$ for these three mole-

TABLE I

Calculated values of α_e for different functions

Potential function	Molecule		
	N_2	OH	OH^+
Experimental[a]	0.0187	0.714	0.7494
Morse[b]	0.01996 (+6.2)	0.714 (0.0)	
Rydberg[b]	0.01844 (+1.4)	0.6425 (−11.1)	
Third[b]	0.01665 (−10.9)	0.6319 (−11.5)	
Empirical[b]	0.01349 (−27.3)	0.5207 (−24.1)	
Present work	0.01727 (−8.3)	0.6234 (−14.0)	0.6654 (−10.0)

TABLE II

Calculated values of $\omega_e X_e$ for different functions

Potential function	Molecule		
	N_2	OH	OH^+
Experimental[a]	14.456	82.81	78.515
Morse[b]	17.42 (+20.5)	94.36 (±13.9)	—
Rydberg[b]	15.97 (+10.4)	86.5 (+4.4)	—
Lippincott[b]	13.82 (−4.4)	77.84 (−6.0)	—
Empirical[b]	13.15 (−9.0)	80.19 (−3.2)	—
Present work	14.46 (+0.06)	82.42 (0.05)	78.49 (−0.04)

[a] Spectra of diatomic molecules, G. Herzberg (1958).
[b] Varshni, *Rev. Mod. Phys.* **29**, 664 (1957).
Values in the brackets represent the per cent error when compared with the experimental values.

cules are in excellent agreement with experimental values than the previous models used in the table for comparison.

These tests, based on Varshni's criterion, suggest that a modified Morse potential function satisfies the criterion for the true potential.

4.2. Computations for the internuclear distance, r_i

We next computed the values of r_i using Eq. (5). The computations for r_1 and r_2 are given in Tables III, IV and V for the molecules studied and are compared with computa-

TABLE III

Comparison of values of turning points from different methods for $N_2(\chi^1\Sigma_g^+, r_e = 1.094$ Å)

Vibrational quantum number v	Potential energy U [cm^{-1}]	r_1 [Å]				r_2 [Å]			
		A	B	C	D	A	B	C	D
0	1176.40	1.051	1.051	1.051	1.051	1.142	1.142	1.142	1.142
1	3506.87	1.023	1.022	1.023	1.023	1.180	1.180	1.180	1.180
2	5808.68	1.005	1.004	1.004	1.004	1.209	1.209	1.209	1.208
3	8081.55	0.991	0.990	0.990	0.989	1.234	1.233	1.234	1.233
4	10326.52	0.979	0.978	0.979	0.977	1.256	1.255	1.256	1.254
5	12540.60	0.970	0.968	0.968	0.966	1.278	1.277	1.277	1.274
6	14726.70	0.961	0.959	0.960	0.958	1.298	1.296	1.296	1.294
7	16883.95	0.953	0.951	0.951	0.949	1.317	1.315	1.315	1.311
8	19012.20	0.946	0.944	0.944	0.941	1.336	1.354	1.334	1.327
9	21181.65	0.940	0.937	0.937	0.933	1.354	1.352	1.350	1.343
10	23182.14	0.934	0.931	0.931	0.927	1.372	1.367	1.367	1.359
11	25223.72	0.928	0.925	0.925	0.925	1.389	1.387	1.388	1.375
12	27236.38	0.923	0.920	0.919	0.914	1.406	1.404	1.399	1.390
13	29220.14	0.918	0.915	0.914	0.908	1.423	1.421	1.415	1.409
14	31174.98	0.914	0.910	0.909	0.902	1.440	1.438	1.431	1.417
15	33100.91	0.910	0.906	0.904	0.897	1.457	1.454	1.447	1.431
16	34997.93	0.906	0.902	0.899	0.892	1.473	1.471	1.462	1.444
17	36866.03	0.901	0.897	0.895	0.887	1.490	1.488	1.477	1.457
18	38083.23	0.899	0.894	0.890	0.882	1.507	1.504	1.492	1.470
19	40515.20	0.895	0.890	0.886	0.878	1.523	1.521	1.508	1.481

A — Modified Jarmain's formula, B — Modified Morse formula of Jarmain, C — Sandeman formula
D — Present work.

tions given by Jarmain with his two different expressions and with those of Sandeman [10]. These results can be summarised as follows:

(*i*) Our results are generally less compared to those of Jarmain's, but are in very good agreement with those of Sandeman [10].

(*ii*) The maximum difference between our values and those of Jarmain's, even at $V = 19.5$, is about 1 per cent for N_2, whereas we found 3 per cent for OH and 4 per cent

TABLE IV

Comparison of values of turning points from different methods for OH ($\chi^2\pi_i$, r_e = 0.9706 Å)

Vibrational quantum number v	Potential energy U [cm^{-1}]	r_1 [Å]				r_2 [Å]			
		A	B	C	D	A	B	C	D
0	1846.90	0.883	0.882	0.883	0.882	1.080	1.079	1.080	1.079
1	3416.50	0.830	0.829	0.830	0.827	1.178	1.177	1.177	1.174
2	8820.44	0.799	0.797	0.797	0.792	1.257	1.256	1.254	1.246
3	12058.80	0.776	0.773	0.773	0.765	1.330	1.328	1.323	1.309
4	15131.40	0.750	0.754	0.752	0.743	1.399	1.398	1.386	1.365
5	18038.60	0.743	0.739	0.735	0.723	1.468	1.468	1.449	1.416
6	20980.10	0.731	0.726	0.719	0.706	1.537	1.539	1.508	1.464

A — Modified Jarmain's formula, B — Modified Morse formula of Jarmain, C — Sandeman formula, D — Present work.

TABLE V

Comparison of values of turning points from different methods for OH^+ ($\chi^3\Sigma_-$, r_e = 1.0289 Å)

Vibrational quantum number v	Potential energy U [cm^{-1}]	r_1 [Å]				r_2 [Å]			
		A	B	C	D	A	B	C	D
0	1537.60	0.934	0.933	0.934	0.933	1.150	1.149	1.150	1.149
1	4493.40	0.878	0.875	0.878	0.873	1.260	1.257	1.260	1.254
2	7292.70	0.846	0.841	0.843	0.836	1.349	1.344	1.347	1.335
3	9935.00	0.823	0.817	0.818	0.806	1.430	1.434	1.425	1.434
4	12420.25	0.806	0.798	0.782	0.782	1.507	1.499	1.499	1.467
5	14748.16	0.792	0.784	0.779	0.761	1.582	1.575	1.569	1.524
6	16919.66	0.781	0.773	0.762	0.743	1.656	1.648	1.644	1.576

A — Modified Jarmain's formula, B — Modified Morse formula of Jarmain, C — Sandeman formula, D — Present work.

for OH^+ at $v = 6$. These differences are only between theoretical computations and can, therefore, be considered as insignificant at this stage. Moreover, our potential function is tested for Varshni's criterion and, therefore, our computations can be expected to be more reliable for the eventual comparison with experimental values. Even for $v = 19$, for instance in the case of N_2, the maximum error in turning points does not exceed 4 per cent.

We, therefore, plan to obtain the wave functions and intensities as a part of our subsequent investigations for comparison with our experimental values of intensities.

5. Equivalence of different approach-calculations of half-widths

We next illustrate that the three approaches, viz. of Sandeman [10], Davies–Vanderslice [11] and ours described in Section 2 coincide the expressions of the half-width.

(*i*) Sandeman's [10] formula for half-width can be written as:

$$(r_1-r_e)/r_e = (U/a_0)^{1/2}+C_1(U/a_0)+C_2(U/a_0)^{3/2}, \tag{16}$$

$$(r_2-r_e)/r_e = -(U/a_0)^{1/2}+C_1(U/a_0)-C_2(U/a_0)^{3/2}, \tag{17}$$

which after subtraction leads to:

$$f = (r_2-r_1)/2 = -\left(\frac{U}{a_0}\right)^{1/2}\cdot r_e\left[1+C_2\left(\frac{U}{a_0}\right)\right].$$

Substituting for $C_2 = \omega_e X_e/3B_e$ and $a_0 = \omega_e^2/4B_e$ and omitting the negative sign for obvious reasons we obtain

$$f = \frac{2(U)^{1/2}}{\omega_e}\left(\frac{h}{8\pi^2 C\mu}\right)^{1/2}\left(1+\frac{U}{3D_e}\right). \tag{18}$$

(*ii*) The Davies–Vanderslice [11] equation for half-width is

$$f = (r_2-r_1)/2 = (h^2/2\pi^2\mu)^{1/2}\sum_{n=1}(n+\tfrac{1}{2})g_n b_n U^{n-1/2}, \tag{19}$$

where

$$g_n = 2^{2n}(n!)^2/(2n+1)! \tag{20}$$

in which they calculated the values of b_n. Thus up to the first two terms

$$\begin{aligned} f &= (h^2/2\pi^2\mu)^{1/2}\,(\tfrac{3}{2}\,g_1 b_1 U^{1/2}+\tfrac{5}{2}\,b_2 g_2 U^{3/2}+\ldots) \\ &= (h^2/2\pi^2\mu)^{1/2}\,(b_1 U^{1/2}+\tfrac{4}{3}\,b_2 U^{3/2}+\ldots). \end{aligned} \tag{21}$$

Substituting from their tables for

$$b_1 = -\frac{1}{\omega_e}\cdot\frac{1}{(hc)^{1/2}},$$

$$b_2 = -\frac{1}{\omega_e(hc)^{1/2}}\cdot\left(\frac{\omega_e X_e}{\omega_e^2}\right)$$

and rearranging we get:

$$f = \left(\frac{2U^{1/2}}{\omega_e}\right)\cdot\left(\frac{h}{8\pi^2 C\mu}\right)\cdot\left(1+\frac{U}{3D_e}\right). \tag{22}$$

(*iii*) We directly obtain from Eq. (3) by writing equations for r_1 and r_2 separately, and subtracting:

$$f = \left(\frac{2U^{1/2}}{\omega_e}\right) \cdot (h/8\pi^2 C\mu)^{1/2} \cdot \left(1 + \frac{U}{3D_e}\right). \tag{23}$$

We thus illustrate, that although these approaches differ in obtaining expressions for classical turning points, they coincide the important result, namely half-width of:

$$f = (r_2 - r_1)/2.$$

This fact, coupled with the results obtained for individual values of turning points, illustrates the utility of our simple approach.

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APPENDIX

Evaluation of the Sandeman C_i coefficients

We next investigate the C_i coefficients in Sandeman's Eq. (12) (paper [10]):

$$R = (r_i - r_e)/r_e = \pm(U/a_0)^{1/2}[1 \pm C_1(U/a_0)^{1/2} + C_2(U/a_0) \pm \ldots], \tag{24}$$

where

$$a_0 = \omega_e^2/4B_e$$

and the other symbols have their usual meaning.

Sandeman had evaluated C_i values from spectroscopic constants after an extensive computation. We, however, felt that this was unnecessary and the same information could have been obtained in the manner described below.

Equating and rewriting Eq. (24) we obtain

$$U = a_0 R^2[1 + C_1(U/a_0)^{1/2} + C_2(U/a_0) \pm \ldots]^{-2}. \tag{25}$$

We note that Dunham [7] gave an expression for potential energy, U, in terms of R directly as:

$$U = a_0 R^2(1 + a_1 R + a_2 R^2 + \ldots). \tag{26}$$

Comparing Eqs. (25) and (26) and noting that $R = (U/a_0)^{1/2}$ to a first approximation we find that

$$C_1 = -a_1/2 \tag{27}$$

for other constants. These are the conversion formulae (Eq. 13) that he has derived after much considerable labour from experimental data.

REFERENCES

[1] O. Oldenburg, *Z. Phys.* **56**, 563 (1929).
[2] R. Rydberg, *Z. Phys.* **73**, 376 (1931).
[3] R. Rydberg, *Z. Phys.* **80**, 344 (1933).
[4] O. Klein, *Z. Phys.* **76**, 226 (1932).
[5] A. L. G. Rees, *Proc. Phys. Soc.* (London) **A59**, 998 (1947).
[6] W. R. Jarmain, *Can. J. Phys.* **38**, 217 (1960).
[7] J. L. Dunham, *Phys. Rev.* **41**, 713, 721 (1932).
[8] Y. P. Varshni, *Rev. Mod. Phys.* **29**, 664 (1957).
[9] N. Y. Mehendale, S. R. Gogawale, A. D. Tillu, Proc. Symp. on Spectroscopic Studies of Astrophysical Interest, Hyderabad, India 1972 p. 173.
[10] I. Sandeman, *Proc. Roy. Soc.* (Edinburgh) **60**, 210 (1940).
[11] R. H. Davies, J. T. Vanderslice, *Can. J. Phys.* **44**, 219 (1966).