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Comparative Study of Potential Energy Functions for Diatomic Molecules

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INTRODUCTION

THE correct representation of potential energy of a set of atoms as a function of the interatomic distance is of fundamental importance in molecular structure. A good deal of information about the structure of a molecule is summarized in its potential energy (P.E.) curves. Potential energy minima determine the bond lengths. The second derivatives of the P.E. with respect to distance give the force constants. And these determine the vibrational and rotational levels of the molecule. Anharmonicity constants depend on higher derivatives of the P.E. curve.

For molecular structure, the problem assumes its simplest form in the case of diatomic molecules where the interatomic distance is the one independent variable.

It is possible to plot the P.E. curves by making use of the energy levels themselves. Oldenberg (O1),[1] Rydberg (R6, R7), and Klein (K1) have developed methods of doing this, and Klein's method has been used with success by Rosenbaum (R5) and by Almy and Beiler (A1) for the upper electronic states of LiH and KH, respectively.

This method is very laborious and further it cannot be applied with accuracy at low vibrational quantum numbers for which the power series expansion method of Crawford and Jorgenson (C5) has to be applied. This power series for the potential energy in terms of the displacement of the atoms from the equilibrium position does not converge rapidly for any range of displacements and involves even more computation than the Rydberg-Klein method. Rees (R1, R2) has given an analytical formulation of the Klein-Rydberg method which enables the P.E. curve to be evaluated with accuracy in the region of the minimum and has applied it to certain states of Br_2.

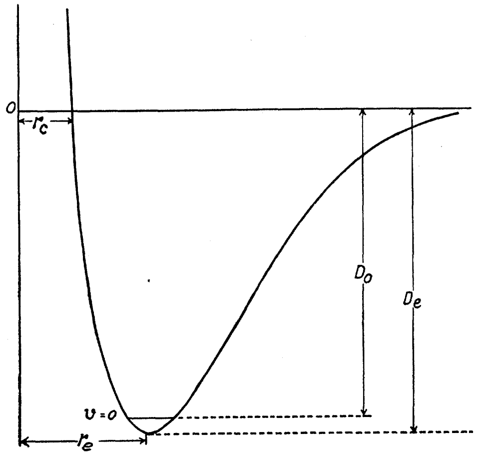

FIG. 1. Simple potential energy curve of a diatomic molecule.

On the theoretical side, by quantum-mechanical methods, it has not been found possible to calculate the P.E. curve to any great degree of accuracy due to mathematical and computational difficulties, except in the case of the simplest molecules like H_2^+ (Teller T3, Chakravarty C2), H_2 (James and Coolidge J1), etc. Classical electrostatic models for ionic molecules like alkali halides have yielded good results (Rittner R3, Varshni V2).

The most widely used method is to represent the P.E. curve by a suitable function—empirical or semi-empirical, and many functions have been suggested. First we formulate the criteria that a good potential function must satisfy. We are not concerned here with repulsive states. These criteria (Morse M6, Frost and Musulin F1, Lippincott and Schroeder L6) can be divided in two parts, (a) necessary and (b) desirable.

(a) Necessary:

(1) It should come asymptotically to a finite value as $r\rightarrow\infty$.

(2) It should have a minimum at $r=r_e$.

(3) It should become infinite at $r=0$. This need not be very strict, because results are practically the same if U becomes very large at $r=0$. Also if nuclear structure and forces are taken into account, this criterion is not exactly true. However, for our purposes, the change in the P.E. function at internuclear distances of 10^{-12} cm is of no consequence.

(b) Desirable:

(4) The above three criteria give a conventional form of P.E. curve as shown in Fig. 1. However, it is not the only possible form for the curve. Potential energy curves with at least one maximum between the main minimum and the dissociation limit are certainly known (Gaydon G1, Mulliken M7, M8, Herzberg H3, Barrow B3). Gaydon (G1) does not exclude the possibility of multiple maxima and minima.

The maximum often arises when an "attractive" potential curve in a low approximation is crossed by a "repulsive" potential curve. Because of the finer

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[1] References are listed at the end of this article.

interaction, the intersection is avoided leading to a potential maximum of the lower of the resulting potential curves if the interaction is not too strong (Fig. 2). A few cases of such potential curves with maximum have been observed by means of predissociation phenomenon, for example for AlH and BH (Herzberg and Mundie H4). Maxima also arise due to Van der Waals interaction. Another case when the maximum is below the asymptote is shown in Fig. 3.

Thus to accommodate such states the potential function should be capable of giving rise to at least one maximum under certain conditions.

Frost and Musulin (F1) have given a theoretical discussion of the various criteria. In analogy with the wave-mechanical calculations, they consider the potential energy as the algebraic sum of two parts:—(i) the nuclear repulsive potential corresponding to merely a Coulomb potential $Z_1Z_2e^2/r$ where Z_1 and Z_2 are effective atomic numbers; (ii) the purely electronic energy defined as U_e which is also a function of r. Thus

$$U=\frac{Z_1Z_2e^2}{r}+U_e.$$

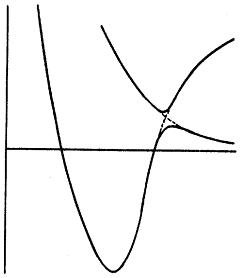

FIG. 2. Potential energy curve with one maximum. The maximum lies above the dissociation limit.

They have shown that an ideal potential function should also satisfy the following additional criteria. Somewhat similar ideas were advanced by Davidson and Price (D2) and Newing (N1) earlier.

(5) (a) U_e is finite at $r=0$.
(b) $U_e=U_e^0$ at $r=0$, where U_e^0 is the known "united" atom energy.
(6) $U_e \propto -Z_1Z_2e^2/r$ for large r.
(7) $\dfrac{dU_e}{dr}=0$ at $r=0$.

This condition is known to exist for H_2^+ as its electronic energy approaches the united atom He^+ (Matsen M3). This is believed to be correct also for other diatomic molecules, but the proof has apparently not been given.

(8) Van der Waals terms should introduce terms of the form $1/r^n$ (Coulson C4, Pauling and Beach P2).

Criteria 4 to 8 need not be exactly true.

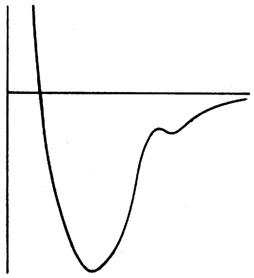

FIG. 3. Another case of potential energy curve with a maximum, the maximum lying below the dissociation limit.

The experimental constants which are available for fitting the curve are: 1. r_e—internuclear distance at equilibrium; 2. D_e—dissociation energy; 3. k_e—force constant; 4. α_e; 5. ω_ex_e; 6. ω_ey_e; 7. r_c—the critical distance, a quantity obtained indirectly from mass spectrometry appearance potentials. r_c is the value of r, less than r_e, at which $U=0$ or the same as at $r=\infty$; 8. U_e^0.

For most molecules only the first five are available. ω_ey_e is known only for a few of the more extensively investigated molecules, and that too not very accurately. So far, the r_c value is available only for H_2^+ (Stevenson S2). U_e^0 can only be used in conjunction with criterion 5b, which is a stringent condition and may not be satisfied by a function satisfactory from other criteria. Thus we are left with the first five constants.

Two types of analytical functions have been used: (1) power series of the type

$$U=c_1(r-r_e)+c_2(r-r_e)^2+c_3(r-r_e)^3\cdots, \qquad (1)$$

(2) closed formulas.

The first type has been investigated by Kratzer (K4) on old quantum theory and by Dunham (D5) and Chakravorti (C1) by wave mechanics. Dunham's work has been extended and simplified by Sandeman (S1).

Though this function has the advantage that the corresponding wave equation can be solved to a very good degree of accuracy, there is one serious objection. The series is not convergent and unsuitable for high r (the P.E. as obtained from this function tends to plus or minus infinity as r becomes infinite, instead of going to the dissociation limit), though it can be used to give a very accurate P.E. curve close to the minimum. Also this is not a very convenient expression from computational viewpoint. The only advantage that can be claimed for Dunham's expression is flexibility.

Numerous empirical or semiempirical functions have been proposed to represent the P.E. curve.

Comparative tests for some of the functions on a few molecules have been made (Lotmar L10, Coolidge, James, and Vernon C3, Davies D3). However, no extensive examination has been made so far to test the relative merits of the various functions.

In view of the fact that five constants are available, for maximum flexibility, one can keep five parameters in the functions, but such functions are only useful for plotting the P.E. curve.

Functions with fewer constants (3 or 4) have also been suggested. Because the number of parameters is less than the available spectroscopic constants, such functions also yield relations between the different constants. This gives rise to another question: is it possible to find interrelation between the different constants, irrespective of the type of binding, etc.? Special emphasis is laid on this point in this paper.

In principle we can utilize any of the known constants (in all equal to the number of parameters in the function) for fitting the function. However, this is not always satisfactory for two reasons: firstly, the expressions for the parameters in terms of constants usually are much simpler for r_e, k_e, D_e than for α_e and $\omega_e x_e$; secondly, the values of α_e and $\omega_e x_e$ are not known with the accuracy that the k_e and r_e values are known (at times values of α_e and/or $\omega_e x_e$ are not known at all). Hence, as a uniform policy we would determine the curve from k_e, r_e, and D_e when there are three constants. The function can be tested in two ways—(a) by comparing it with the experimental curve, (b) by evaluating the values of the coefficients in the series or the unused constants and comparing them with the actual values. Here we only utilize method (b).

Comparison of α_e and $\omega_e x_e$ is a more direct method, rather than of the coefficients of the series. Further it is more convenient for comparing different functions. Hence we adopt this method.

The condition that a satisfactory function should be capable of yielding the correct α_e and $\omega_e x_e$ values is only necessary but not sufficient. A function may yield correct α_e and $\omega_e x_e$, but still may not be satisfactory in the neighborhood of $r=0$. (See also Wu and Chao W2.)

To find the parameters from the experimental constants we have to solve the corresponding wave equation and compare the resulting coefficients of the terms with the series

$$G(v)=\omega_e(v+\tfrac{1}{2})-\omega_e x_e(v+\tfrac{1}{2})^2+\omega_e y_e(v+\tfrac{1}{2})^3+\cdots. \quad (2)$$

However, this is not always possible. The Schrödinger equation is exactly solvable in only a very limited number of cases (Manning M1, Eisenhart E1) and perturbation methods are often cumbersome. Hence the following procedure is adopted. The closed analytical function can be expanded as follows:

$$U(r)=\frac{1}{\underline{|2}}U''(r_e)(r-r_e)^2+\frac{1}{\underline{|3}}U'''(r_e)(r-r_e)^3+\frac{1}{\underline{|4}}U^{\mathrm{iv}}(r_e)(r-r_e)^4+\cdots \quad (3)$$

which is the same as series (1) with

$$c_2=\frac{U''(r_e)}{\underline{|2}}$$

$$c_3=\frac{U'''(r_e)}{\underline{|3}}$$

$$c_4=\frac{U^{\mathrm{iv}}(r_e)}{\underline{|4}}.$$

Dunham (D5) has shown that

$$\alpha_e=-\left[\frac{c_3}{c_2}r_e+1\right]\frac{6B_e^2}{\omega_e} \quad (4)$$

and

$$\mu\omega_e x_e=\left[\frac{15}{8}\left(\frac{c_3}{c_2}\right)^2-\frac{3}{2}\left(\frac{c_4}{c_2}\right)\right]\frac{h}{8\pi^2 c}, \quad (5)$$

where B_e = rotational constant and μ = reduced mass. Actually there are some further terms but they are negligible. We put

$$U'''(r_e)/U''(r_e)=X$$
$$U^{\mathrm{iv}}(r_e)/U''(r_e)=Y.$$

Then in terms of X, Y, and μ_A (reduced mass in atomic weight units)

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

$$\begin{aligned}\omega_e x_e&=\left[\frac{5}{3}X^2-Y\right]\frac{h}{64\pi^2 c\times 1.6597\times 10^{-24}\mu_A}\\&=\left[\frac{5}{3}X^2-Y\right]\frac{2.1078\times 10^{-16}}{\mu_A}\\&=\left[\frac{5}{3}X^2-Y\right]\frac{W}{\mu_A}\end{aligned} \quad (7)$$

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

If we are dealing with a three constant curve we can fit the curve from k_e, r_e, and D_e and deduce the value of α_e and $\omega_e x_e$ from (6) and (7). The curve can be fitted from the following three conditions

$$U(r_e)-U(\infty)=-D_e \quad (8a)$$

$$\left(\frac{dU}{dr}\right)_{r=r_e}=0 \quad (8b)$$

and

$$\left(\frac{d^2U}{dr^2}\right)_{r=r_e}=k_e. \quad (8c)$$

The relative merits of the functions can be tested by calculating the values of α_e and $\omega_e x_e$ and comparing them with the experimental values. For a broad behavior of the function a new graphical method is used, which very clearly shows the applicability of a function without detailed calculations. In (6) and (7) it is only the quantities

$$\left[\frac{Xr_e}{3}+1\right] \quad \text{and} \quad \left[\frac{5}{3}X^2-Y\right]$$

which will be different for different functions. For most of the functions

$$-\left[\frac{Xr_e}{3}+1\right]=F \tag{9}$$

$$\left[\frac{5}{3}X^2-Y\right]r_e^2=G \tag{10}$$

can be represented as functions of the dimensionless parameter Δ where

$$\frac{k_e r_e^2}{2D_e}=\Delta. \tag{11}$$

This Δ may be called *Sutherland parameter* in honor of Sutherland (S3) who was the first to emphasize its importance. Then

$$\alpha_e=F\cdot\frac{6B_e^2}{\omega_e} \tag{12}$$

$$\omega_e x_e=G\cdot\frac{W}{\mu_A r_e^2}. \tag{13}$$

From the later analysis, it appears that those functions which give α_e and $\omega_e x_e$ values higher than those given by the Morse function can be safely ruled out.

The following symbols are used:

$$\rho=r-r_e$$

$$\xi=\frac{r-r_e}{r_e}.$$

A, B, C $\cdots$ a, b, c $\cdots$ m, n, etc. are constants. Though often the constants in different functions are represented by the same symbols, the value of the constants for different functions is different and should not be confused.

DOUBLE-EXPONENTIAL AND MORSE FUNCTIONS

Assuming that the repulsive and attractive terms both vary in an exponential manner, the potential function can be put as

$$U=Ae^{-mr}-Be^{-nr}. \tag{14}$$

Morse (M6) suggested a special form of this:

$$U=D_e[1-e^{-a(r-r_e)}]^2. \tag{15}$$

This satisfies criteria (1) and (2) and although at $r=0$, U is not infinite, it is nevertheless a satisfactorily large quantity.

Applying conditions (8 a, b, c) one easily gets

$$a=(k_e/2D_e)^{\frac{1}{2}}.$$

Morse solved his function for a special case and found that

$$G(v)=\omega_e(v+\tfrac{1}{2})-\omega_e x_e(v+\tfrac{1}{2})^2$$

for the vibrational energy levels without any higher power of $(v+\frac{1}{2})$. However Ter Haar (T4) has shown that this conclusion is not rigorously true.

Pekeris (P4, P5) solved the Schrödinger equation for the Morse curve by a perturbation method and found that to a good approximation

$$\alpha_e=6B_e x_e\left[\left(\frac{B_e}{\omega_e x_e}\right)^{\frac{1}{2}}-\frac{B_e}{\omega_e x_e}\right]. \tag{16}$$

Since

$$U''(r_e)=2a^2D_e$$
$$U'''(r_e)=-6a^3D_e$$
$$U^{\text{iv}}(r_e)=14a^4D_e,$$

from Eqs. (6) and (7) we easily get

$$\alpha_e=(\Delta^{\frac{1}{2}}-1)\frac{6B_e^2}{\omega_e} \tag{17}$$

$$\omega_e x_e=8a^2\frac{W}{\mu_A}=8\Delta\frac{W}{r_e^2\mu_A}. \tag{18}$$

Equation (17) is equivalent to (16) by virtue of (18). Equation (16) has been tested by Pekeris and found to yield good results.

On the other hand (18) has been examined by Huggins (H5, H6), Linnett (L1), etc., and found to give very poor results.

Equation (18) can be simplified to

$$D_e=\frac{\omega_e^2}{4\omega_e x_e} \tag{19}$$

which corresponds to the linear Birge-Sponer extrapolation. Gaydon (G1) has shown that usually this method gives rather high values for the dissociation energies.

For hydrogen halides, Davies (D3) found the values of $U'''(r_e)$ and $U^{\text{iv}}(r_e)$ to be satisfactory.

This function predicts for H_2^+, $r_e=0.50$ A or 16% low as compared with Stevenson's (S2) experimental value of 0.595 A.

Badger (B2) has proposed the following empirical rule for estimating "a" for single bonds:

$$a=1.15/(r_e-d_{ij})$$

where d_{ij} is the constant occurring in Badger's relation (B1) between k_e and r_e.

Huggins (H5, H6) modified the Morse function by putting a in (15) equal to $e^{mr_{12}}$, both r_{12} and m being the same for all electronic states of the same diatom. This gave satisfactory values of r_e from observed values of k_e and $\omega_e x_e$. But when he attempted to use the same function with the same values of r_{12} and m to calculate the heats of dissociation, the results were quite unsatisfactory, the errors being of the order of 100–200%. It appears that the function of Huggins gives an adequate representation of the relation between U and r in the neighborhood of r_e, but departs widely from the actual relation outside this region.

EXTENDED MORSE FUNCTION

Coolidge, James, and Vernon (C3) examined the following extended version of the Morse curve:

$$\frac{U}{D_e}=\sum_{n=2,3\cdots} c_n[1-e^{-a'(r-r_e)}]^n. \tag{20}$$

In actual calculations on certain states of H_2, Coolidge, James, and Vernon have taken 7 terms in this series. The form is flexible, but it has one serious disadvantage: a' is difficult to determine, and in fact loses its significance as we take more terms in the extended Morse curve.

HULBURT-HIRSCHFELDER FUNCTION

Hulburt and Hirschfelder (H7) modified the simple Morse function in this way:

$$U=D_e[(1-e^{-x})^2+cx^3e^{-2x}(1+bx)] \tag{21}$$

where

$$x=2\beta\xi=\frac{\omega_e}{2(B_eD_e)^{\frac{1}{2}}}\cdot\frac{r-r_e}{r_e}$$

and b and c are simple algebraic functions of the five spectroscopic constants. This has the great practical advantage that it uses just those five parameters which are most readily obtained from the study of band spectrum. Hulburt and Hirschfelder give a list of the numerical values of the parameters for 25 common diatomic molecules. With only a few exceptions, their potential curves lie above the Morse curves.

Recent work of Tawde and Gopalkrishnan (T1) on the transition probabilities in the C_2 (Swan) system suggests that this function is only satisfactory in the region $r>r_e$.

RYDBERG FUNCTION

Rydberg (R6) proposed:

$$U=-D_e(1+b\rho)e^{-b\rho} \tag{22}$$

which is similar to the radial wave function $R_{20}(r)$ of the hydrogen atom. This satisfies criteria (1) and (2), but like the Morse function, does not become ∞ at $r=0$, though it is sufficiently large at that point.

From the three conditions (8 a, b, c) one gets

$$b=(k_e/D_e)^{\frac{1}{2}}.$$

Further we have

$$U'''(r_e)=-2D_eb^3$$

$$U^{\mathrm{iv}}(r_e)=3D_eb^4$$

whence we get

$$\alpha_e=\left[\frac{2\sqrt{2}}{3}\Delta^{\frac{1}{2}}-1\right]\frac{6B_e^2}{\omega_e} \tag{23}$$

$$\omega_ex_e=\frac{22}{3}\Delta\cdot\frac{W}{r_e^2\mu_A}. \tag{24}$$

In predicting transition probabilities of C_2 (Swan) system, the Rydberg function gives better performance than the Morse or Hulburt-Hirschfelder functions (Tawde and Gopalkrishnan T1).

ROSEN-MORSE FUNCTION

In its simple form the Rosen-Morse (R4) curve is

$$U=A\tanh(r/d)-C\,\mathrm{sech}^2(r/d). \tag{25}$$

This does not satisfy the 3rd criterion. The relations to observed constants are

$$\tanh(r_e/d)=-A/2C$$

$$D_e=(A+2C)^2/4C.$$

Let

$$f=1/C^2\cdot(4C^2-A^2)^2$$

then

$$k_e=U''(r_e)=f/8d^2C$$

$$U'''(r_e)=3Af/8d^3C^2$$

$$U(r_e)=(9A^2-8C^2)f/8d^4C^3.$$

We define another parameter p given by

$$r_e/d=p.$$

Then we have

$$\Delta=p^2(1+\tanh p)^2 \tag{26}$$

$$\alpha_e=(2p\tanh p-1)\cdot\frac{6B_e^2}{\omega_e} \tag{27}$$

$$\omega_ex_e=8p^2(3\tanh^2p+1)\frac{W}{r_e^2\mu_A}$$

$$=8\Delta\frac{(3\tanh^2p+1)}{(1+\tanh p)^2}\cdot\frac{W}{r_e^2\mu_A}$$

$$=8\Delta(1-e^{-2p}+e^{-4p})\frac{W}{r_e^2\mu_A}. \tag{28}$$

Variation of F and G with p and Δ is tabulated in Table I.

Other methods of fitting the curve have been given by Lotmar (L10), Kronig (K6), and Davies (D3). Davies found that for hydrogen halides it gives results no better than Morse function. An extended four constant version of the Rosen-Morse function has been suggested by Lotmar (L10) which has been tested by Tawde and Gejji (T2).

MANNING-ROSEN-NEWING FUNCTION

The Manning-Rosen (M2) function is

$$U=\frac{1}{kd^2}\left[\frac{\beta(\beta-1)e^{-2r/d}}{(1-e^{-r/d})^2}-\frac{Ae^{-r/d}}{1-e^{-r/d}}\right] \tag{29}$$

which may be put as

$$U=-\frac{Be^{-r/d}+Ce^{-2r/d}}{(1-e^{-r/d})^2}. \tag{30}$$

It obeys the 3 necessary criteria. However, Manning and Rosen found that for this function "the dissociation energy . . . is greater than the quantity $\omega_e^2/4\omega_e x_e$ given by the Morse function." Thus

$$D_e=\frac{\omega_e^2}{4\omega_e x_e}+\delta$$

or

$$\omega_e x_e=\frac{\omega_e^2}{4(D_e-\delta)}>\frac{\omega_e^2}{4D_e}.$$

Thus it gives $\omega_e x_e$ values even higher than does the Morse function (which itself gives much higher values), and hence this function is not suitable.

Newing (N1, N2) studied the function

$$U=-D_e+D_e\left[\frac{(1-e^{-a\rho})e^{ar_e}}{e^{ar_e}-e^{-a\rho}}\right]^2. \tag{31}$$

(There is a misprint in the original equation as given in his paper. The first term in the denominator has been printed as e^{-ar_e}, whereas it should be e^{ar_e}.)

This expression on simplification takes the form of function (30).

PÖSCHL-TELLER FUNCTION

The function due to Pöschl and Teller (P6) has the form

$$U=A\ \mathrm{cosech}^2\alpha(r-r_0)-B\ \mathrm{sech}^2\alpha(r-r_0) \tag{32a}$$

which uses 4 constants.

We examine here the simpler version

$$U=M\ \mathrm{cosech}^2(r/d)-N\ \mathrm{sech}^2(r/d). \tag{32b}$$

This obeys the three criteria.

Table I. Rosen-Morse function.

p	Δ	F	G
0.7	1.26	−0.1539	8.208
0.8	1.77	0.0624	11.89
0.9	2.39	0.289	16.45
1.0	3.10	0.523	21.92
1.1	3.94	0.761	28.43
1.2	4.84	1.001	35.55
1.3	5.86	1.240	43.63
1.4	6.96	1.479	52.49
1.6	9.45	1.949	72.68
1.8	12.28	2.408	95.63
2.0	15.43	2.856	121.2
2.2	18.89	3.293	149.3
2.4	22.67	3.723	179.8
2.6	26.74	4.144	212.8
2.8	31.13	4.559	248.1

From conditions (8 a, b, c) we get the following relations (Davies D3):

$$\tanh^4(r_e/d)=M/N=y^4\quad\text{(say)}.$$

Then

$$d^2=8D_e/k_e\quad\text{or}\quad\Delta=4r_e^2/d^2$$

$$y=\tanh(r_e/d)$$

$$N=D_e/(1-y^2)^2.$$

Further

$$U''(r_e)=8N/d^2\cdot(1-y^2)^2$$

$$U'''(r_e)=-24N/yd^3\cdot(1-y^2)(1-y^4)$$

$$U^{\text{iv}}(r_e)=\frac{8}{d^4}\left[15(MN)^{\frac{1}{2}}\left\{\frac{1-y^4}{y^2}\right\}^2-32N(1-y^2)^2\right]$$

whence we get

$$\alpha_e=[\Delta^{\frac{1}{2}}\coth\Delta^{\frac{1}{2}}-1]\frac{6B_e^2}{\omega_e} \tag{33}$$

$$\omega_e x_e=8\Delta\cdot\frac{W}{r_e^2\mu_A}. \tag{34}$$

While the value of α_e is different from the Morse function, the value of $\omega_e x_e$ comes out to be the same as in the Morse function.

Davies (D3) examined this function on hydrogen halides and from the values of $U'''(r_e)$ and $U^{\text{iv}}(r_e)$ concluded that it is slightly superior to the Morse function.

HYLLERAAS FUNCTION

Hylleraas (H8, H9, H10) introduced the potential:

$$U=D_e\left[1-\frac{(1+a)(1+c)(z+b)}{(z+a)(z+c)(1+b)}\right] \tag{35}$$

where

$$z=e^{2(1+k)\beta\xi}$$

and the intermediate quantities a, b, c are defined by

$$a=(k-k_2)/(1+k_2)$$
$$b=\{k-(k_1+k_2)\}/(1+k_1+k_2)$$
$$c=(k-k_1)/(1+k_1)$$

k, k_1, k_2 being the parameters.

The function involves 6 parameters which are difficult to determine. Coolidge, James, and Vernon (C3) have given complicated equations for finding them. Obviously this function cannot furnish any relation between the molecular constants. This passes into the Morse curve upon making $k=k_1=0$, so that $a=b$, $c=0$. The Pöschl-Teller function is also a special case $k=0$, $k_1=\frac{1}{2}[\tanh(r/d)-1]$, $k_2=\frac{1}{2}[\coth(r/d)-1]$.

KRATZER FUNCTION

The Kratzer (K5) function approximates to the form

$$U=D_e\left[\frac{r-r_e}{r}\right]^2. \tag{36}$$

This has the drawback that it makes use of only two constants. The solution of the corresponding wave equation was first given by Fues (F3).

While it satisfies the three necessary criteria, application of conditions (8 a, b, c) leads to the abnormal result

$$\Delta=k_er_e^2/2D_e=1. \tag{37}$$

This value is not found in any of the 23 molecules considered in the present paper. Even H_2 (which has the lowest value of Δ) has a value higher than 2, and it is extremely unlikely that any other molecule will satisfy this condition. Hence this function is not applicable to molecular problems. A modified form is considered later.

DAVIDSON FUNCTION

Davidson (D1) examined the function

$$U=a\left[\frac{r}{r_e}-\frac{r_e}{r}\right]^2. \tag{38}$$

This does not satisfy the criterion that U should be finite when $r=\infty$. Also only two constants are used. However, on applying conditions (8 a, b, c), this leads to the interesting result

$$k_er_e^2=8a=\text{constant}. \tag{39}$$

Although this is not a universal relation, it is well satisfied by ground states of hydrogen halides (Kratzer K4, Glasstone G3, Davies D3, Heath, Linnett, and Wheatley H1).

It is easily deduced that

$$\alpha_e=2\cdot\frac{6B_e^2}{\omega_e} \tag{40}$$

$$\omega_ex_e=0. \tag{41}$$

F always comes out to be equal to 2, contrary to fact, and (40) does not hold for any molecule.

MECKE-SUTHERLAND FUNCTION

Mecke (M4) and Sutherland (S3) suggested

$$U=\frac{a}{r^m}-\frac{b}{r^n}. \tag{42}$$

Here both the attractive and the repulsive terms are of the reciprocal type. This type of function was used before by Grüneisen (G6), Mie (M5), etc., for forces in the solid state. A special case ($m=2$, $n=1$) has been treated by Fues (F3). Baughan (B4) used such a function for interaction between nonbonded atoms.

From conditions (8 a, b, c),

$$D_e=\frac{a}{r_e^m}\left(\frac{m-n}{n}\right)=\frac{b}{r_e^n}\left(\frac{m-n}{m}\right) \tag{43}$$

$$k_e=am(m-n)/r_e^{m+2}=bn(m-n)/r_e^{n+2} \tag{44}$$

whence

$$2\Delta=k_er_e^2/D_e=mn. \tag{45}$$

Sutherland found that for the same class of molecules $k_er_e^2/D_e$ is approximately constant, which led him to conclude that m and n are constant for similar molecules.

We can further deduce

$$\alpha_e=(m+n)\cdot\frac{2B_e^2}{\omega_e} \tag{46}$$

$$\omega_ex_\epsilon=\left[\frac{2}{3}m^2+\frac{7}{3}mn+\frac{2}{3}n^2+4(m+n)+4\right]\frac{W}{r_e^2\mu_A}. \tag{47}$$

From considerations of the relation between k_e and r_e, Linnett (L1) thinks that this function is not satisfactory.

Equation (42) is a four-constant function and we can determine their values from k_e, r_e, D_e, and α_e by (44), (45), and (46) and then try to evaluate ω_ex_e from (47) (actually we need calculate only m and n for finding ω_ex_e). However, as we are restricting ourselves to three constant potentials we will not attempt it.

Sutherland (S4) later modified it by replacing r by $(r-d)$, so that it becomes

$$U=\frac{a}{(r-d)^m}-\frac{b}{(r-d)^n}. \tag{48}$$

This modified Sutherland function can be used (V3) to derive a series of very fruitful relations connecting the various molecular constants, by making certain assumptions regarding a, d, m, and n. These will be published later on.

Lovera (L11) applied (48) to 4b–6b group of molecules.

LINNETT FUNCTION

Linnett (L1, L2) investigated the function

$$U=\frac{a}{r^m}-be^{-nr}. \tag{49}$$

Conditions (8 a, b, c) provide the following relationships:

$$D_e=\frac{a}{r_e^m}\left[\frac{m-nr_e}{nr_e}\right] \tag{50}$$

$$k_e=am(m+1-nr_e)/r_e^{m+2} \tag{51}$$

$$k_er_e^{m+2}=ma+\frac{m^2D_er_e^m}{1+D_er_e^m/a}. \tag{52}$$

Assuming $m(=3)$ to be constant for the KK period of molecules, and a to be constant for all states of a given molecule, he showed that (52) gives a satisfactory relation between k_e and r_e. He further deduced

$$\omega_ex_e=\left[\frac{5}{3}\cdot\left\{\frac{20-(nr_e)^2}{4-nr_e}\right\}^2-\left\{\frac{120-(nr_e)^3}{4-nr_e}\right\}\right]\frac{2.098}{r_e^2\mu_A} \tag{53}$$

where r_e is in angstroms.

The mean percentage error in ω_ex_e values over the states considered was found to be 16, compared to 46 by the Morse function—a considerable improvement.

Linnett also traced regularities in the value of a and later (L2) extended the function to other periods. This function is capable of giving rise to a low maximum between $r=r_e$ and $r=\infty$, and such a behavior of the function was found with ${}^1\Sigma_g^+$ and ${}^3\Pi_g$ states of N_2, however, experimental evidence does not favor such a maximum in these states.

α_e and ω_ex_e can be deduced in terms of parameter t $(=nr_e)$ which can be found from

$$\Delta=\frac{m(m+1-t)t}{2(m-t)}. \tag{54}$$

Then

$$\alpha_e=\left[\frac{(m+1)(m+3)-t^2-t}{m+1-t}\right]\frac{6B_e^2}{\omega_e} \tag{55}$$

$$\omega_ex_e=\left[\frac{5}{3}\left\{\frac{(m+1)(m+2)-t^2}{m+1-t}\right\}^2-\left\{\frac{(m+1)(m+2)(m+3)-t^3}{m+1-t}\right\}\right]\frac{W}{r_e^2\mu_A}. \tag{56}$$

TABLE II. Linnett function.

t	Δ	F	G
0	0	6	11.67
1	2.25	7.33	27.2
1.5	3.75	8.1	37.28
2.0	6.0	9.0	50.6
2.25	7.875	9.53	59.4
2.5	11.25	10.17	70.47
2.6	13.65	10.46	75.92
2.7	17.55	10.78	82.16
2.75	20.625	10.95	83.69
2.8	25.2	11.13	89.96
3.0	∞	12	108.7

The expression for ω_ex_e coincides with that of Linnett for $m=3$.

Table II gives the variation of F and G with t and Δ for the special case of $m=3$.

WU-YANG FUNCTION

Wu and Yang (W3) used a function similar to the Born-Mayer function used for crystal forces:

$$U=ae^{-mr}-b/r^n. \tag{57}$$

This differs from the Linnett function in that the attractive and repulsive terms have been exchanged.

This satisfies only the first and second criteria. At $r=0$, this gives $U=-\infty$! Conditions (8 a, b, c) yield

$$k_er_e^{n+1}=-bn(n+1)/r_e+bnm. \tag{58}$$

For each molecular period Wu and Yang plotted $k_er_e^{n+1}$ against $1/r_e$ with different values of n. They obtained straight lines for a certain value of n, whence they concluded that n, m and b are constant in each period. This function will be examined in detail for α_e and ω_ex_e in a later publication.

PUPPI FUNCTION

Puppi (P7) derived a reduced functional relation, his reduced distance variable being

$$y=(r-r_e)/r_eD_e^{\frac{1}{2}}.$$

This was obtained by assuming a Morse function and introducing an empirical relation, equivalent to $k_er_e^2$ $=$const. Puppi's reduced equation is not universal as $k_er_e^2$ remains constant only within small groups of molecules. Furthermore, his variable y is complicated in that it mixes distance and energy.

LIPPINCOTT FUNCTION

Recently Lippincott (L3, L4) has given the following function for which he also gives a semitheoretical justification:

$$U=D_e[1-\exp(-n\rho^2/2r)][1+af(r)]. \tag{59}$$

Here $f(r)$ is a function of the internuclear distance, chosen such that $f(r)=\infty$ when $r=0$ and $f(r)=0$ when

$r=\infty$. Lippincott says that for many purposes the $f(r)$ term is unimportant, and neglects it to a first approximation. Thus

$$U=D_e[1-\exp(-n\rho^2/2r)]. \tag{60}$$

At $r=0$, r_e, and ∞, it has the values D_e, 0, and D_e, respectively.

Then from conditions (8 b, c) we get $n=k_e r_e/D_e$. Further

$$\alpha_e=-\tfrac{1}{2}\cdot\frac{6B_e^2}{\omega_e} \tag{61}$$

$$\omega_e x_e=(6\Delta+3)\cdot\frac{W}{r_e^2\mu_A} \tag{62}$$

$$=(3nr_e+3)\frac{W}{r_e^2\mu_A}.$$

Calculations of $\omega_e x_e$ have been reported by Lippincott and Schroeder (L6). They have calculated it in terms of n, where n is empirically given by

$$n=n_0(I/I_0)^{\frac{1}{2}}{}_A(I/I_0)^{\frac{1}{2}}{}_B$$

where $(I/I_0)_A$ and $(I/I_0)_B$ are the ionization potentials of atoms A and B, respectively, relative to those of the corresponding atoms in the same row and first column of the periodic table. For the H atom I/I_0 has been assigned the value 0.88 rather than 1. For diatomic alkali metal and alkali hydrides, $n_0=4.21\times10^8$, for most of the others $n_0=6.32\times10^8$.

For α_e, Lippincott and Schroeder report that (60) gives $\alpha_e=0$. [As (61) shows, this appears to be in error.]

Hence later they have used (59) with

$$af(r)=-a(r_e/r)^6[1-\exp(-b^2nr^{11}/2r_e^{12})]^{\frac{1}{2}}$$
$$+a(r_e/r)^{12}[1-\exp(-b^2nr^{11}/2r_e^{12})]$$

and deduced the following expressions

$$D_e=\omega_e^2/2nr_eB_e$$

$$\alpha_e=ab\left(\frac{nr_e}{2}\right)^{\frac{1}{2}}\cdot\frac{6B_e^2}{\omega_e}$$

$$\omega_e x_e=1.5B_e[0.25+nr_e/4+ab(nr_e/2)^{\frac{1}{2}}$$
$$+(5a^2b^2-ab^2)nr_e/2].$$

TABLE III. Frost-Musulin function.

s	Δ	F	G
0	0	0	3
1	1.5	0.555	15.29
2	4	1.17	34.42
3	7.5	1.8	60.60
4	12	2.44	93.96
5	17.5	3.09	134.6
5.5	20.625	3.47	157.6

Utilizing the fact that ab and b are found to be nearly constant for most molecules, they computed α_e and $\omega_e x_e$ from the above expressions. The calculated values agree well with the experimental values for the molecules considered.

The simple equation (60) has also been applied to the problem of the hydrogen bond by Lippincott and Schroeder (L5).

FROST-MUSULIN FUNCTION

Another recent function is due to Frost and Musulin (F1). From semitheoretical reasoning they have constructed

$$U=e^{-ar}(1/r-b). \tag{63}$$

This satisfies the three criteria. Its special feature is that the united atom energy can be utilized in determining the constants a and b. Frost and Musulin found quite satisfactory results with this function for H_2^+ and H_2.

α_e and $\omega_e x_e$ are best represented in terms of a parameter s, defined by

$$\Delta=s^2/2+s \quad \text{or} \quad s=-1+(1+2\Delta)^{\frac{1}{2}}.$$

Then

$$\alpha_e=\left[\frac{2s^2+3s}{3(s+2)}\right]\frac{6B_e^2}{\omega_e} \tag{64}$$

$$\omega_e x_e=\left[\frac{11s^4+66s^3+156s^2+144s+36}{3(s+2)^2}\right]\frac{W}{r_e^2\mu_A}. \tag{65}$$

A short table of the variation of functions F and G with s and Δ is given in Table III.

Frost and Musulin (F2) have also attempted to obtain a "universal" potential energy function in terms of reduced potential energy U/D_e and reduced internuclear distance $(r-r_{ij})/(r_e-r_{ij})$, where r_{ij} is a constant for a given molecule formed from atoms i and j. They interpret r_{ij} as a measure of inner shell radii and correlate with Badger's d_{ij}. However, the results obtained for $U^{\mathrm{III}}(r_e)$ and $U^{\mathrm{IV}}(r_e)$ are rather poor, the average percentage deviations being 13.2 and 42, respectively, for the 23 molecules examined.

IONIC P.E. FUNCTIONS

For ionic molecules, P.E. functions based on a classical model have been used. These usually consist of several terms, including a Coulomb attractive term, a repulsive term and polarization terms etc. For details reference may be made to papers by Rittner (R1) and Varshni (V2).

SOME NEW POTENTIAL ENERGY FUNCTIONS

In the above, we have considered the various potential energy functions suggested by different authors.

Now we consider a few new potential energy functions and their possible applicability to diatomic molecules.

FIRST

$$U=D_e\{1-\exp[-b(r^2-r_e^2)]\}^2. \tag{66}$$

This satisfies criteria 1 and 2 and is sufficiently large at $r=0$.

We easily get

$$b=(k_e/8D_er_e^2)^{\frac{1}{2}}=\Delta^{\frac{1}{2}}/2r_e^2$$

$$\alpha_e=(\Delta^{\frac{1}{2}}-2)\frac{6B_e^2}{\omega_e} \tag{67}$$

$$\omega_ex_e=[8\Delta-12\Delta^{\frac{1}{2}}+12]\frac{W}{r_e^2\mu_A}. \tag{68}$$

Table IV shows the variation of F and G.

TABLE IV. First function.

Δ	F	G
0	−2	12
1	−1	8
2	−0.586	11.03
3	−0.268	15.22
4	0	20.00
6	+0.4495	30.61
8	0.8284	42.06
10	1.162	54.06
14	1.742	78.89
18	2.243	105.1
22	2.690	131.7
24	2.899	145.2
26	3.099	158.9

SECOND

$$U=D_e\left[1-\frac{r_e}{r}e^{-\alpha(r-r_e)}\right]^2. \tag{69}$$

This satisfies all the three criteria.

$$\alpha+\frac{1}{r_e}=\frac{\Delta^{\frac{1}{2}}}{r_e}$$

$$\alpha_e=\left[\Delta^{\frac{1}{2}}+\frac{1}{\Delta^{\frac{1}{2}}}-1\right]\frac{6B_e^2}{\omega_e} \tag{70}$$

$$\omega_ex_e=\left[8\Delta+12-\frac{8}{\Delta^{\frac{1}{2}}}+\frac{12}{\Delta}\right]\frac{W}{r_e^2\mu_A}. \tag{71}$$

Obviously α_e values by this function would be higher than those by Morse and because

$$\frac{12}{\Delta^{\frac{1}{2}}}\left[\Delta^{\frac{1}{2}}+\frac{1}{\Delta^{\frac{1}{2}}}\right]>\frac{8}{\Delta^{\frac{1}{2}}}.$$

TABLE V. Third function.

Δ	F	G
1	1.0	24
2	0.828	23.04
3	0.887	29.46
4	1.0	36.75
6	1.266	51.46
8	1.535	65.94
10	1.796	79.74
14	2.276	108.4
18	2.714	138.0
22	3.116	165.4
24	3.307	179.6
26	3.693	193.9

ω_ex_e values calculated by this function will also be higher than those by Morse.

THIRD

As the first function gave too low values, and second function high, hence a mixture was attempted

$$U=D_e\left\{1-\frac{r_e}{r}\exp[-\beta(r^2-r_e^2)]\right\}^2. \tag{72}$$

This also obeys the three criteria.

$$\beta=\frac{1}{2r_e^2}[\Delta^{\frac{1}{2}}-1]$$

$$\alpha_e=[\Delta^{\frac{1}{2}}+2/\Delta^{\frac{1}{2}}-2]\frac{6B_e^2}{\omega_e} \tag{73}$$

$$\omega_ex_e=[8\Delta-12\Delta^{\frac{1}{2}}+66-111/\Delta^{\frac{1}{2}}+73/\Delta]\frac{W}{r_e^2\mu_A}. \tag{74}$$

Table V depicts the variation of F and G with Δ.

FOURTH

$$U=B(A+e^{b/r})^2 \tag{75}$$

fulfills the three criteria.

Conditions (8 a, b, c) furnish

$$A=e^{b/r_e}$$

$$D_e=B(e^{b/r_e}-1)^2$$

$$b=r_e\ln A$$

$$\Delta=\left[\frac{\ln A}{1-1/A}\right]^2.$$

We get

$$\alpha_e=(\ln A+1)\frac{6B_e^2}{\omega_e} \tag{76}$$

$$\omega_ex_e=[8(\ln A)^2+24\ln A+64]\frac{W}{r_e^2\mu_A}. \tag{77}$$

As Δ is ~5 or higher, $(\ln A)^2\approx\Delta$. To this approxi-

TABLE VI. Sixth function.

Δ	F	G
1	−1	16
2	−0.293	15.66
3	+0.1546	20.62
4	0.5	27.00
6	1.041	41.27
8	1.474	56.33
10	1.846	71.77
14	2.475	103.0
18	3.007	134.5
22	3.477	166.3
24	3.695	182.1
26	3.903	198.0

mation

$$\alpha_e \approx [\Delta^{\frac{1}{2}}+1]\frac{6B_e^2}{\omega_e}$$

$$\omega_e x_e \approx [8\Delta+24\Delta^{\frac{1}{2}}+64]\frac{W}{r_e^2\mu_A}.$$

FIFTH

$$U = D_e\left[1-\left(\frac{r_e}{r}\right)^n\right]^2. \tag{78}$$

This is a generalization of Kratzer function and a special case of the Mecke-Sutherland function.

$$n^2 = \Delta$$

$$\alpha_e = \Delta^{\frac{1}{2}}\frac{6B_e^2}{\omega_e} \tag{79}$$

$$\omega_e x_e = [8\Delta+12\Delta^{\frac{1}{2}}+4]\frac{W}{r_e^2\mu_A}. \tag{80}$$

SIXTH

$$U = D_e\left[1-\frac{r}{r_e}e^{-a(r-re)}\right]^2[1+Kf(r)] \tag{81}$$

where $f(r)$ is a function such that at $r=0$, $f(r)=\infty$ and at $r=\infty$, $f(r)=0$. This general function satisfies the three criteria. Neglecting the $f(r)$ term, we get

$$U = D_e\left[1-\frac{r}{r_e}e^{-a(r-r_e)}\right]^2. \tag{82}$$

This gives $U=D_e$ at $r=0$.

We have

$$ar_e = \Delta^{\frac{1}{2}}+1$$

$$\alpha_e = [\Delta^{\frac{1}{2}}-1/\Delta^{\frac{1}{2}}-1]\frac{6B_e^2}{\omega_e} \tag{83}$$

$$\omega_e x_e = [8\Delta-12+8/\Delta^{\frac{1}{2}}+12/\Delta]\frac{W}{r_e^2\mu_A}. \tag{84}$$

Notice the similarity in coefficients of the terms in bracket in $\omega_e x_e$ with similar terms of the second function.

F and G values are recorded in Table VI.

SEVENTH

$$U = -Ar^n e^{-ar}[1-Kf(r)] \tag{85a}$$

where, as before, $f(r)$ is a function such that at $r=0$, $f(r)=\infty$ and at $r=\infty$, $f(r)=0$. This function is very similar to the Lippincott function.

As before, neglecting the $f(r)$ term

$$U = -Ar^n e^{-ar}. \tag{85b}$$

The general function (85a) satisfies the three criteria. However, the simplified version (85b) gives $U=0$ at $r=0$.

The values of the constants in (85b) can be obtained from conditions (8 a, b, c):

$$a = n/r_e$$

$$A = D_e/r_e^n e^{-n}$$

$$n = 2\Delta.$$

α_e and $\omega_e x_e$ are given by

$$\alpha_e = -\tfrac{1}{3}\frac{6B_e^2}{\omega_e} \tag{86}$$

$$\omega_e x_e = [6\Delta+\tfrac{2}{3}]\frac{W}{r_e^2\mu_A}. \tag{87}$$

Here the F and G values are very similar to those of the Lippincott function; F comes out to be negative and G is only slightly less than Lippincott's value.

COMPARISON

For testing any potential function, we require accurate data for the various molecular constants. A search of the available experimental data reveals that there are only 23 neutral molecules for which reliable values are available. Even for these the situation is not quite satisfactory for all of them. Dissociation energies of N_2, CO, and NO are still an open question. Two values for N_2, three for CO, and two for NO have been widely discussed. Reference is made to recent reviews by Gaydon and Penney (G2), Long (L7, L8, L9), Pauling and Sheehan (P3), Glockler (G5), Valatin (V1), Gaydon (G1), and Douglas (D4). We have used all the values considered probable in our calculations. Recent experiments of Hendrie (H2) and Brook and Kaplan (B7) lend a strong support to the higher value (9.756 ev) for N_2.

Quantum-mechanical calculations by Kopineck (K2, K3) also support the high value of N_2. However, Wolfsberg (W1) considers that some of the approximations used by Kopineck are not justified and his calculations should not be used as an argument favoring the 9.8 ev value for $D_e(\mathrm{N}_2)$.

The dissociation energy for HF is also not certain. We have used the value given by Herzberg (H3). For Li_2 also there is slight uncertainty in the dissociation energy; again Herzberg's value has been followed.

The data for the 23 diatomic molecules for the ground states are given in Tables VII (a) and (b), collected from Herzberg (H3). For O_2, a more recent value of $D_0(=5.115 \text{ ev})$ recommended by Brix and Herzberg (B5, B6) has been used. D_e has been calculated from the usual relation

$$D_e = D_0 + \tfrac{1}{2}\omega_e.$$

and k_e from $k_e = 4\pi^2\mu c^2\omega_e^2 = 5.8883\times10^{-2}\mu_A\omega_e^2$ dyne/cm.

Dissociation energies favored by Gaydon are marked with an asterisk. Most of the D_e values are given to 4 significant figures and some even to 5. These values are not that accurate. Because the conversion factors led to these values, and to keep consistency with original values, sometimes extra figures were retained.

For SO it is not yet certain that it is the ground state.

Some authors (e.g., Hulburt and Hirschfelder H7) use the "corrected" dissociation energies of molecules at absolute zero by subtracting the rotational, vibrational, and translational heat contents. Others have applied corrections to get the value of r_e at absolute zero (e.g., Verwey and de Boer V5). Such corrections are difficult to determine and often uncertain, hence we have completely omitted them.

While for most of the diatoms under consideration, the experimental evidence suggests a conventional potential energy curve, perhaps such is not the case with ZnH, CdH, and HgH. Dissociation energies determined by Birge-Sponer linear extrapolation come too high than the actual values. Mulliken (M7, M8) suspects that there might be a maximum and a long distance minimum in the P.E. curves of these molecules due to the approach of two interacting states. Glockler and Sister Horst (G4) have constructed a P.E. curve for HgH taking into account the fact that at large r, the molecule can change from a structure bonded by exchange forces to a quasi-molecule held together by London dispersion forces which leads to a small maximum.

The experimental values of F and G are given by

$$F = -\left[\frac{X\cdot r_e}{3}+1\right] = \frac{\alpha_e\omega_e}{6B_e^2} \tag{88}$$

$$G = \left[\frac{5}{3}X^2 - Y\right] r_e^2$$

$$= \frac{\omega_e x_e r_e^2 \times 64\pi^2 c \times 1.6597\times10^{-24}\mu_A}{h}. \tag{89}$$

TABLE VII.

(a)

Molecule figures in	μ_A	ω_e cm^{-1}	α_e cm^{-1}	$\omega_e x_e$ cm^{-1}
H_2	0.5041	4395.2	2.993	117.99
ZnH	0.9928	1607.6	0.2500	55.14
CdH	0.9992	1430.7	0.218	46.3
HgH	1.0031	1387.1	0.312	83.01
CH	0.930	2861.6	0.534	64.3
OH	0.9484	3735.2	0.714	82.81
HF	0.9573	4138.5	0.7705	90.069
HCl	0.9799	2989.7	0.3019	52.05
HBr	0.9956	2649.7	0.226	45.21
HI	1.0002	2309.5	0.183	39.73
Li_2	3.509	351.43	0.00704	2.592
Na_2	11.498	159.23	0.00079	0.726
K_2	19.488	92.64	0.000219	0.354
N_2 (i)	7.0038	2359.6	0.0187	14.456
N_2 (ii)*	7.0038	2359.6	0.0187	14.456
P_2	15.492	780.43	0.00142	2.804
O_2	8.000	1580.4	0.01579	12.073
SO	10.665	1123.7	0.00562	6.116
Cl_2	17.489	564.9	0.0017	4.0
Br_2	39.958	323.2	0.000275	1.145
I_2	63.466	214.6	0.000117	0.6127
ICl	27.422	384.18	0.000536	1.465
CO (i)	6.8584	2170.2	0.01748	13.46
CO (ii)	6.8584	2170.2	0.01748	13.46
CO (iii)*	6.8584	2170.2	0.01748	13.46
NO (i)	7.4688	1904	0.0178	13.97
NO (ii)*	7.4688	1904	0.0178	13.97

(b)

Molecule figures in	k_e 10^5 dynes/cm	r_e 10^{-8} cm	B_e cm^{-1}	D_e 10^{-12} erg
H_2	5.734	0.7417	60.809	7.607
ZnH	1.511	1.594	6.6794	1.523
CdH	1.204	1.762	5.437	1.228
HgH	1.137	1.740	5.549	0.740
CH	4.482	1.12	14.457	5.843
OH	7.792	0.971	18.871	7.340
HF	9.655	0.9171	20.939	10.65
HCl	5.157	1.275	10.591	7.394
HBr	4.117	1.414	8.473	6.277
HI	3.142	1.604	6.551	5.125
Li_2	0.2552	2.672	0.6727	1.685
Na_2	0.1717	3.078	0.1547	1.185
K_2	0.0985	3.923	0.0562	0.8322
N_2 (i)	22.96	1.094	2.010	12.046
N_2 (ii)*	22.96	1.094	2.010	15.863
P_2	5.556	1.894	0.3033	8.137
O_2	11.76	1.207	1.4457	8.351
SO	7.93	1.493	0.7089	6.522
Cl_2	3.279	1.988	0.2438	4.021
Br_2	2.457	2.284	0.08091	3.190
I_2	1.721	2.667	0.03736	2.489
ICl	2.296	2.321	0.11416	3.486
CO (i)	19.02	1.128	1.9314	14.865
CO (ii)	19.02	1.128	1.9314	15.602
CO (iii)*	19.02	1.128	1.9314	18.01
NO (i)	15.944	1.151	1.7046	8.673
NO (ii)*	15.944	1.151	1.7046	10.57

We have seen that F and G depend on the parameter Δ [defined in (11)]. It is these F and G values which differ for different functions. F determines α_e and G determines $\omega_e x_e$. The experimental values of Δ, F, and G have been tabulated in Table VIII. Figures 4 and 6 show respectively the actual values of F and G against Δ.

F and G values as given by various functions have been compared in Tables IX and X. Their variation

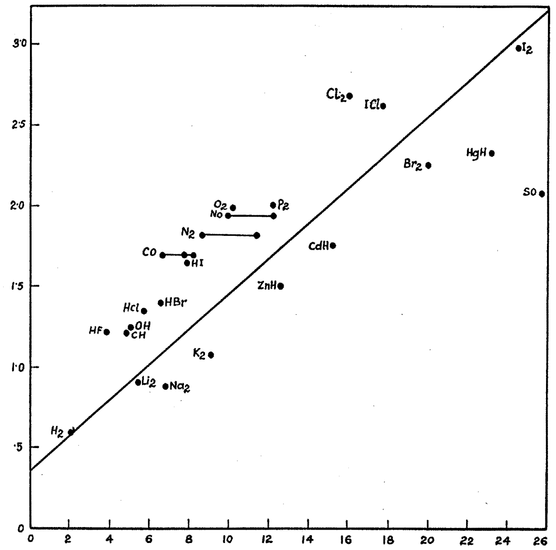

FIG. 4. Experimental values of the function F plotted against Sutherland parameter Δ.

with Δ for a few of the important functions have been shown graphically in Figs. 5 and 7, respectively. (To avoid confusion, the curves were not drawn in Figs. 4 and 6.)

Table VII (a) gives the experimental values of α_e and $\omega_e x_e$. Numerical calculations of α_e and $\omega_e x_e$ for a few of the functions along with percentage errors have been reported in Tables XI (a), (b) and XII (a), (b), (c), respectively. For calculating average percentage errors, only those values of N_2, CO, and NO which are favored by Gaydon (marked with an asterisk) have been taken into account.

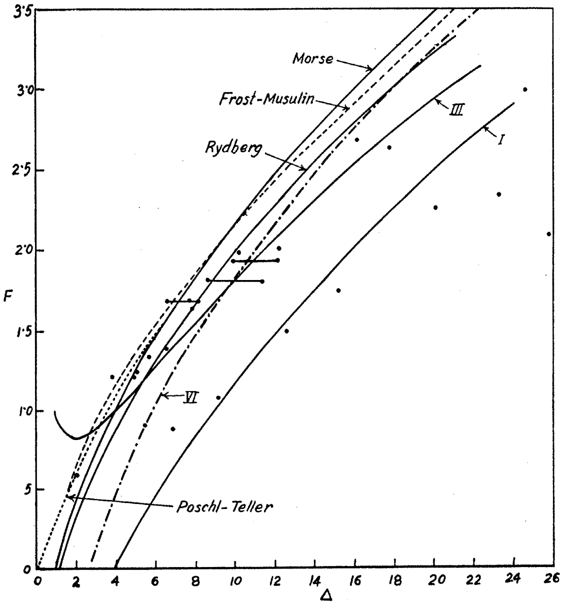

FIG. 5. Behavior of function F according to various potential energy functions. Experimental points are shown as dots.

DISCUSSION

A few important facts emerge clearly from Figs. 4 and 6. In case of both F and G, points are scattered. For F, they are rather too widely scattered. Had it been possible to represent all molecules by a "universal" P.E. curve, we should have obtained smooth curves passing through all the points. Thus the possibility that a "universal" P.E. curve exists can be ruled out. This agrees with what one expects theoretically. The shape of a P.E. curve depends on the electron configuration as well as on the position of neighboring electronic states and it is quite clear that any general relation cannot have exact validity. Of course, this is only relevant when we utilize only a limited number of molecular constants for fitting the P.E. curve, and try to find other constants from them. If the P.E. curve is made sufficiently flexible by including all the available molecular constants, no such question arises.

TABLE VIII.

Diatom	Δ	F	G
H_2	2.073	0.5928	15.52
ZnH	12.62	1.500	66.01
CdH	15.23	1.758	68.14
HgH	23.25	2.343	119.6
CH	4.814	1.218	35.58
OH	5.003	1.248	35.14
HF	3.813	1.213	34.40
HCl	5.669	1.342	39.33
HBr	6.554	1.390	42.69
HI	7.881	1.642	48.51
Li_2	5.408	0.9065	30.80
Na_2	6.864	0.8758	37.53
K_2	9.107	1.070	50.37
N_2 (i)	11.40	1.820	57.49
N_2 (ii)*	8.662	1.820	57.49
P_2	12.25	2.008	73.94
O_2	10.26	1.990	66.74
SO	25.81	2.093	131.5
Cl_2	16.12	2.693	131.2
Br_2	20.09	2.262	113.3
I_2	24.58	2.997	131.2
ICl	17.74	2.633	98.06
CO (i)	8.139	1.694	55.73
CO (ii)	7.752	1.694	55.73
CO (iii)*	6.719	1.694	55.73
NO (i)	12.18	1.944	65.58
NO (ii)*	9.995	1.944	65.58

It may be thought that in view of the different nature of binding, HgH, CdH, and ZnH should be treated on somewhat different footing from other molecules for P.E. curve considerations. However, the position of these points in Figs. 4 and 6 does not seem to justify such an exclusion.

Nevertheless, Figs. 4 and 6 show that broadly speaking, F and G both increase with increasing Δ. This shows that it is possible to have "universal" potential curves broadly describing such a behavior, though not

TABLE IX.

	F values
Morse	$\Delta^{\frac{1}{2}}-1$
Rydberg	$2\sqrt{2}\Delta^{\frac{1}{2}}/3-1$
Rosen-Morse	$2p\tanh p-1$
Pöschl-Teller	$\Delta^{\frac{1}{2}}\coth\Delta^{\frac{1}{2}}-1$
Linnett	$(24-t^2)/(4-t)$
Lippincott	$-\frac{1}{2}$
Frost-Musulin	$(2s^2+3s)/3(s+2)$
I	$\Delta^{\frac{1}{2}}-2$
II	$\Delta^{\frac{1}{2}}+1/\Delta^{\frac{1}{2}}-1$
III	$\Delta^{\frac{1}{2}}+2/\Delta^{\frac{1}{2}}-2$
IV	$\Delta^{\frac{1}{2}}+1$
V	$\Delta^{\frac{1}{2}}$
VI	$\Delta^{\frac{1}{2}}-1/\Delta^{\frac{1}{2}}-1$
VII	$-\frac{1}{3}$

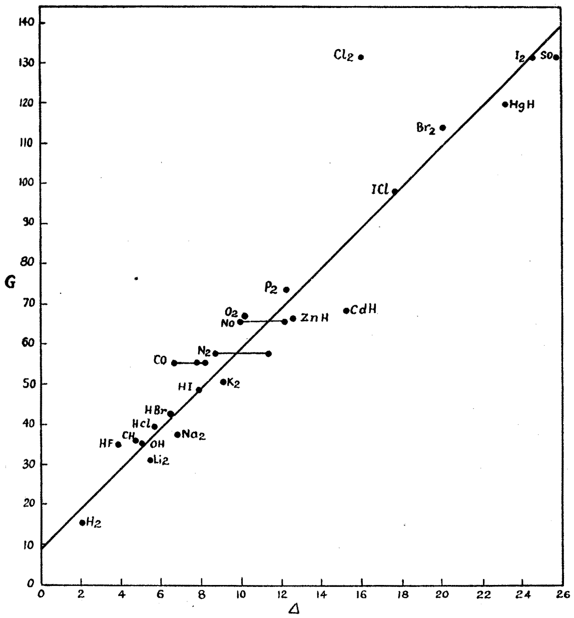

FIG. 6. Experimental values of the function G *versus* Sutherland parameter Δ.

very accurately. It is with this point of view that we will consider the various functions.

We can also represent the variation of F and G with Δ empirically. As a first approximation, straight lines have been drawn in both cases. In case of G, the points are not so widely distributed and excepting a few points, a straight line would be a good approximation. However, in case of F one is tempted to draw two straight lines—one for the low-lying points and another for higher points. Then the question arises that for an unknown molecule, which line will be taken for prediction. On the lower line we may count H_2, Li_2, Na_2, K_2, ZnH, CdH, Br_2, HgH, SO. There does not seem to be any characteristic feature regarding such molecules for distinguishing them from others. While several of them belong to $s-s$ type of binding, and three of them are perhaps van der Waals molecules, there are still Br_2 and SO. Hence only one straight line was drawn. The equations of the two lines are:

$$F=0.11\Delta+0.36 \tag{90}$$

$$G=5\Delta+9. \tag{91}$$

One more question arises: While it is not possible to have exact "universal" P.E. function for *all* molecules, is it possible to have such a function for molecules with similar linkage, i.e., those belonging to the same

TABLE X.

	G values
Morse	8Δ
Rydberg	$22\Delta/3$
Rosen-Morse	$8\Delta(1-e^{-2p}+e^{-4p})$
Pöschl-Teller	8Δ
Linnett	$\frac{5}{3}\left[\frac{20-t^2}{4-t}\right]^2-\left[\frac{120-t^3}{4-t}\right]$
Lippincott	$6\Delta+3$
Frost-Musulin	$(11s^4+66s^3+156s^2+144s+36)/3(s+2)^2$
I	$8\Delta-12\Delta^{\frac{1}{2}}+12$
II	$8\Delta+12-8/\Delta^{\frac{1}{2}}+12/\Delta$
III	$8\Delta-12\Delta^{\frac{1}{2}}+66-111/\Delta^{\frac{1}{2}}+73/\Delta$
IV	$8\Delta+24\Delta^{\frac{1}{2}}+64$
V	$8\Delta+12\Delta^{\frac{1}{2}}+4$
VI	$8\Delta-12+8/\Delta^{\frac{1}{2}}+12/\Delta$
VII	$6\Delta+\frac{2}{3}$

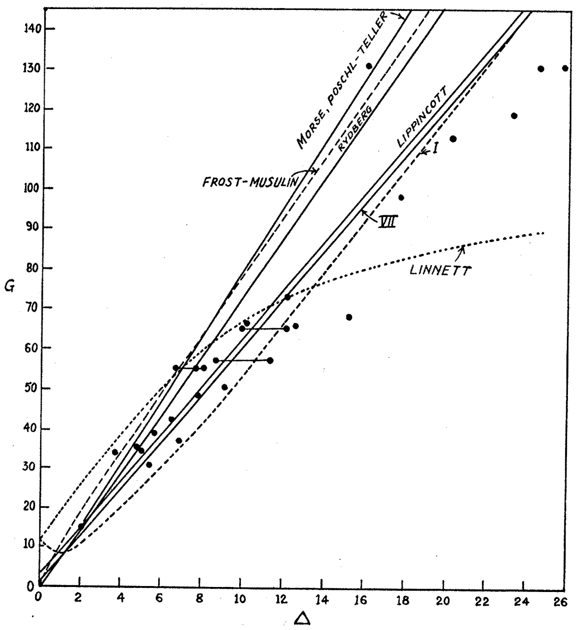

FIG. 7. Behavior of function G according to various potential energy functions. Experimental points are shown as dots.

Table XI.

(a)

	Morse		Rydberg	
Diatom	α_e calc	% error	α_e calc	% error
H_2	2.222	−25.8	1.853	−38.1
ZnH	0.4248	+69.9	0.3950	+58.0
CdH	0.3599	+65.1	0.3355	+54.0
HgH	0.5090	+63.1	0.4765	+52.7
CH	0.5238	−1.9	0.4744	−11.2
OH	0.7141	0	0.6425	−11.1
HF	0.5822	−24.4	0.5429	−29.5
HCl	0.3109	+3.3	0.2836	−6.0
HBr	0.2540	+7.9	0.2326	+3.0
HI	0.2015	+9.2	0.1857	+1.5
Li_2	0.0103	+46.3	0.00938	+30.0
Na_2	0.00146	+84.8	0.001342	+70.0
K_2	0.000412	+88.1	0.0003813	+74.1
N_2 (i)	0.02864	(+53.2)	0.02266	(+21.2)
N_2 (ii)*	0.01996	+6.2	0.01844	+1.4
P_2	0.00177	+24.7	0.001644	+15.8
O_2	0.00175	+10.8	0.01619	+2.5
SO	0.01095	+94.8	0.01026	+82.5
Cl_2	0.00190	+11.8	0.001775	+4.4
Br_2	0.000423	+53.8	0.0003957	+43.8
I_2	0.000154	+31.6	0.0001446	+23.6
ICl	0.000654	+22.0	0.000689	+13.6
CO (i)	0.01912	(+9.4)	0.01762	(+0.9)
CO (ii)	0.01844	(+5.5)	0.01694	(−3.0)
CO (iii)*	0.01643	−6.0	0.01506	−13.8
NO (i)	0.0228	(+28.1)	0.02117	(+18.1)
NO (ii)*	0.0198	+11.2	0.01832	+3.0
Average		±33.1		±28.0

(b)

	Third		Empirical	
Diatom	α_e calc	% error	α_e calc	% error
H_2	4.186	+39.8	2.969	−0.9
ZnH	0.3523	+40.9	0.291	+16.4
CdH	0.2996	+37.4	0.2524	+15.8
HgH	0.4311	+38.5	0.3886	+24.6
CH	0.4837	−9.4	0.3898	−27.0
OH	0.6319	−11.5	0.5207	−24.1
HF	0.6210	−19.4	0.4953	−35.7
HCl	0.2749	−8.9	0.2215	−26.6
HBr	0.2181	−3.5	0.1758	−22.2
HI	0.1694	−7.4	0.1369	−25.2
Li_2	0.009204	+30.7	0.007415	+4.1
Na_2	0.001247	+57.8	0.001006	+27.3
K_2	0.0003439	+57.0	0.0002786	+27.2
N_2 (i)	0.02023	(+8.2)	0.01659	(−11.3)
N_2 (ii)*	0.01665	−10.9	0.01349	−27.3
P_2	0.001464	+3.1	0.001207	−15.0
O_2	0.01450	−8.2	0.01181	−25.2
SO	0.009324	+65.8	0.008586	+52.8
Cl_2	0.001588	−6.6	0.001283	−24.5
Br_2	0.0003558	+29.1	0.0003127	+13.0
I_2	0.0001311	+12.0	0.0001196	+2.2
ICl	0.0005468	+2.1	0.0004706	−12.2
CO (i)	0.01603	(−8.3)	0.01293	(−26.0)
CO (ii)	0.01550	(−11.3)	0.01251	(−28.4)
CO (iii)*	0.01405	−19.6	0.01133	−35.2
NO (i)	0.01888	(+6.1)	0.01556	(−12.6)
NO (ii)*	0.01643	−7.7	0.01336	−24.9
Average		±22.9		±22.1

molecular group (Varshni and Majumdar V4)? Very few points are available to throw light on this question.

In case of G (Fig. 6), HF, HCl, HBr, and HI seem to be on a regular curve. The case with Li_2, Na_2, and K_2 is similar. Neglecting Cl_2, we can consider ICl, Br_2, and I_2 to be in a straight line. ZnH, CdH, and HgH are erratic which is not surprising in view of the irregular behavior of their molecular constants.

However, for F the situation is worse. Only for HF, HCl, HBr, and HI a regular curve can be drawn quite close to these points. Others do not show any regular behavior. In short, we can say that there is not sufficient evidence to give any definite conclusion on this point.

Now we consider the relative merits of each function.

Morse Function

This simple function though very widely used, to quote Partington (P1), "has been overworked in many branches of investigation," gives rather a poor performance.

α_e: (see Fig. 5, Table XI a): Excepting H_2, HF, and one point of CO, all other experimental points lie below the curve. Corresponding results are obtained in the numerical calculations which show the high average percentage error of 33.1.

$\omega_e x_e$: (see Fig. 7, Table XII a): The case here is similar. Only Cl_2, one point of CO, and HF lie above the Morse line. As expected, the average percentage error is high, being 31.2.

In a way, the Morse function sets an upper limit to F and G values. A satisfactory P.E. function should give F and G values which are lower than Morse's. As mentioned earlier, previous workers also found unsatisfactory results with this function. On the whole, this function is not suitable for using with a randomly chosen molecule.

Rydberg Function

From a comparison of F and G values of Morse and Rydberg functions, the latter gives lower values so the trend is in the right direction.

α_e: (see Fig. 5, Table XI a): There is a significant improvement from the Morse function, though even now only about 8 points lie above the curve. The average percentage error has slightly decreased to 28.

$\omega_e x_e$: (see Fig. 7, Table XII a): Though better than Morse, still only about 5 points are above the Rydberg line. The average percentage error has decreased to 23.1.

On the whole, this function is distinctly better than the Morse function.

Rosen-Morse Function

α_e: (see Table I): From the expression for F when p is small (i.e., Δ is small), this gives lower values than Morse function, as p increases (i.e., Δ increases), the Rosen-Morse F approaches the F of the Morse function.

$\omega_e x_e$: (see Table I): Behavior of G is very similar to that of F.

Thus, the Rosen-Morse function is somewhat better than Morse function, though more complicated.

TABLE XII.

(a)

Diatom	Morse, Poschl-Teller $\omega_e x_e$ calc	% error	Rydberg $\omega_e x_e$ calc	% error
H_2	126.3	+7.0	115.8	−1.9
ZnH	84.35	+52.9	77.32	+40.2
CdH	82.80	+78.8	75.90	+63.9
HgH	129.2	+55.6	118.4	+42.6
CH	69.58	+8.2	63.78	−5.5
OH	94.36	+13.9	86.5	+4.4
HF	79.86	−11.3	73.2	−18.7
HCl	60.00	+15.3	55.00	+5.6
HBr	55.53	+22.8	50.9	+12.6
HI	51.64	+30.0	47.34	+24.2
Li_2	3.639	+37.3	3.336	+24.8
Na_2	1.048	+44.3	0.9605	+32.3
K_2	0.512	+44.6	0.4692	+32.5
N_2 (i)	22.93	(+58.0)	21.02	(+45.4)
N_2 (ii)*	17.42	+20.5	15.97	+10.4
P_2	3.717	+32.5	3.408	+21.5
O_2	14.85	+23.0	13.61	+12.7
SO	9.615	+57.2	8.814	+44.1
Cl_2	3.932	−1.7	3.604	−9.9
Br_2	1.624	+41.8	1.489	+30.0
I_2	0.9183	+49.8	0.8418	+37.4
ICl	2.101	+43.4	1.926	+31.5
CO (i)	15.76	(+17.1)	14.45	(+7.4)
CO (ii)	14.98	(+11.3)	13.73	(+2.0)
CO (iii)*	12.99	−3.5	11.91	−11.5
NO (i)	20.75	(+48.5)	19.02	(+36.1)
NO (ii)*	17.04	+21.9	15.62	+11.9
Average		±31.2		±23.1

(b)

Diatom	Lippincott $\omega_e x_e$ calc	% error	First $\omega_e x_e$ calc	% error
H_2	117.6	−0.3	86.14	−27.0
ZnH	65.77	+19.3	58.76	+6.5
CdH	64.13	+38.5	59.12	+27.7
HgH	98.93	+19.2	97.27	+17.2
CH	57.59	−10.4	47.31	−26.4
OH	77.84	−6.0	59.37	−28.3
HF	67.76	−24.7	49.94	−44.5
HCl	48.97	−5.9	36.77	−29.3
HBr	44.81	−0.9	35.70	−21.0
HI	41.19	+3.7	33.88	−14.7
Li_2	2.983	+15.1	2.218	−14.4
Na_2	0.8547	+17.7	0.6863	−5.5
K_2	0.4051	+14.4	0.3418	−3.4
N_2 (i)	17.96	(+24.2)	15.77	(+9.1)
N_2 (ii)*	13.82	−4.4	11.56	−20.0
P_2	2.902	+3.4	2.578	−8.1
O_2	11.68	−3.3	10.24	−15.2
SO	7.352	+20.2	7.335	+1.9
Cl_2	3.041	−23.4	2.83	−29.3
Br_2	1.248	+9.0	1.202	+5.0
I_2	0.7028	+14.7	0.6965	+13.7
ICl	1.621	+10.6	1.531	+4.5
CO (i)	12.52	(−7.0)	10.43	(−22.5)
CO (ii)	11.96	(−11.1)	9.806	(−27.1)
CO (iii)*	10.45	−22.4	8.370	−37.8
NO (i)	16.21	(+16.0)	14.39	(+3.0)
NO (ii)*	13.42	−4.0	11.51	−17.6
Average		±12.7		±18.2

(c)

Diatom	Seventh $\omega_e x_e$ calc	% error	Empirical $\omega_e x_e$ calc	% error
H_2	99.06	−16.0	147.5	+25.8
ZnH	63.81	+15.7	60.23	+9.2
CdH	62.38	+35.4	57.86	+24.9
HgH	97.27	+17.2	86.96	+4.7
CH	53.38	−16.8	59.74	−7.1
OH	72.33	−12.6	80.19	−3.2
HF	61.65	−31.5	73.48	−18.4
HCl	45.88	−11.8	49.42	−5.1
HBr	42.36	−6.3	44.23	−2.2
HI	39.27	−1.2	39.64	−0.2
Li_2	2.786	+7.4	3.033	+17.0
Na_2	0.8091	+11.5	0.8362	+15.2
K_2	0.3887	+9.8	0.3832	+8.2
N_2 (i)	17.37	(+20.0)	16.60	(+14.8)
N_2 (ii)*	13.23	−8.5	13.15	−9.0
P_2	2.813	+0.3	2.664	−5.0
O_2	11.26	−6.7	10.90	−9.7
SO	7.243	+18.4	6.428	+5.1
Cl_2	2.970	−25.7	2.732	−31.7
Br_2	1.226	+7.1	1.107	−3.3
I_2	0.6763	+10.4	0.616	+0.5
ICl	1.586	+8.3	1.446	−1.3
CO (i)	11.96	(−11.1)	12.00	(−10.9)
CO (ii)	11.40	(−15.3)	11.53	(−14.3)
CO (iii)*	9.9	−26.5	8.172	−39.3
NO (i)	15.71	(+12.5)	14.89	(+6.6)
NO (ii)*	12.93	−7.5	12.56	−10.1
Average		±13.6		±11.1

Pöschl-Teller Function

α_e: (see Fig. 5): Since $\coth\Delta^{\frac{1}{2}}>1$, it will always give higher values than the Morse function. However, as Δ increases, this almost merges with the Morse value.

$\omega_e x_e$: (see Fig. 7, Table XII a): Same expression, as given by the Morse function.

Thus this function is slightly inferior to the Morse function, though the difference is not large. The fact that Davies (D3) found it slightly superior to the Morse function for HF, HCl, and HI, is because he compared $U'''(r_e)$ and $U^{\text{iv}}(r_e)$, rather than α_e and $\omega_e x_e$. $U'''(r_e)$ depends on α_e, while $U^{\text{iv}}(r_e)$ depends both on α_e and $\omega_e x_e$. As Tables VI and IX of Davies' paper show, he obtained $U'''(r_e)$ for the Pöschl-Teller higher than $U'''(r_e)$ for the Morse. This is in agreement with our Fig. 5. However, for $U^{\text{iv}}(r_e)$, the effect of α_e and $\omega_e x_e$ got mixed up. While the effect of $\omega_e x_e$ remained the same on both the functions, α_e effected an increase in $U^{\text{iv}}(r_e)$ for the Pöschl-Teller over the Morse. As Davies found $U^{\text{iv}}(r_e)$ for the Morse lower than experimental, he concluded that the Pöschl-Teller is slightly superior.

Actually only for HF, the Pöschl-Teller is superior to the Morse; for HCl and HI, it is inferior, as is evident from Fig. 5.

Linnett Function

α_e: (see Table II): F values given by this function are too high. Indeed the smallest value of $F=6$ (for $\Delta=0$) given by this function is almost twice the highest value of F found in the 23 molecules under consideration. Hence for α_e it is quite unsatisfactory.

$\omega_e x_e$: (see Fig. 7, Table II): The course of the G curve is very peculiar. For low Δ it is greater even than the Morse, for high Δ it is too low.

At least for $m=3$, this is not a very useful function.

Simple Lippincott Function

α_e: It gives a negative value which is meaningless.

$\omega_e x_e$: (see Fig. 7, Table XII b): From the expression for $\omega_e x_e$, for $\Delta > 2$ (which is usually the case) the values are much lower than from the Morse function (almost three-fourth of the Morse function). Table XII b shows that the average percentage error is much lower (± 12.7) as compared to the Morse (± 31.2) and the Rydberg (± 23.1) functions, indicating a significant improvement.

The simple function (60) does not satisfy the third criterion; to achieve this the $f(r)$ term has to be introduced. The $f(r)$ given by Lippincott and Schroeder makes the function a five constant function and thus rather complicated. Only by assuming that ab and b are constant can one predict α_e and $\omega_e x_e$. As we are confining ourselves to three-constant functions, calculations for α_e and $\omega_e x_e$ have not been carried out.

From the spread of points in Fig. 7, when two or more D_e have been suggested for a diatom, there is no reason to assume the value favored by this function as the "correct" one. Thus, Lippincott's statement that "where two or more alternative values have been proposed, this function should suggest which is the correct one" seems to be rather optimistic.

Frost-Musulin Function

α_e: (see Fig. 5, Table III): For low Δ it is slightly higher than Morse function, but for high Δ it is slightly lower than Morse function.

$\omega_e x_e$: (see Fig. 7, Table III): Behavior of G is very similar to that of F.

On the whole this function is very close to the Morse function, though slightly more complex.

First Function

α_e: (see Fig. 5, Table IV): This gives much lower values for F than the Morse function, which is also evident from Fig. 5.

$\omega_e x_e$: (see Fig. 7, Tables IV and XII b): Usually gives lower values. Average percentage error (18.2) is lesser than that for the Morse and Rydberg functions.

Second Function

As shown before, both for α_e and $\omega_e x_e$ it would give higher values than the Morse function and hence is unsuitable.

Third Function

α_e: (see Fig. 5, Tables V and XI b): The average percentage error (22.9) is significantly lower than that by Morse (33.1) and Rydberg (28.0) functions.

$\omega_e x_e$: (see Table V): At low Δ (but >2), it is midway between the Linnett and Frost-Musulin curves; as Δ increases it almost follows the Frost-Musulin curve (to avoid overlapping, the curve has not been drawn).

Fourth Function

This gives much higher values for F and G than the Morse function, and hence can be dismissed.

Fifth Function

This also gives higher values than the Morse for both F and G and hence is not applicable.

Sixth Function

α_e: (see Fig. 5, Table VI): Course of the F curve is encouraging. However, for $\Delta < 2.5$, it is negative.

$\omega_e x_e$: (see Table VI): Very close to the Rydberg function.

Seventh Function

α_e: It gives a negative value of F $(=-\frac{1}{3})$ which is absurd.

$\omega_e x_e$: (see Fig. 7, Table XII c): Slightly lower than, and parallel to the Lippincott function. Consequently, the average percentage error (13.6) is also very near to that of Lippincott (12.7).

The results given by this function have a striking resemblance to those of the Lippincott function.

Empirical Relations

α_e: (Fig. 4, Table XI b): As can be expected, the average percentage error is lowest, being 22.1. However, this is not far from the third function (22.9).

$\omega_e x_e$: (Fig. 6, Table XII c): Here also the average percentage error is lowest, being 11.1.

CONCLUSIONS

We may summarize as follows:

It is not possible to find three-constant "universal" potential energy functions, and consequently, there are no "universal" relations connecting α_e and $\omega_e x_e$ with Δ.

Several functions give relations which may be used for estimating α_e and $\omega_e x_e$. Further, $\omega_e x_e$ can be estimated to a greater degree of accuracy than α_e. A surprising fact emerges that a function which may be useful for calculating $\omega_e x_e$, may fail completely to reproduce α_e (e.g. Lippincott, Seventh).

On the basis of these 23 diatoms, for α_e, the functions in order of increasing accuracy are:

(i) Morse, Pöschl-Teller, Rosen-Morse, Frost-Musulin
(ii) Rydberg
(iii) Third, Sixth.

And for $\omega_e x_e$:
(i) Morse, Pöschl-Teller, Rosen-Morse, Frost-Musulin, Third, Sixth
(ii) Rydberg
(iii) Lippincott, Seventh.

Thus for over-all representation of the P.E. curves, the Rydberg, Third, and Sixth functions are the most useful.

Such diverse looking functions as those of Morse, Pöschl-Teller, Rosen-Morse, and Frost-Musulin are actually extremely close to each other.

The best values of α_e and $\omega_e x_e$ are obtained from

$$\alpha_e = (0.11\Delta + 0.36) 6 B_e^2 / \omega_e \tag{92}$$

$$\omega_e x_e = (5\Delta + 9) W / r_e^2 \mu_A . \tag{93}$$

Equation (93) can be transformed as

$$D_e = \frac{5 W k_e r_e^2}{2 \omega_e x_e r_e^2 \mu_A - 9W} . \tag{94}$$

For estimating dissociation energies, (94) deserves to be employed in preference to $D_e = \omega_e^2 / 4\omega_e x_e$. However, this cannot serve as a strong argument for favoring any of the values when several appear to be possible (e.g. NO, CO, N_2, etc.).

In Table VIII the Sutherland parameter Δ varies regularly in a molecular group (V4) and increases with increasing μ_A.

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