Potential Energy Functions for Diatomic Molecules*

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The usual Morse functions are determined from the energy of dissociation, the equilibrium separation of the nuclei, and the fundamental vibration frequency. Two additional spectroscopic constants, $\omega_e x_e$ and α_e, are available for most of the common diatomic molecules and permit us to add a two-parameter correction term to the Morse curve. Both the potential $V/D = (1 - e^{-x})^2 + cx^3(1 + bx)e^{-2x}$ and the extended Morse curve of the Coolidge, James and Vernon type, $V/D = C_2(1 - e^{-x})^2 + C_3(1 - e^{-x})^3 + C_4(1 - e^{-x})^4$ agree with accurate potentials in those cases where they are known. Here $x = 2\beta(r - r_e)/r_e$. The constants for the first of these potentials are easy to evaluate and are given for 25 common diatomic molecules. With only a few exceptions, the improved potentials lie above the Morse curves and the corrections for moderately large internuclear separations may amount to ten percent of the energy of dissociation. Our treatment is based on the work of Dunham and the analysis of Coolidge, James and Vernon.

IN this paper the five spectroscopic constants which are available for most of the common diatomic molecules are used to improve the usual three-parameter Morse curves.[1] The two parameters in our correction term are easy to determine. In those cases where accurate potentials are known, our functions are satisfactory. With only a few exceptions, the improved potentials lie above the Morse curves and the corrections for moderately large internuclear separations may amount to ten percent of the energy of dissociation. The corrections are so large for some of the molecules that we are led to speculate on the existence of a hump or maximum in the potential energy. The higher vibrational energy levels are not known for most molecules, so that it is not possible to determine the potential uniquely for large internuclear separations from the existing experimental data. For these distances, it may be feasible to compute the potentials from the first- and second-order quantum-mechanical perturbation schemes. Our treatment is based on the work of Dunham[2] and the analysis of Coolidge, James and Vernon.[3]

The vibrational and rotational energy levels of a diatomic molecule are usually expressed in the form of a double infinite series

$$E_{v,K} = \sum_{i,j} Y_{ij}(v + \tfrac{1}{2})^i K^j (K+1)^j, \qquad (1)$$

where v is the vibrational and K is the rotational quantum number. The Y_{ij} are the usual spectroscopic constants and are better known in the nomenclature:

$$
\begin{aligned}
&Y_{00} = D, \quad Y_{10} = \omega_e, \quad Y_{20} = -\omega_e x_e, \\
&\qquad\qquad Y_{30} = \omega_e y_e, \quad Y_{40} = -\omega_e z_e, \\
&Y_{01} = B_e, \quad Y_{11} = -\alpha_e \cdots, \\
&Y_{02} = -D_e, \quad Y_{12} = -\beta_e \cdots.
\end{aligned}
\qquad (2)
$$

Our problem is to determine the potential energy, $V(r)$, as a function of the internuclear separation r from a knowledge of these experimental constants. To do this we must assume a mathematical form for $V(r)$ which contains a number of parameters. These parameters are then adjusted to give the best fit to the observed spectroscopic constants.

The Morse curve has been used quite generally because of the simplicity of its form and the convenience of obtaining the energy levels in closed form. It may be written:

$$V_M = D[1 - \exp(-x)]^2, \qquad (3)$$

where

$$x = 2\beta\xi; \quad \xi = (r - r_e)/r_e;$$

β is a parameter for the Morse curve which has

[1] P. M. Morse, Phys. Rev. **34**, 57 (1929).
[2] J. L. Dunham, Phys. Rev. **41**, 713, 721 (1932).
[3] A. S. Coolidge, H. M. James and E. L. Vernon, Phys. Rev. **54**, 726 (1938).

the value

$$\beta = \omega_e / 4 (B_e D)^{\frac{1}{2}}$$

and r_e is the equilibrium separation. When the rotational quantum number is zero, the Schrödinger equation for this potential can be integrated exactly to give

$$\omega_e x_e = \omega_e^2 / 4D, \quad \omega_e y_e = \omega_e z_e = \cdots = 0. \quad (4)$$

Pekeris[4] has calculated the rotational energy by a perturbation method. He found that to a good approximation:

$$\alpha_e = 6 B_e x_e \left[\left(\frac{B_e}{x_e \omega_e} \right)^{\frac{1}{2}} - \frac{B_e}{x_e \omega_e} \right], \quad D_e = \frac{4 B_e^3}{\omega_e^2}. \quad (5)$$

Often spectroscopists assume *a priori* that $D_e = 4 B_e^3 / \omega_e^2$ and fit their curves accordingly. Actually this form for D_e should only be true if the coupling between the rotation of the molecule and the spins and motions of the electrons is negligible. Deviations from this relation should be of interest but most of the published spectroscopic constants are computed in such a manner as not to show them. When the special relations of Eqs. (4) and (5) are not satisfied, it is obvious the Morse curve must be corrected.

I. DUNHAM'S METHOD

The potential energy of a diatomic molecule may be expressed in the form:

$$V = a_0 \xi^2 [1 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 + \cdots] hc, \quad (6)$$

where $\xi = (r - r_e)/r_e$, h is Planck's constant and c is the velocity of light. This expansion converges rapidly for small values of ξ and is therefore useful in calculating the energy of the lowest vibrational states. This potential should be used in the Schrödinger equation to determine the vibrational and rotational energy levels in terms of the constants a_n. But the difficulties inherent in the integration of the Schrödinger equation for general values of the a_n made it necessary for Dunham[2] to use the WBK method. To this approximation he found that:

$$a_0 = \omega_e^2 / 4 B_e, \quad (7)$$

$$a_1 = -1 - \alpha_e \omega_e / 6 B_e^2, \quad (8)$$

[4] C. L. Pekeris, Phys. Rev. **45**, 98 (1934).

$$a_2 = \frac{5}{4} a_1^2 - \frac{2}{3} \frac{x_e \omega_e}{B_e}, \quad (9)$$

$$a_3 = \frac{\gamma_e \omega_e^2}{30 B_e^3} - 2 a_1 + \frac{3}{5} a_2 + \frac{13}{5} a_1 a_2$$
$$- \frac{3}{2} (a_1^2 + a_1^3) - 1, \quad (10)$$

$$a_4 = \frac{(y_e \omega_e) \omega_e}{5 B_e^2} + \frac{7}{2} a_1 a_3 + \frac{17}{20} a_2^2$$
$$- \frac{45}{8} a_1^2 a_2 + \frac{141}{64} a_1^4. \quad (11)$$

Two other equations show that $\omega_e c$ is the classical fundamental frequency for the potential $V = a_0 h c \xi^2$ and that $B_e = h / (8 \pi^2 \mu r_e^2 c)$ where μ is the reduced mass of the molecule. One curious feature of these equations is that the coupling between the vibrational and rotational states manifests itself in a_1; while the first anharmonic correction in the vibrational energy levels, $\omega_e x_e$, does not appear until a_2. This has some interesting consequences in the selection of an appropriate potential function, as we shall show later. Dunham[2] subsequently improved upon the WBK approximation by adding corrections good to the third power of h. However, the numerical values of the correction terms are so small that we may neglect them in this treatment. For example, in the case of the ground state of hydrogen where the correction has its maximum effect, we find that ω_e should differ from its classical value by only one part in 6000 and B_e differs by one part in 12,000 from the above definition.

To test further the accuracy of WBK approximation, one may expand the Morse function to obtain the a_n's; then, substitute these a_n's into Dunham's expressions for the spectroscopic constants. The vibrational constants ω_e, $\omega_e x_e$, $\omega_e y_e$, and $\omega_e z_e$ obtained in this manner agree exactly with the expressions of Eq. (4) obtained by actual integration of the Schrödinger equation. While α_e calculated in this manner, agrees with the correct expression (5), the other rotational constants show some disagreement. This may be caused either by the approximations in the usual integration of the Schrödinger

equation as discussed by Pekeris[4] or it may be caused in part by the WBK approximation. In any case we conclude that the WBK method is satisfactory for use in the determination of accurate potential energy functions. Experimental errors in the constants are larger in most cases than any errors which could be introduced by the use of this method.

II. THE FIVE-CONSTANT POTENTIAL FUNCTIONS

Any acceptable form for a potential energy function should have a large value (if not infinite) as the nuclei come together; it should pass through a minimum at the equilibrium separation; and it should approach the energy of dissociation as the nuclei become far apart. At large separations, the slope of the function should be in agreement with the van der Waals forces but this is a refinement which has not received attention up to this time. There are an infinite number of functions which have a shape suitable for potential functions. Of these, the Morse function is the simplest and most generally useful. The three-parameter Manning and Rosen[5] function,

$$V = -\frac{A \exp(-cr) + B \exp(-2cr)}{[1 - \exp(-cr)]^2} \quad (12)$$

has all of the general attributes of a good potential function and even gives the vibrational energy levels in closed form. But this function has never been generally adopted because most people prefer to use functions with greater flexibility, i.e., more parameters. The Pöschl-Teller[6] function has the same vibrational levels as the Morse function but a fourth parameter makes it possible to give a better adjustment to the rotational levels. It has the form:

$$V = D\left[\frac{\sinh^4 a}{\sinh^2(a+\beta\xi)} - \frac{\cosh^4 a}{\cosh^2(a+\beta\xi)}\right]. \quad (13)$$

The potential curve of Hylleraas[7] gives excellent agreement with the experimental energy levels but it has two disadvantages. It has six parameters, which is one more than we usually have

[5] M. F. Manning and N. Rosen, Phys. Rev. **44**, 953 (1933).
[6] G. Pöschl and E. Teller, Zeits. f. Physik **83**, 143 (1933).
[7] E. A. Hylleraas, Zeits. f. Physik **96**, 661 (1935).

experimental data to fit, and it is difficult to determine the constants. The Hylleraas potential has the form:

$$V = D\left[1 - \frac{[1+a][1+b][\exp(2\beta'\xi)+c]}{[\exp(2\beta'\xi)+a][\exp(2\beta'\xi)+b][1+c]}\right]^2,$$

where a, b, c, β', D and of course, the r_e in ξ are the adjustable constants. The extended Morse curve of Coolidge, James and Vernon[3] appears more useful. It has the form:

$$\frac{V}{D} = \sum_{n=2, 3, \cdots} C_n[1 - e^{-2\beta'\xi}]^n. \quad (14)$$

In actual computations, Coolidge, James and Vernon have taken 7 terms in this series. This form of potential is flexible but it has one disadvantage, β' is difficult to determine and in fact loses its significance as we take more terms in the extended Morse curve. The three-term extended Morse function which uses five parameters is quite comparable in accuracy with the other five-parameter functions which we consider. The greater difficulty in evaluating these parameters makes it slightly less desirable.

For most diatomic molecules the four spectroscopic constants ω_e, $\omega_e x_e$, B_e, and α_e are known and listed in convenient tables. In addition the heats of dissociation are known from thermochemical or spectroscopic data. Therefore, we sought a potential function with five parameters which could be determined easily from the spectroscopic constants. Three of these constants could be used to determine the usual Morse function leaving two parameters to describe the corrections to the Morse curve. We find the following function satisfactory:

$$V = D[(1 - e^{-x})^2 + cx^3 e^{-2x}(1 + bx)]. \quad (15)$$

Here

$$x = 2\beta\xi = \frac{\omega_e}{2(B_e D)^{\frac{1}{2}}}\left[\frac{r - r_e}{r_e}\right]$$

as in Eq. (3). The constants b and c are determined by the relation:

$$c = 1 + a_1(D/a_0)^{\frac{1}{2}}, \quad (16)$$

$$b = 2 + \left[\frac{7}{12} - \frac{Da_2}{a_0}\right]\Big/ c, \quad (17)$$

TABLE I.

	ω_e (CM^{-1})	$x_e\omega_e$ (CM^{-1})	B_e (CM^{-1})	α_e (CM^{-1})	r_e (A)	ENERGY OF DISSOC. (KCAL.)	D (CM^{-1})	a_0 (CM^{-1})	$-a_1$	a_2	2β	c	b
Hydrogen													
H$_2$	4405.3	125.325	60.872	3.0671	0.7414	103.23	38,292	79,703	1.60774	1.85848	1.4426	−0.1145	−0.704
HD	3817.1	94.958	45.668	1.9931	0.7413	104.06	38,292	79,762	−1.60798	1.84578	1.4433	−0.1141	−0.654
D$_2$	3118.8	64.15	30.429	1.0492	0.7417	105.03	38,292	79,915	1.58901	1.75071	1.4446	−0.1000	−0.556
H$_2$($^2\Sigma_g{}^+$)	2665.9252	72.79390	34.22051	1.694884	0.9888	66.09	24,460	51,913	1.64090	1.95250	1.45672	−0.059533	−0.6543
Metal hydrides													
ZnH	1607.6	55.135	6.6794	0.2500	1.5947	19.6	7660	96,729	2.50138	2.31816	3.5536	0.2961	0.6501
CdH	1430.7	46.3	5.437	0.218	1.762	15.63	6184	94,119	2.75847	3.83430	3.901	0.2929	0.869
HgH	1432.7	108.8	5.58	0.373	1.741	8.58	3695	91,964	3.86052	5.63068	4.844	0.3099	0.671
Hydrogen halides													
HF	4141.305	90.866	20.967	0.879	0.9166	147.9	53,826	204,493	2.38007	4.19177	1.949	−0.2212	−0.351
HCl	2988.95	51.65	10.5909	0.3019	1.2747	102.16	37,244	210,884	2.34080	3.59797	2.379	0.0161	5.236
HBr	2649.67	45.21	8.471	0.226	1.414	86.73	31,674	207,200	2.39085	3.58717	2.558	0.0653	1.466
HI	2309.53	39.73	6.551	0.183	1.604	70.38	24,628	203,554	2.64138	4.67794	2.8098	0.0599	2.153
Halogens													
Cl$_2$	564.9	4.0	0.2438	0.0017	1.989	57.2	20,298	327,227	3.69278	6.10788	4.015	0.0803	−0.545
ICl	384.18	1.465	0.11414	0.000502	2.321	49.64	17,563	323,274	3.46724	6.47045	4.291	0.1920	0.793
Br$_2$	323.2	1.07	0.08091	0.00027	2.284	45.44	16,063	322,760	3.22156	4.15668	4.482	0.2812	0.661
I$_2$	214.36	0.593	0.03736	0.00012	2.667	35.56	12,550	307,483	4.07157	10.14034	4.950	0.1775	1.046
Oxides													
O$_2$	1580.36	12.073	1.4456	0.0158	1.2076	117.2	41,802	431,921	2.99143	5.61814	3.2145	0.0694	1.429
CO	2168.2	13.04	1.9310	0.01744	1.1284	210.8	74,840	608,634	2.69017	4.54428	2.8518	0.0567	1.568
NO	1906.52	14.504	1.709	0.0183	1.150	122.0	43,644	531,717	2.99094	5.52423	3.490	0.1430	1.092
SO	1123.73	6.116	0.70894	0.00562	1.4935	92.27	32,842	445,302	3.09425	6.21665	3.6823	0.1597	1.219
OH	3727.95	78.15	18.862	0.693	0.9710	99.0	36,548	184,201	2.21025	3.34436	2.2450	0.0155	7.181
Alkalies													
Li$_2$	351.346	2.557	0.67293	0.00719	2.6723	26.3	9379	45,861	1.92976	2.12179	2.211	0.1272	0.825
Na$_2$	159.23	0.726	0.15471	0.00079	3.079	18.0	6379	40,971	1.87592	1.27041	2.534	0.2597	0.516
K$_2$	92.64	0.354	0.05622	0.000219	3.923	11.85	4193	38,163	2.06982	1.15739	3.017	0.3139	0.547
Miscellaneous													
N$_2$	2359.61	14.445	2.007	0.018	1.095	170.2	60,738	693,542	2.75738	4.70575	3.379	0.1840	1.070
C$_2$	1641.55	11.67	1.6334	0.0149	1.3121	83	29,865	412,436	2.52793	3.22498	3.718	0.2725	1.017

where a_0, a_1 and a_2 are the Dunham coefficients of Eq. (6). Table I gives the values of b and c for 25 common diatomic molecules.

In making these calculations we were limited to those molecules for which the energy of dissociation is known reasonably accurately. The spectroscopic constants are those given by Herzberg.[8] The energies of dissociation are taken from Bichowsky and Rossini[9] after subtracting the rotational, vibrational, and translational heat contents at 18°C to get the energy of the molecules at absolute zero. The energies of dissociation of C$_2$ and of CO are still uncertain because of the heat of sublimation of graphite. We use the values recommended by Herzberg.

In all of those cases considered except Cl$_2$ the potential becomes large and positive when the nuclei come together. This spurious minimum for Cl$_2$ is completely unimportant since it does

not appear for any physically attainable nuclear separation. For example, this potential gives an energy equal to the energy of dissociation when the nuclei are only 0.06A closer than the corresponding separation given by the Morse curve. However, all argument could be avoided in this case by using the potential:

$$V = D[(1 - \exp(-x))^2 + cx^3(1+x) \exp(-(3-b)x)]. \quad (18)$$

This function does not have the spurious minimum and still it has all of the other desirable properties of Eq. (15). For some molecules the potential of Eq. (18) seems to be a little more accurate. But since this function is not generally applicable and in the other cases the difference between (15) and (18) is always small, we shall not use (18) for any general considerations.

Our confidence in the potential of Eq. (15) is bolstered by comparing it with the few accurate potentials for diatomic molecules which are available—the $1s\sigma 2s\sigma^3\Sigma_g{}^+$, state of H$_2$, the ground state of CdH, and the ground state of N$_2$.

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[8] G. Herzberg, *Molecular Spectra and Molecular Structure, I* (Prentice-Hall, 1939).
[9] F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Co., 1936).

1. The $1s\sigma 2s\sigma^3\Sigma^+_g$ state of H_2

Coolidge, James and Vernon[2] made use of the extensive experimental data available for this state to examine fourteen different types of potential functions and to compare them with an excellent nine-constant Morse function which fits the energy levels almost perfectly. Our five-parameter function (15) is better than any of the functions which they considered except a six-parameter Hylleraas function and a specially fitted Pöschl-Teller function. At $r=1.11A$ ($x=0.1811$) our function (15) is only 0.017 kcal. higher than their nine-parameter function and at $r=1.43A$ ($x=0.6491$) it is only 0.15 kcal. higher. At the same separation the usual Morse function is 0.043 and 0.34 kcal. higher, respectively. A five-parameter extended Morse function,[10] i.e., three terms of Eq. (14), gives an energy which agrees almost perfectly with the nine-parameter extended Morse function at $r=1.11A$, but is 0.11 kcal. lower than the nine-parameter function at $r=1.43A$. The three-term extended Morse function is thus about as far below the correct potential as (15) is above it.

2. The CdH molecule

All of the vibrational levels are known for CdH and Rydberg[11] constructed an accurate potential function to fit the experimental data. Rydberg[11] used a graphical method based on the WBK approximation. Subsequently Hylleraas[12] fitted a six-parameter potential curve by Dunham's method and obtained excellent agreement with Rydberg's potential. In Fig. 1 we have plotted the Rydberg-Hylleraas potential, the three-term extended Morse curve of the Coolidge, James and Vernon type (C.J.V.) and our potential (15). The constants for the extended Morse curve are

$$2\beta' = 5.1067, C_2 = 0.5836, C_3 = 0.2684, C_4 = 0.1480.$$

The maximum deviation of our potential from the Rydberg curve is only 0.35 kcal. whereas the Morse function deviates by as much as 1.8 kcal. The extended Morse curve gives about

[10] We have taken $2\beta' = 1.4858$; $C_2 = 0.9614$; $C_3 = -0.1004$; $C_4 = 0.1390$ in Eq. (14).
[11] R. Rydberg, Zeits. f. Physik 73, 376 (1932); 80, 514 (1933).
[12] E. A. Hylleraas, Zeits. f. Physik 96, 661 (1935).

as good agreement as our potential, the principal difference being that our correction is slightly too large while theirs is slightly too small (falls 0.30 kcal. below the Rydberg-Hylleraas curve). Actually our potential (18) agrees with the Rydberg-Hylleraas potential to within the width of the ink lines. Our only reason for not stressing (18) is that for some molecules it gives extremely large corrections which do not seem physically reasonable. All of these five-parameter functions therefore agree and are satisfactory for CdH.

3. The normal N_2 molecule

Hylleraas[10] has fitted the first 22 vibrational levels of N_2 with his six-parameter function. In Fig. 2 we have plotted his potential. The maximum deviation of the Morse curve from the Hylleraas curve is 14 kcal. For this case potentials (15) and (18) are almost identical. Both agree almost perfectly with the Hylleraas function although again the deviation from the Morse curve is large. The five-parameter extended Morse curve (C.J.V.) again falls below the Hylleraas curve, being 4.39 kcal. too low at $r=1.743A$. ($x=2$). The constants for this curve are

$$2\beta' = 4.1939, C_2 = 0.6492, C_3 = 0.2223, C_4 = 0.1285.$$

It appears that the extended Morse curve (14) and our potential (15) are of about equal accuracy, but the constants are more readily determined for Eq. (15). Thus we gain confidence that our corrections are real rather than illusory.

In Table II we have used Eq. (15) to calculate the magnitude of the corrections to the Morse
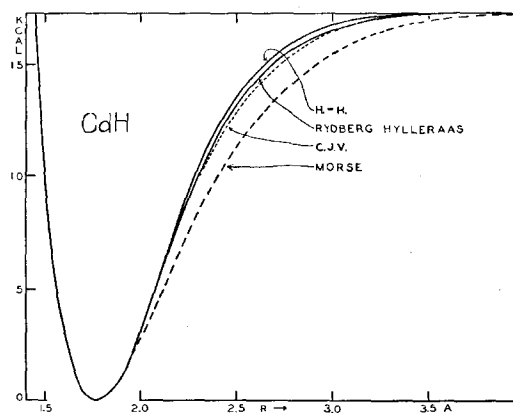

FIG. 1.

curves for three different corresponding internuclear separations $x=1$, $x=2$, $x=3$ where the Morse function gives 40 percent, 75 percent, and 90 percent of the energy of dissociation, respectively. Figure 3 indicates where these points occur. Let us consider the molecules individually.

4. The hydrogen molecule

The potential curves for H_2, HD, and D_2 should be nearly the same. The differences, as
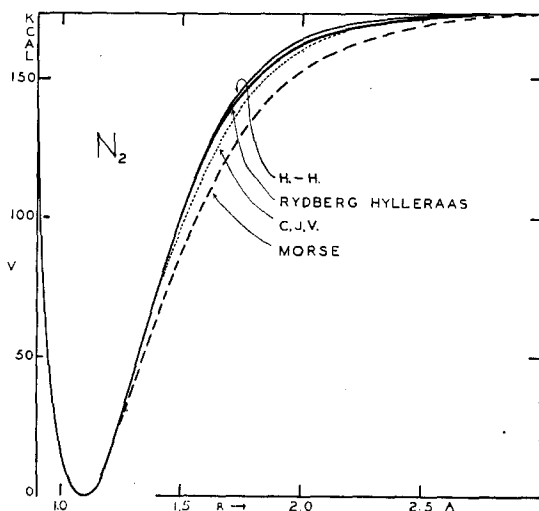

FIG. 2.

shown in Tables I and II, are caused primarily by the experimental errors which occur normally with the two-meter vacuum spectrograph used to photograph the spectra.[13] According to Professor Dieke,[14] more accurate experimental data should be forthcoming. These discrepancies show the order of accuracy of a_0, a_1, and a_2 which are probably present for other molecules in our table.

The corrections to the Morse curve for hydrogen are slight. The coupling between the rotation and vibration, α_e, indicates that the true potential should rise less steeply than the Morse curve; but the first anharmonic correction to the vibrational levels, $\omega_e x_e$, indicates that the Morse curve does not rise steeply enough. Fortunately these facts are not incompatible since α controls a_1 and $\omega_e x_e$ controls a_2. The correction term in Eq. (15) starts out negative

at r_e and becomes positive for large separation of the nuclei. Qualitatively this must be the proper behavior but we cannot be sure that Eq. (15) handles this complicated effect quantitatively. Actually this function is an improvement on the Morse curve for small values of the internuclear separations and also for the large values but in the intermediate range the correction term may not change sign at the proper point. More work on this potential should be carried out as soon as the more accurate experimental data is available.

5. The metal hydrides

The potential curves for the metal hydrides rise much more steeply than the Morse function as is illustrated in Fig. 1 for CdH. Professor Mulliken[15] has warned us to look out for the possibility of a maximum and a long distance minimum in the potential curves for ZnH, CdH, and HgH due to the tendential approach of two interacting states. While Eq. (15) does not lead to these maxima, it is easy to make a slight change in the potential which does give the

TABLE II.

MOLECULE	V/D $x=1$	V/D $x=2$	V/D $x=3$	MAXIMUM CORRECTION KCAL.
Hydrogen				
H_2	−0.0046	0.0068	0.0085	<1
HD	− .0053	.0051	.0073	<1
D_2	− .0060	.0016	.0045	<1
Metal hydrides				
ZnH	.0661	.0998	.0585	2.2
CdH	.0741	.1175	.0707	2.1
HgH	.0701	.1063	.0625	1.1
Hydrogen halides				
HF	− .0194	−.0096	.0008	−3.0
HCl	.0136	.0271	.0180	2.9
HBr	.0218	.0376	.0236	3.4
HI	.0256	.0466	.0299	3.4
Halogens				
Cl_2	.0049	−.0011	−.0034	<1
ICl	.0466	.0727	.0434	3.6
Br_2	.0632	.0957	.0561	4.4
I_2	.0491	.0804	.0491	2.9
Oxides				
OH	.0170	.0346	.0231	3.6
CO	.0197	.0344	.0216	7.3
O_2	.0228	.0392	.0245	4.7
NO	.0405	.0667	.0409	8.3
SO	.0479	.0804	.0497	7.6
Alkalies				
Li_2	.0314	.0494	.0296	1.3
Na_2	.0533	.0773	.0443	1.4
K_2	.0657	.0963	.0555	1.2
Miscellaneous				
C_2	.0744	.1211	.0739	10.3
N_2	.0515	.0846	.0518	14.7

[13] C. R. Jeppeson, Phys. Rev. **49**, 797 (1936).
[14] G. H. Dieke, Phys. Rev. **47**, 661 (1935).
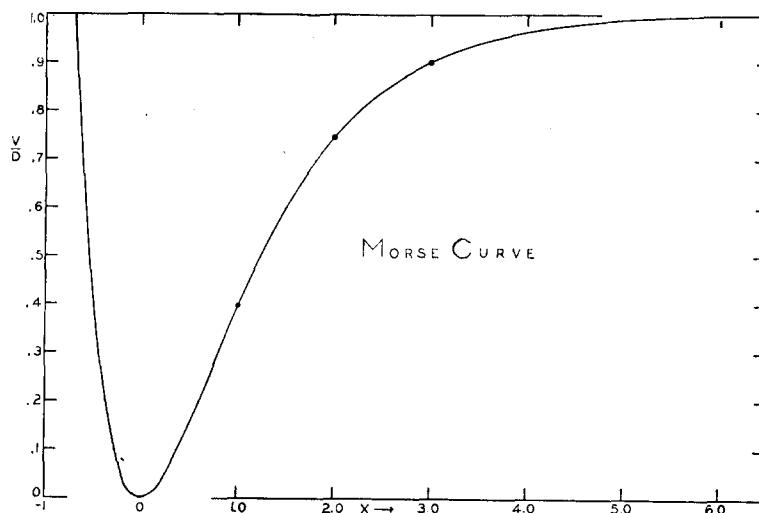
[15] Robert S. Mulliken, J. Phys. Chem. **41**, 5 (1937).

maximum and is still consistent with all of the experimental information.

7. The hydrogen halides

The corrections to the Morse curve for the hydrogen halides increase as we go down the series HF, HCl, HBr, and HI. However, only the lowest few vibrational levels are known for these molecules. The corrections to the Morse curve for HF are small and may not be significant. This may be another example showing that the Morse curve works best for those molecules which do not have inner shells.

The potential for HCl is shown in Fig. 4. Here the correction is fairly small and agrees with that which we would expect on the basis of the three-term extended Morse curve.

$$2\beta' = 2.6089, \quad C_2 = 0.8319, \quad C_3 = 0.0855, \quad C_4 = 0.0826.$$

The potential curves for HBr and HI behave perfectly normally. The maximum corrections are 3.5 and 4.5 kcal., respectively. The large anharmonicity of the HI molecule accounts in part for the difficulty of computing the equilibrium constants for $H_2 + I_2 \rightleftarrows 2HI$ from the spectroscopic data.[16,17]

Since only the three lowest vibrational levels of HI are known, there may be considerable

experimental error in ω_e, $\omega_e x_e$ and hence in our correction term.

8. The halogens

The potential curves for ICl, Br_2, and I_2 rise more steeply than the Morse curve, have maximum corrections of three or four kcal., but otherwise behave quite normally, as seen in Fig. 5. The potential hump for ICl which is indicated from the absorption spectra and predissociation work of Brown does not appear from our potential.[15]

The potential for Cl_2 deviates very little from the Morse function.

9. The alkalies

A great deal of experimental information is available for the alkalies and it would be desirable to construct very accurate potentials for them. According to Eq. (15), the true potentials rise more steeply than the Morse curves, have maximum corrections to the Morse curves of about a kilocalorie, and seem to behave perfectly normally. Our potential for Na_2 gives a fifth vibrational energy level which differs from the experimental value by only 0.015 kcal.

10. The oxides and OH

Here the corrections to the Morse curve are quite large but the potentials appear quiet normal.
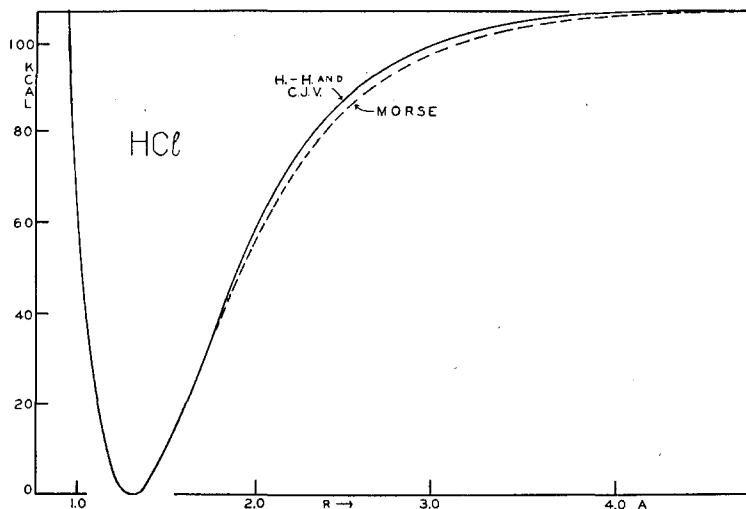
[16] G. M. Murphy, J. Chem. Phys. **4**, 344 (1936).
[17] Our energy of dissociation of HI was obtained from some unpublished data of Crist which he gave us in a private communication.

FIG. 4.

11. C₂ and N₂

The C_2 molecule appears normal with a rather large correction to the Morse curve. The molecule N_2 has been discussed previously. The corrections to the Morse curve are very large at intermediate distances, but Eq. (15) reproduces the accurate Hylleraas potential almost exactly.

IV. SIGNIFICANCE OF THE SPECTROSCOPIC CONSTANTS

In this treatment we adjusted the potential function to fit the spectroscopic constants. These constants are readily available and our method is convenient. But as Coolidge, James and Vernon have pointed out,[3] greater accuracy can be obtained by making a least square fit of the individual energy levels. The reason for this is that the spectroscopic constants contain both random experimental errors and systematic errors resulting from the particular polynomial formula which the energy levels are supposed to obey. Often (as in the case of N_2) it is found that one polynomial is adequate for expressing the lower vibrational levels, whereas an altogether different polynomial is required for the higher states. This phenomena may be due to the fact that a true expression for the energy levels might contain an exponential, as for example:

$$E_v = A[1 - \exp(-\tfrac{1}{2}(v + \tfrac{1}{2}))]$$
$$\times [1 + 0.1(v + \tfrac{1}{2}) - 0.005(v + \tfrac{1}{2})^2].$$

For small values of $(v + \tfrac{1}{2})$ the energy levels would be given by the power series:

$$E_v = 0.5(v + \tfrac{1}{2}) - 0.075(v + \tfrac{1}{2})^2 + \cdots$$

but for large quantum numbers, the power series is:

$$E_v = 1 + 0.1(v + \tfrac{1}{2}) - 0.005(v + \tfrac{1}{2})^2 + \cdots.$$

The reason for this difference is that exponentials of large negative numbers are asymptotically zero. Thus it is never safe to trust the accuracy of power series developments.

This same criticism can be made of the Dunham method for obtaining the potential functions. It is obvious that the power series expansion of the potential does not converge
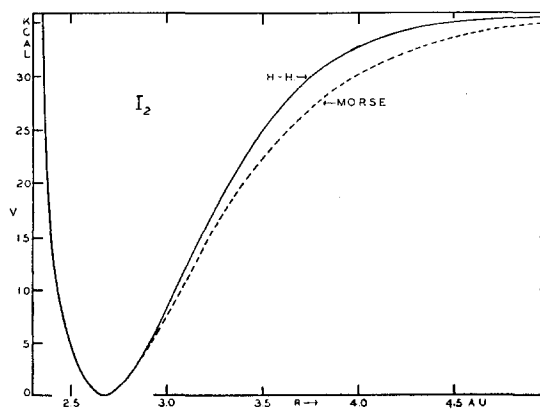

FIG. 5.

rapidly for large internuclear distances and therefore Dunham's method is not adapted to the calculations of the higher vibrational levels. For this purpose we would suggest either one of two methods. First, one could substitute the assumed potential directly into the Schrödinger equation and carry out the integrations numerically to find the corresponding energy levels. Or, one could develop a perturbation method using the Morse potential and the Morse wave functions for the unperturbed state. The integrals of Pekeris[4] would make this method easy to carry out. At the present time these refinements are not warranted by the accuracy of the spectroscopic data for most molecules.

Thus we have made a rough survey of the corrections which must be made to the Morse curve for all of the common diatomic molecules. In some cases the corrections are large. As Mulliken[15] has pointed out, there does not seem to be any universal form for a potential energy function, each molecule having its own peculiar properties. Significant advances in the determination of molecular potential functions will come through closer coöperation of the quantum mechanician and the spectroscopist.

Force Constants in Some Organic Molecules*

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Consistent normal coordinate treatments, involving force-constants which are related to bond structures and which may be transferred from one molecule to another, are applied to hydrogen cyanide, methyl cyanide, and the methyl halides. The connection with previous treatments of acetylene, ethane, and methyl and dimethyl acetylene is discussed. A method of setting up such a consistent treatment is described, and a table of force constants for a number of bond structures is given. The structural significance of these force constants is briefly discussed.

IN analyzing the vibrational spectra of polyatomic molecules, it has become increasingly common to carry out normal coordinate treatments. One important reason for such a treatment is the aid thus given in fixing the fundamental frequencies of complicated molecules. When a few fundamentals are unambiguously assigned, as through symmetry selection rules or from polarization data, it often becomes possible to locate less certain frequencies, at least approximately, by means of a normal coordinate calculation in which the force constants are evaluated from the unambiguous assignments. In view of the difficulty of vibrational analyses for complex molecules, the importance of such aids can scarcely be overemphasized.

Of more fundamental importance are the magnitudes of the force constants which are evaluated. If a valence-force potential is used, these force constants are an additional property of the bonds involved in the molecule, and they may be used to study the character of different bonds and their variation in different molecules. The connection which has been found between the force constant of a diatomic molecule and its bond length[1] shows us the type of correlation we may expect.

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[1] R. M. Badger, J. Chem. Phys. **2**, 128 (1934); C. H. Douglas-Clark, Phil. Mag. **18**, 459 (1934); and later papers.