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On the Determination of Molecular Potential Curves from Spectroscopic Data

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The problem of determining accurately a molecular potential curve from spectroscopic data on the system is analyzed, and the difficulties are discussed in detail. In general the principal difficulty arises from the importance in the energy expression of terms in high powers in the quantum numbers; to deal with this, recourse may be taken to a method employing graphical integration. Formulas based on the first order of the W.B.K. approximation are usually but not always adequate. One can obtain markedly better results in determining potential curves by dealing directly with the energy levels which it is desired to reproduce, rather than by the usual method of making the curve reproduce a limited number of spectroscopic constants. A method of successive approximations has proved to be particularly effective in giving accurate results. Formulas are given for the convenient manipulation of potential curves of the types suggested by Morse, Pöschl and Teller, Hylleraas, Dunham, and also a generalization of the Morse curve. This last curve has proved to be most satisfactory, combining great flexibility with relative ease of manipulation; explicit solutions for vibrational wave functions are not obtainable for it, however. The discussion is illustrated by extensive computations on the lowest $^3\Sigma_g$ state of H_2, for which a potential curve very accurate in the range of nuclear separations $1.3 \leqslant r \leqslant 2.9\ a_H$ is obtained.

§1. INTRODUCTION

IN the course of a careful theoretical study of the $1s\sigma 2s\sigma\ ^3\Sigma_g$ state of H_2 by a variational method, two of us[1] have found values for the energy of this state which differ in a surprising manner from the values given by a Morse curve constructed in the usual way to represent the experimental results. The computed and observed values of the energy agreed well at the potential minimum, for a nuclear separation $r=1.87a_H$. For $r=1.3a_H$, however, the computed energy was *lower* than the Morse curve energy by more than 0.1 electron volt, and for $r>2.7a_H$ a disagreement in the same direction, but of smaller magnitude, was found. Since our variational process could lead only to energy values above the exact theoretical value, this apparent contradiction of theory and experiment caused us to make a careful check on our theoretical work, but no errors were detected. This led us to make a critical examination of the Morse function as an approximation to the potential curve accurately derived from all available spectroscopic data, which showed that it is surprisingly in error even in the neighborhood of the minimum. Our efforts to find a better representation, accurate over the relatively small range of r in which we were interested, showed that this is a problem of unexpected difficulty, and that it is easy to overestimate the accuracy with which potential curves can be constructed by the methods used in the past.

In the present paper we wish to discuss the problem of determining analytical approximations to molecular potential curves from spectroscopic data, to describe more accurate methods than have been used heretofore, and to exhibit the accuracy of various methods, old and new, as applied to the $1s\sigma 2s\sigma\ ^3\Sigma_g$ state of H_2.

Two general methods have been employed in constructing potential curves. First we may mention that of Rydberg.[2] This is a graphical method designed to produce a curve which will give the observed vibrational and rotational energies, when these are computed by the Bohr theory with half-integral quantum numbers (or, what is the same thing, the usual approximation of the Wentzel-Brillouin-Kramers method in wave mechanics). To this approximation the energy levels depend only on the form of that part of the potential curve which lies between the limits of classical motion of the system for the energy in question. It is thus possible to construct the potential curve step by step, the energy E_v of the vth vibrational level and spacing of the rotational levels of that vibrational level providing two conditions on the construction of the potential curve for energies between E_{v-1} and E_v. Though an excellent method for determining the general form of the curve, it is of

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[1] H. M. James and A. S. Coolidge, J. Chem. Phys. **6**, 730 (1938).

[2] R. Rydberg, Zeits. f. Physik **73**, 376 (1932); **80**, 514 (1933).

rather limited accuracy as concerns details, principally because of its graphical character.

The second method consists in the representation of the potential curve by an analytical expression having a generally appropriate character and containing a number of parameters; these parameters are adjusted to values appropriate to each molecular state considered. The curve most widely employed is that of Morse,[3] while other useful curves are those of Rosen and Morse,[4] Manning and Rosen,[5] Pöschl and Teller[6] and Hylleraas.[7] In each case the spectroscopic constants associated with a given curve can be determined, usually by approximate methods, as functions of the parameters in the curve; these parameters are then determined by so adjusting them as to reproduce the observed spectroscopic constants as well as possible. (The method of Hylleraas departs slightly from this procedure, as will be discussed later.)

In applying this method one encounters three difficulties, each of which may be of practical significance: the rotational levels associated with the analytical curve are always, the vibrational levels usually, known only as more or less satisfactory approximations; the "spectroscopic constants" of the state are not definite constants, but depend on the amount of observational material available and the care with which the energy levels are approximated by power series; the curves to be fitted to the data are of limited flexibility, and there may be a wide choice as to which of the observed spectroscopic properties of the system the approximate potential curve is to reproduce.

In the next three sections of this paper we shall discuss these difficulties in more detail, and shall describe a technique for dealing with them to best advantage, when the accuracy desired will justify some care in the determination of the curve. We shall then give formulas useful in fitting to observational data in various ways the curves of Morse, Pöschl and Teller, and Hylleraas, and certain series discussed by Dunham.[8] Finally we shall present and compare the results of fitting curves in a large number of ways, illustrating thereby certain principles involved in the adjustment of curves of limited flexibility, and in the deduction of the nature of the errors in a potential curve from the errors in the spectroscopic constants or energy levels associated with it.

§2. Significance of Spectroscopic Constants

We may regard as the primary spectral data for any given state the term values of the vibration-rotation levels, or the energy differences of these levels. From this it is customary to derive "spectroscopic constants," the definition of which is subject to some arbitrariness. Thus one may write

$$E_{v,\,K}=E_v+B_vK(K+1)-D_vK^2(K+1)^2+\cdots.$$

The energies $E_{v,\,K}$ are expressed in wave numbers. For any given v there will be a limited number of rotational levels known, and the coefficients E_v, B_v, $\cdots$ of this expansion will not be uniquely determined; the values depend on the number of terms used in setting up the expansion. Regarding E_v, B_v, $\cdots$ as functions of v approximately fixed for integral v, but not for other values of v, we see that in the expansions

$$E_v=C_e+\omega_e(v+\tfrac{1}{2})-\omega_ex_e(v+\tfrac{1}{2})^2+\cdots,$$
$$B_v=B_e-\alpha_e(v+\tfrac{1}{2})+\gamma_e(v+\tfrac{1}{2})-\cdots,$$

the spectroscopic constants ω_e, ω_ex_e, B_e, $\cdots$ are not definite quantities, but may depend, among other things, on the amount of spectral data available and the number of terms used in the expansions. In particular it must be realized that these expansions cannot be relied upon to give term values for vibrational levels outside of the set used in constructing them.

This point is nicely illustrated by the work of Hylleraas[9] on the $^1\Sigma_g$ state of N_2. With this state, for v up to 15, E_v can be expressed quite accurately by a series ending with the term in ω_ex_e; extrapolation of this series leads to a dissociation energy in error by 60 percent. As a second example we take the results of Sandeman[10] on the $1s\sigma 2s\sigma\ ^3\Sigma_g$ state of H_2, which form the experimental basis of the computations to be presented in this paper. He finds that the observed term

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[3] P. M. Morse, Phys. Rev. **37**, 57 (1929).
[4] N. Rosen and P. M. Morse, Phys. Rev. **42**, 210 (1932).
[5] N. F. Manning and N. Rosen, Phys. Rev. **42**, 953 (1933).
[6] G. Pöschl and E. Teller, Zeits. f. Physik **83**, 143 (1933).
[7] E. A. Hylleraas, Zeits. f. Physik **96**, 643, 661 (1935).
[8] J. L. Dunham, Phys. Rev. **41**, 721 (1932).
[9] E. A. Hylleraas, Zeits. f. Physik **96**, 661 (1935).
[10] I. Sandeman, Proc. Roy. Soc., Edinburgh **55**, 49 (1935).

differences, for v up to 7, are practically all reproduced to within a few hundredths of a wave number by the series[11]

$$E_v = 4.90 + 2665.9252(v+\tfrac{1}{2}) - 72.79390(v+\tfrac{1}{2})^2 + 1.429492(v+\tfrac{1}{2})^3 - 0.1473890(v+\tfrac{1}{2})^4 + 0.01246012(v+\tfrac{1}{2})^5 - 0.000585323(v+\tfrac{1}{2})^6,$$

$$B_v = 34.22051 - 1.694884(v+\tfrac{1}{2}) + 0.03454932(v+\tfrac{1}{2})^2 - 0.002034446(v+\tfrac{1}{2})^3 + 0.00000733776(v+\tfrac{1}{2})^4.$$

The occasional deviations of greater magnitude he attributes to perturbations by other electronic levels, which have no place in a discussion of potential curves and will be ignored in this paper. He also gives a series containing a smaller, but still relatively large, number of terms:

$$E_v = 5.00 + 2665.4861(v+\tfrac{1}{2}) - 72.18137(v+\tfrac{1}{2})^2 + 1.068784(v+\tfrac{1}{2})^3 - 0.04863957(v+\tfrac{1}{2})^4$$

also fitted by least squares, and of course reproducing the observed term differences less accurately. Omission of terms in $(v+\frac{1}{2})^5$ and $(v+\frac{1}{2})^6$ has here changed the coefficient of $(v+\frac{1}{2})^4$ by a factor of three, and even the coefficient of $(v+\frac{1}{2})^2$, almost always used in curve fitting, is changed by one percent. But even in the more elaborate expression the cutting off of the series changes the coefficients by amounts which are appreciable in calculating E_v for $v > 7$. One must expect an expansion adequate to represent all the vibrational levels[12] to continue well beyond the terms here given, with fairly regularly decreasing coefficients. Extrapolating Sandeman's series, we would expect as the next term $+0.00002(v+\frac{1}{2})^7$, which for $v=7$ would contribute some 27 cm^{-1} to E_v. Neglect of this and higher terms in the series has been compensated, for $v \leqslant 7$, by proper modifications of the other constants, but this compensation will not extend outside the range in question. Thus for $v=10$, when the contribution of the term in $(v+\frac{1}{2})^7$ would be some ten times greater, the error in the representation must be expected to be of this order, and to increase rapidly with v.

§3. Energy Levels of a Potential Curve

We now turn to the problem of determining the energy levels of an analytic potential curve $U(r)$, having a minimum, which it is convenient to take as the zero for energy, at $r=r_e$ and an asymptotic value $U(\infty)=D$ which it approaches so rapidly that there is only a finite number of discrete vibrational levels E_v. (We shall throughout express U in cm^{-1}, and r in Bohr radii.) For this there is one generally useful method, that of Wentzel-Brillouin-Kramers, which provides an asymptotic expansion which converges at first very rapidly, so that only two terms, at most, need be taken. To this approximation we write, for the case of no rotation, $E_v = E_v' + E_v''$; E_v' is the first W. B. K. approximation, E_v'' the correction which arises from the second approximation. Employing the results of Dunham[13] we find

$$\oint P_v' d\rho = 2\pi B_e^{\frac{1}{2}}(v+\tfrac{1}{2}), \tag{1}$$

$$\oint P_v'' d\rho - (B_e/32) \oint (U')^2 (P_v'')^{-5} d\rho = 2\pi B_e^{\frac{1}{2}}(v+\tfrac{1}{2}), \tag{2}$$

where $\rho = r/r_e, \quad B_e = Rm/\mu r_e^2, \quad U' = dU/dr,$

$$(P_v')^2 = E_v' - U, \quad (P_v'')^2 = E_v' + E_v'' - U,$$

and R is the Rydberg constant, μ the reduced mass of the nuclei, m the mass of the electron. The case of rotation may be treated similarly by introducing the effective potential $U(\rho) + B_e K(K+1)/\rho^2$, assuming an energy expansion of the form $E = E_v' + E_v'' + K(K+1) \times (B_v' + B_v'')$ + higher terms in $K(K+1)$, and equating to zero separately the coefficient of each power of $K(K+1)$ in Dunham's relations. We thus find

$$B_v' \oint (P_v')^{-1} d\rho = B_e \oint \rho^{-2} (P_v')^{-1} d\rho, \tag{3}$$

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[11] We have added the constant term in E_v, which was obtained in the computations to be described later.

[12] There is, of course, no uniquely defined correct expansion of the functions E_v, B_v, which are specified only for a finite number of points.

[13] J. L. Dunham, Phys. Rev. **41**, 713 (1932).

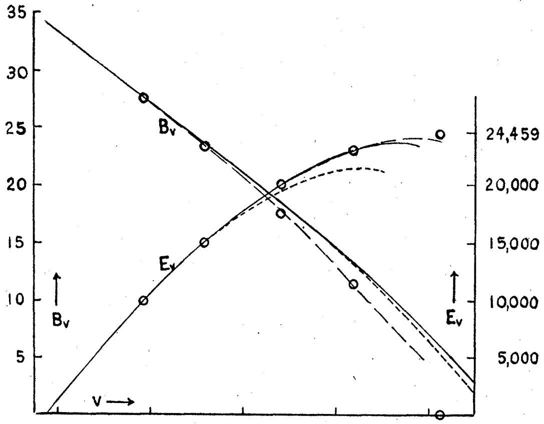

FIG. 1. E_v and B_v as determined by various methods. O, graphical integration of Eqs. (1) and (3), curve 14. ----calculated with Y's used in determining curve 14. — — calculated with additional Y's as described. —— calculated with Sandeman's complete constants.

$$(B_v'+B_v'')\left\{\oint(P_v'')^{-1}d\rho+(5B_e/32)\oint(U')^2(P_v'')^{-7}d\rho\right\}$$
$$=B_e\oint\rho^{-2}(P_v'')^{-1}d\rho+(5B_e^2/32)\oint(U')^2\rho^{-2}(P_v'')^{-7}d\rho-(B_e^2/4)\oint U'\rho^{-3}(P_v'')^{-5}d\rho. \quad (4)$$

When analytical evaluation of these expressions is impracticable they can be evaluated numerically, by assuming values of E and using Eq. (1) or (2) to determine the corresponding value of v, afterward interpolating to integral values of v.

Dunham has given the results of this method in very useful form, expanding E_v, etc., in series like those employed by spectroscopists:

$$E_v=Y_{00}+Y_{10}(v+\tfrac{1}{2})+Y_{20}(v+\tfrac{1}{2})^2+\cdots, \quad (5)$$

$$B_v=Y_{01}+Y_{11}(v+\tfrac{1}{2})+Y_{21}(v+\tfrac{1}{2})^2+\cdots. \quad (6)$$

Expanding $U(r)$ about r_e in powers of

$$\xi=(r-r_e)/r_e,$$

he defines coefficients a_n by

$$U(r)=a_0\xi^2(1+a_1\xi+a_2\xi^2+\cdots). \quad (7)$$

He gives formulas for Y_{lj}' and Y_{lj}'', the parts of Y_{lj} arising from the first and second approximations of the W. B. K. method, as functions of the a_n so far as this is possible without going beyond a_6, namely, up to Y_{20}'', Y_{40}', Y_{11}'', Y_{31}', Y_{02}'', Y_{22}', Y_{13}', Y_{04}'.

In applying the results of Dunham, the principal limitation does not arise from the lack of higher terms in the W. B. K. approximation, which are of the order of the uncertainties arising from the imperfect separability of nuclear and electronic coordinates, i.e., arising from the essential vagueness in the definition of a molecular potential function. Rather, it is due to the lack of such coefficients Y_{lj} as depend on $a_7, \cdots$, and may play an essential role in determining the location of the levels for moderately large values of v. The extension of Dunham's formulas is of course possible; we believe, however, that it is more practical to estimate the necessary additional Y's by a process which is the inverse of Rydberg's, determining by numerical integration the values of E_v and B_v for large v, and so adjusting the values of the higher Y's as to reproduce these values. Thus, by graphical integration of Eq. (1) with various values of E_v', we obtain the corresponding (in general nonintegral) values of v. The resulting curve of E_v against v is tangent to the line $E=D$ for some finite value $v=v_0$ such that the next largest integer is the number of discrete vibrational levels. Similarly, the curve for B_v' (the main term in B_v), is obtained from Eq. (3); it vanishes for $v=v_0$, but it can be shown that at this point all its derivatives are infinite, so that the end-point should be disregarded when fitting the curve by a power series. These curves are, of course, subject to the errors of numerical integration as well as those due to neglect of the higher terms in the W. B. K. approximation, but they suffice to determine the higher Y's with ample precision when they are to be used only for lower v's, where they have the character of small correction terms.

An example of this procedure is illustrated in Fig. 1, which is based upon the curve numbered 14 in Table II. As will be described later, this curve was set up to reproduce the values of $Y_{10}\cdots Y_{40}$, $Y_{01}\cdots Y_{31}$ given by Sandeman for $1s\sigma 2s\sigma\ {}^3\Sigma_g$ H_2; no control of the higher Y's was

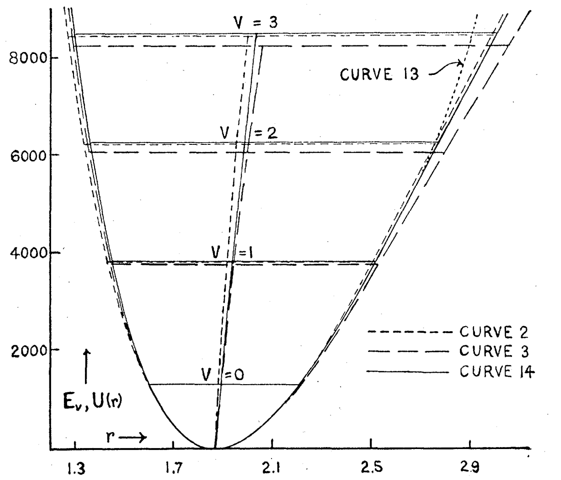

FIG. 2. Relations between E_v, r_v, and potential curves. Horizontal tie lines show values of E_v. Nearly vertical lines intersect tie lines at $r = r_v = [Rm/\mu B_v]^{\frac{1}{2}}$.

possible, and they were estimated by graphical integration. The procedure in the case of Eq. (1) is obvious; in the case of Eq. (3) the occurrence of infinities in the integrand was avoided by a change of variables:

$$\oint \rho^{-2}(E-U)^{-\frac{1}{2}}d\rho$$

$$=4\int_{r=a}^{r=g}(\rho-a)^{\frac{1}{2}}\rho^{-2}(E-U)^{-\frac{1}{2}}d(\rho-a)^{\frac{1}{2}}$$

$$+4\int_{r=b}^{r=g}(b-\rho)^{\frac{1}{2}}\rho^{-2}(E-U)^{-\frac{1}{2}}d(b-\rho)^{\frac{1}{2}}. \quad (8)$$

Here a and b are the values of ρ at the classical turning-points, and $a<g<b$. We obtain the following results:

E	10000	15000	20000	23000	24459
v	3.705	6.33	9.64	12.7	16.5
B	27.53	23.25	17.47	11.38	0.

These results lead to the following values for the higher Y's:

$Y_{50} = 0.01061$, $Y_{60} = -0.000705$,
$Y_{70} = 0.0000202$, $Y_{80} = -0.00000022$,
$Y_{41} = -0.0001$, $Y_{51} = -0.000004$,
$Y_{61} = 0.0000005$.

Fig. 1 shows E_v and B_v as computed with these Y's, and for comparison the values computed with, first, only the Y's with reference to which the curve was constructed, and, second, the complete results of Sandeman, introduced for later reference. The higher Y's derived here make appreciable contributions to E_v and B_v, even for quite low values of v. Thus they contribute 14 cm^{-1} to E_v and -0.044 cm^{-1} to B_v for $v=4$, while for $v=9$ they contribute 396 cm^{-1} to E_v and -0.76 cm^{-1} to B_v.

§4. DETERMINATION OF EXPERIMENTAL POTENTIAL CURVES

We shall consider as an "experimental potential curve" any potential curve having as its energy levels the observed discrete energy levels of the molecule. Such a curve is of course not uniquely defined by the finite number of observed energy levels, but a reasonable, smooth curve which reproduces these energies should be well defined and of good accuracy everywhere. If strong perturbations affect the electronic state in question there may exist no curve whatsoever with the desired properties; a potential curve for this state is then of significance only in an intermediate stage in the theoretical treatment of these levels.

The usual process in determining an experimental potential is to refer, not to the energy levels, but to certain of the spectroscopic constants, determining a potential curve $U(r)$ such that a limited number of the Y's have the same values as the corresponding spectroscopic constants ω_e, $\omega_e x_e$, $\cdots$ in some analysis of the electronic state. The energy levels of the curve then differ from the observed energies insofar as the spectroscopic constants not used in determining the curve differ from the corresponding uncontrolled Y's of the curve. Now the spectroscopic constants appearing in the analysis are chosen to give the best possible fit on the assumption that those constants not explicitly introduced are zero. Then even if one determines the potential curve using all the available constants there remain errors in the energy levels due to the higher Y's of the curve, which will not in general be zero, and which may affect the energy levels appreciably even for low values of the quantum numbers. In any case, it is clear that the greatest difficulties will arise in properly determining the higher energy levels, and it will be correspondingly difficult properly to determine the potential curve near the classical turning points for these higher levels. The magnitude of the errors which will appear in the energy levels even under the most favorable circumstances is illustrated in Fig. 1, while Fig. 2 will illustrate the errors in the potential curve when less careful methods of curve fitting are employed.

This difficulty can be overcome, so far as the limited flexibility of the potential curve will permit, by a process of successive approximations based on the observed energy levels rather than the derived spectroscopic constants. Let it be desired to determine a potential curve of a particular form which will approximate as well as possible to the experimental curve up to a height E_w above the minimum. This is clearly to be accomplished by making the differences in the energy levels of this curve, for $E_v < E_w$, approximate as well as possible, say in a least-squares sense, to the observed energy level differences. The behavior of the energy levels and the potential curve outside of the specified region will be disregarded. As a first approximation to the desired curve we take a curve constructed in the usual way to reproduce a certain set of spectroscopic constants, which we call the controlled constants. Let the values of the uncontrolled Y's for this curve be determined; these will have roughly the same values as for the final curve. Deducting from the observed energy values the contributions to $E_{v,\,K}$ of these uncontrolled Y's, we obtain a set of values which we would like to reproduce by a series containing only the controlled Y's. Fitting such a series to these values by a least-squares process we obtain new values for these Y's, which serve to determine the second approximation to the desired curve. Next, the values of the uncontrolled Y's for this curve can be determined and in turn employed in a repetition of this procedure, and so on, until repetition produces no essential improvement.

We have applied this process in representing the $1s\sigma 2s\sigma\,{}^3\Sigma_g$ state of H_2 by a Pöschl-Teller curve, and find that it converges rapidly, requires no excessive labor, and produces a curve which bears comparison with another curve involving twice as many disposable constants fixed in the usual way. This curve is the curve 6 of §6; where its construction and characteristics are indicated in more detail; some of its properties are tabulated in Tables II to VI.

It should be possible to form estimates of the errors in any approximate potential curve on the basis of the errors, as compared with experimental values, of the corresponding spectroscopic constants or, much better, of the energy level separations. From the point of view of the Rydberg process, one sees that an excessive computed difference of E_v and E_{v+1} indicates that the potential curve is on the average too narrow in the range between these energies, while an excessive value of B_v indicates that the mean value of the classical turning points for the vth vibration is too small. From the point of view of perturbation theory, it is clear that a depression of the potential curve in any region will depress most strongly those energy levels with turning points in the given region, and will increase or decrease the corresponding values of B_v according as the depression affects the inner or the outer branch of the potential curve. The latter effect is more clearly indicated by the behavior of the quantity $\bar{r}_v = (Rm/B_v\mu)^{\frac{1}{2}}$, the effective nuclear separation for the vth level, the error in which should be a rough measure of the average lateral errors of the two branches in the neighborhood of E_v. It is also clear that an error in the curve of alternating sign will lead to errors of generally smaller magnitude in the energy levels affected.

These considerations lead also to some general principles which are useful when methods of determining a potential curve less careful than that described above are to be employed. For instance, a curve which reproduces perfectly the observed vibrational levels of a molecule may still contain very large errors if the rotational levels do not also come out right. Thus, in choosing a set of controlled constants for the construction of a curve one ought to include rotational as well as vibrational constants; a rough equality in the number of constants of each type used will probably lead to most satisfactory results. Correspondingly, to insure a reasonably wide range of application of a particular form of analytic curve it should contain at least four variable parameters, of which two can be used to give proper character to the rotational levels of the curve. Thus four-param-

TABLE I. *Constants of a Morse curve in terms of various spectroscopic constants.*

r_e	β	D	ω_e	$\omega_e x_e$	B_e	α_e
$(Rm/\mu B_e)^{\frac{1}{2}}$	$\omega_e/4(DB_e)^{\frac{1}{2}}$	$\mathbf{D}$	$\boldsymbol{\omega}_\mathbf{e}$	$\omega_e^2/4D$	$\mathbf{B_e}$	$3B_e^{\frac{3}{2}}/D^{\frac{1}{2}}-6B_e^2/\omega_e$
$(Rm/\mu B_e)^{\frac{1}{2}}$	$(\omega_e x_e/4B_e)^{\frac{1}{2}}$	$\omega_e^2/4\omega_e x_e$	$\boldsymbol{\omega}_\mathbf{e}$	$\boldsymbol{\omega}_\mathbf{e}\mathbf{x_e}$	$\mathbf{B_e}$	$6B_e^{\frac{3}{2}}(\omega_e x_e)^{\frac{1}{2}}/\omega_c-6B_e^2/\omega_e$
$(Rm/\mu B_e)^{\frac{1}{2}}$	$(\omega_e\alpha_e/12B_e^2)^{\frac{1}{2}}$	$9\omega_e^2B_e^3/[6B_e^2+\omega_e\alpha_e]^2$	$\boldsymbol{\omega}_\mathbf{e}$	$[6B_e^2+\omega_e\alpha_e]^2/36B_e^3$	$\mathbf{B_e}$	$\boldsymbol{\alpha}_\mathbf{e}$

eter curves such as those of Pöschl and Teller or Rosen and Morse have a marked superiority to the three-parameter curve of Morse. Another obvious consideration is that, when one is interested only in the form of the potential curve near the minimum, as, for instance, in determining vibrational wave functions for low v, one should choose the parameters without regard to errors in the dissociation energy indicated by the curve.

These ideas will be illustrated in §6 of this paper.

§5. FORMULAS FOR THE DETERMINATION OF POTENTIAL CURVES

We here present in a uniform notation formulas useful in determining from experimental data potential curves of Morse, Pöschl and Teller, Hylleraas, and the generalized Morse function suggested by Dunham. We write any potential curve having an asymptotic value D as

$$U(\xi)=DF(\xi),\quad \xi=(r-r_e)/r_e.$$

In addition to D and r_e, a third parameter β occurs in all these curves, while the energy formulas are conveniently expressed in terms of a constant C, where

$$C^2=4R_\infty m\beta^2/\mu r_e^2.$$

(We purposely avoid defining curves in terms of symbols such as B_e and ω_e, which we reserve for use as empirical spectroscopic constants.)

The calculation of the energy levels of any of these curves, referred to the minimum as the zero of energy, can well be based on Dunham's formulas. For the purpose of curve fitting it is convenient to have expressions for the constants defining these curves in terms of certain of the Y's. Upon identifying Y_{10}' with ω_e, $-Y_{20}'$ with $\omega_e x_e$, Y_{01}' with B_e, and $-Y_{11}'$ with α_e, one obtains formulas for computing these constants, as shown below. The error arising from the neglect of higher order terms is trivial in comparison with those due to the essential shortcomings of this method of curve fitting, as already discussed.

Morse curve

The Morse curve is defined by the three basic parameters.

$$F_M=[1-e^{-2\beta\xi}]^2.$$

One finds

$$\begin{aligned}&Y_{00}'=0,\quad Y_{00}''=0,\\&Y_{10}'=2CD^{\frac{1}{2}},\\&Y_{20}'=-C^2,\\&Y_{01}'=C^2/4\beta^2,\\&Y_{11}'=-(3C^3/16\beta^4D^{\frac{1}{2}})(2\beta-1).\end{aligned}$$

Y_{l0}' vanishes for all $l>2$, while Y_{l0}'' vanishes for all l; the Morse curve, for $K=0$, shares with the parabola the property of yielding the exact solution of the energy level problem in the first approximation of the W. B. K. method.

To find the constants of a curve in terms of given spectroscopic constants, one may use Table I, which gives the value of each of the quantities at the top in terms of the quantities in bold-faced type.

Pöschl-Teller curve

To define the Pöschl-Teller curve we introduce a fourth parameter τ:

$$F_P=1+\sinh^4\tau/\sinh^2(\tau+\beta\xi)-\cosh^4\tau/\cosh^2(\tau+\beta\xi).$$

This goes into the Morse curve as $\tau\rightarrow\infty$, $L=\coth 2\tau\rightarrow 1$. For the Pöschl-Teller curve also exact values can be found for the Y_{l0}, though they are not given by the first W. B. K. approximation. Defining

$$D'=D[(\cosh^4\tau+C^2/16D)^{\frac{1}{2}}-(\sinh^4\tau+C^2/16D)^{\frac{1}{2}}]^2,$$

we find

$$\begin{aligned}&Y_{00}=D-D',\\&Y_{10}=2CD'^{\frac{1}{2}},\\&Y_{20}=-C^2,\\&Y_{l0}=0,\quad l>2.\end{aligned}$$

Closed expressions for the rotational terms do not exist, but they can be computed from Dunham's formulas with sufficient accuracy. For Dunham's a_n we find

$$a_0=4D\beta^2,$$
$$a_1=-2L\beta,$$
$$a_2=(5L^2-8/3)\beta^2,$$
$$a_3=-(12L^3-10L)\beta^3,$$
$$a_4=\left(28L^4-\frac{98}{3}L^2+\frac{272}{45}\right)\beta^4,$$
$$a_5=-\left(64L^5-96L^3+\frac{164}{5}L\right)\beta^5.$$

Then
$$Y_{00}'=0,\quad Y_{00}''=\tfrac{1}{4}C^2(L^2-1),$$
$$Y_{10}'=2CD^{\frac{1}{2}},$$
$$Y_{20}'=-C^2,$$
$$Y_{01}'=C^2/4\beta^2,$$
$$Y_{11}'=-(3C^3/16\beta^4D^{\frac{1}{2}})(2L\beta-1).$$

For the determination of the constants of the curve one may use either the first or the second line of the corresponding table for the Morse curves, except for the last column. To find τ one must assume in addition a value for α_e, solving either

$$2\sinh^2\tau=(1-9\omega_e^2B_e^3/D[6B_e^2+\omega_e\alpha_e]^2)^{-\frac{1}{2}}-1$$

in the first case, or, in the second

$$2\sinh^2\tau=(1-36\omega_ex_eB_e^3/[6B_e^2+\omega_e\alpha_e]^2)^{-\frac{1}{2}}-1.$$

Lotmar[14] has given comparable formulas, but they are erroneous, because of a confusion of r_e with r_0, a quantity defined in Pöschl and Teller's original paper, and in our notation given by $r_0=r_e(1-\tau/\beta)$.

Hylleraas curve

The Hylleraas curve involves three more parameters k, k_1, k_2, in terms of which are defined the intermediate quantities

$$x=e^{2(1+k)\beta\xi},\quad a=\frac{k-k_2}{1+k_2},\quad b=\frac{k-(k_1+k_2)}{1+k_1+k_2},$$
$$c=\frac{k-k_1}{1+k_1}.$$

Then
$$F_H=\left[1-\frac{(1+a)(1+c)(x+b)}{(x+a)(x+c)(1+b)}\right]^2.$$

This passes into F_M upon making $k=k_1=0$, so that $a=b$, $c=0$; F_P is also the special case $k=0$, $k_1=\frac{1}{2}(\tanh\tau-1)$, $k_2=\frac{1}{2}(\coth\tau-1)$.

Exact values are not available for the energy levels. We have determined Dunham's a_n for particular curves of this type both by a straightforward expansion of the potential in powers of ξ and by a set of formulas too cumbersome to reproduce. As far as a_4, these formulas may be expressed in terms of the quantities a_1, a_2, a_3, a_4, defined in Hylleraas' paper[15] and lead to the expressions:

$$Y_{00}'=0,\qquad Y_{00}''=\tfrac{1}{4}C^2(a_1^2-a_2),$$
$$Y_{10}'=2CD^{\frac{1}{2}},$$
$$Y_{20}'=-C^2a_2,$$
$$Y_{01}'=C^2/4\beta^2,$$
$$Y_{11}'=-(3C^3/16\beta^4D^{\frac{1}{2}})(2a_1\beta-1).$$

To set up a Hylleraas curve which will reproduce certain selected spectroscopic constants, one begins by finding a set of Dunham's a_n (using a method of successive approximations if high accuracy is desired) such that when they are substituted in Dunham's formulas the desired Y_n will emerge. The task of determining a Hylleraas curve which will reproduce these a_n is most conveniently accomplished by means of the following formulas, in which we put $R=2\beta(1+k)$:

$$(D^{\frac{1}{2}}/a_0^{\frac{1}{2}})\{8R^4-12a_1R^3-(18a_1^2-24a_2)R^2-(144a_3-144a_2a_1+36a_1^3)R+144a_3a_1-144a_2^2+9a_1^4\}$$
$$=24R^3+(144a_2-108a_1^2)R-(288a_3+180a_1^3-432a_1a_2).$$

$$\begin{aligned}
&8640a_4\{4(a_0/D)+4(a_0/D)^{\frac{1}{2}}[-R+a_1]+[R^2-2a_1R+a_1^2]\}\\
&=12(a_0/D)\{-512R^4+360a_1R^3+[2340a_1^2-3120a_2]R^2+[7200a_3-8640a_2a_1+2880a_1^3]R\\
&\quad+2160a_2^2+1080a_2a_1^2-1125a_1^4\}\\
&\quad+24(a_0/D)^{\frac{1}{2}}\{226R^5-406a_1R^4+[1200a_2-720a_1^2]R^3+[-3600a_3+3120a_2a_1-540a_1^3]R^2\\
&\quad+[3600a_3a_1-2160a_2^2-3240a_2a_1^2+1395a_1^4]R+[2160a_2^2a_1-1080a_2a_1^3+45a_1^5]\}\\
&\quad+\{-1136R^6+3432a_1R^5+[-4320a_2-96a_1^2]R^4+[21600a_3-15840a_2a_1+2160a_1^3]R^3\\
&\quad+[-43200a_3a_1+23760a_2^2+24120a_2a_1^2-7155a_1^4]R^2+[21600a_3a_1^2-38880a_2^2a_1\\
&\quad+6480a_2a_1^3+810a_1^5]R+[8640a_2^3-1620a_2a_1^4+270a_1^6]\},
\end{aligned}$$

$$\beta=\tfrac{1}{2}(a_0/D)^{\frac{1}{2}},$$
$$(1+k)=R(D/a_0)^{\frac{1}{2}},$$
$$k_1k_2=1+\tfrac{1}{2}(D/a_0)^{\frac{1}{2}}(a_1-R),$$
$$-(k_1+k_2)\{24+12(D/a_0)^{\frac{1}{2}}(a_1-R)\}=48+36(D/a_0)^{\frac{1}{2}}(a_1-R)+(D/a_0)\{(12a_2-3a_1^2)-12a_1R+8R^2\}.$$

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[14] W. Lotmar, Zeits. f. Physik **93**, 528 (1935).

[15] It is to be noted that the $a_1\cdots a_4$ of Hylleraas' paper are simply related to, but not identical with, these quantities in our notation.

TABLE II. *Constants of potential curves.*

CODE	TYPE	r_e	D	β	τ	k	k_1	k_2
1	*M*	1.8678	24460	0.72836				
2	*M*	1.8678	24637	0.72573				
3	*M*	1.8678	19440	0.81700				
4	*M*	1.8678	20204	0.82725				
5	*P-T*	1.8678	24637	0.72573	0.70697			
6	*P-T*	1.8698	26619	0.69633	0.66959			
7	*H*	1.8678	24460	0.72806		−0.05382	−0.02775	1.22820
8	*H*	1.8678	24460	0.72806		0.12221	−0.36200	0.33728
9	*H*	1.8678	23248	0.74708		0.17427	−0.40643	0.32949
10	*H*	1.8678	24460	0.72836		−0.08041	−0.01249	1.65297
11	*H*	1.8672	23762	0.73930		0.27643	−0.54098	0.36442

In addition, we have considered the three curves (with $r_e=1.8677$)

12 $V(\xi)=51922\xi^2[1-1.6438\xi+1.9588\xi^2-2.0945\xi^3+2.2775\xi^4]$,

13 $V(\xi)=51913\xi^2[1-1.6409\xi+1.9525\xi^2-2.0840\xi^3+2.260\xi^4-2.965\xi^5+4.15\xi^6]$,

14 $V(\xi)=24459X^2[0.72550+0.02948X+0.10522X^2+0.05281X^3+0.05525X^4+0.02573X^5+0.00601X^6]$; $X=1-e^{-2\beta\xi}$; $\beta=0.8552$.

TABLE III. *Dunham coefficients of potential curves.*

CODE	a_0	a_1	a_2	a_3	a_4	a_5	a_6
1	51906	−1.45672	1.23785	−0.77280	0.38776	—	—
2	51906	−1.45146	1.22893	−0.76446	0.38219	—	—
3	51906	−1.63400	1.55747	−1.09068	0.61386	—	—
4	55308	−1.65450	1.59680	−1.13224	0.64525	—	—
5	51906	−1.63400	1.93292	−2.2407	2.6672	−3.1560	—
6	51628	−1.59806	1.89923	−2.24733	2.72171	−3.2602	—
7	51861	−1.63373	1.99851	−2.94412	5.96758	—	—
8	51861	−1.63373	1.99851	−2.36007	2.67414	—	—
9	51903	−1.63396	1.96115	−2.22259	2.36103	−2.3378	2.232
10	51906	−1.63400	1.93292	−2.73312	5.96937	—	—
11	51950	−1.65287	1.99520	−2.11494	1.96573	−1.6746	1.384
12	51922	−1.64380	1.95880	−2.09450	2.27750	0	0
13	51913	−1.64090	1.95250	−2.08400	2.26000	−2.9650	4.150
14	51913	−1.64090	1.95250	−2.08400	2.26000	−2.9650	4.150

If it is desired to reproduce given values of r_e, D, a_0, a_1, a_2, a_3, the first of these equations will serve to determine R; the remaining equations then give the constants of the curve, as well as a_4. If, rather, the value of D given by the curve is of no interest, and it is desired to reproduce values of a_0, a_1, a_2, a_3, a_4, r_e then use of the first two equations will allow one to find the values of R and D needed to reproduce the given a_4, and the values for the parameters of the curves follow as before.

Hylleraas gives another method of adjusting his curve, based on a method which, if consistently carried through, would give just the principal parts of Dunham's terms, the Y_{l0}' and Y_{l1}'. However, he breaks off the vibrational series with Y_{30}', and arbitrarily substitutes a fractional expression (his Eq. (28)) which gives, upon expansion, the proper values for these quantities, and in addition a further set of Y_{l0}' which have no relation to the problem. Thus his expression for the vibrational energies does not accurately reproduce the energy levels of the curve, as he himself states. In the case of $1s\sigma 2s\sigma\ {}^3\Sigma_g$ H_2 this approximate expression is a very poor approximation, and breaks down completely when one attempts to make it reproduce the observed values of ω_e, $\omega_e x_e$, $\omega_e y_e$.

Extended Morse curve

The extended Morse curve is defined by

$$F(\xi)=\sum_{n=2}^{8} c_n[1-e^{-2\beta\xi}]^n,$$

the c's being adjustable parameters. Its manipulation differs little from that of Dunham's power series function. In either case one first finds the a_n needed to reproduce the desired Y_n. The c_n of the extended Morse curve can then be determined from the relations

$$a_0=4\beta^2Dc_2$$

$$a_0a_1=4\beta^3D(-2c_2+2c_3),$$

$$a_0a_2=4\beta^4D(\tfrac{7}{3}c_2-6c_3+4c_4),$$

$$a_0a_3=4\beta^5D(-2c_2+10c_3-16c_4+8c_5),$$

$$a_0a_4=4\beta^6D(\tfrac{62}{45}c_2-12c_3+34\tfrac{2}{3}c_4-40c_5+16c_6),$$

$$a_0a_5=4\beta^7D(-\tfrac{4}{5}c_2+11\tfrac{21}{45}c_3-53\tfrac{1}{3}c_4+106\tfrac{2}{3}c_5-96c_6+32c_7),$$

$$a_0a_6=4\beta^8D(\tfrac{127}{315}c_2-9\tfrac{1}{5}c_3+64\tfrac{4}{5}c_4-200c_5+304c_6-224c_7+64c_8).$$

β may be chosen so as to satisfy the auxiliary condition, $\sum_n c_n=1$, if it is desired to reproduce the observed dissociation energy D, or it may be used simply as an adjustable parameter to satisfy some other condition.

§6. ILLUSTRATIVE COMPUTATIONS ON $1s\sigma 2s\sigma\ {}^3\Sigma_g$ H_2

In Tables II to VI we summarize the results of a variety of treatments of the $1s\sigma 2s\sigma\ {}^3\Sigma_g$ state of H_2. This work was based on Sandeman's analysis of this state, as given in §2, except that some of the cruder curves were fitted to data derived from the results of Richardson and Davidson.[16] The difference for these curves is inappreciable.

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[16] O. W. Richardson and P. M. Davidson, Proc. Roy. Soc. **A125**, 23 (1929).

TABLE IV. *Values of* Y_{lj}.

CURVE	Y_{00}''	Y_{10}'	Y_{10}''	Y_{20}'	Y_{20}''	Y_{30}'	Y_{40}'	Y_{01}'	Y_{01}''	Y_{11}'	Y_{11}''	Y_{21}'	Y_{31}'
1	0	2665.34	0	−72.609	0	0	0	34.216	—	−1.2037	—	−0.03288	—
2	0	2665.34	0	−72.087	0	0	0	34.216	—	−1.1899	—	−0.03276	—
3	0	2665.34	0	−91.356	0	0	0	34.216	—	−1.6709	—	−0.03647	—
4	0	2751.3	0	−93.663	0	0	0	34.216	—	−1.6709	—	+0.02419	—
5	4.82	2665.34	−0.26	−72.087	0	0	0	34.216	—	−1.6709	—	−0.00071	—
6	5.24	2655.41	−0.26	−66.223	0	0	0	34.144	−0.012	−1.5754	+0.0005	0.00292	−0.000218
7	5.66	2664.2	—	−68.66	—	0.1068	—	34.216	—	−1.6709	—	−0.0777	—
8	5.66	2664.2	—	−68.66	—	0.2080	—	34.216	—	−1.6709	—	0.0212	—
9	5.18	2665.3	−0.67	−70.630	0.033	0.2842	−0.063	34.216	−0.008	−1.6708	+0.0006	0.0212	−0.00375
10	4.82	2665.34	+4.60	−72.087	—	1.0715	—	34.216	—	−1.6709	—	−0.0826	—
11	5.16	2667.40	−0.61	−72.920	−0.016	1.2406	−0.1146	34.240	−0.002	−1.7217	−0.0008	0.0476	−0.00466
12	—	2665.92	—	−72.794	—	1.4295	—	34.221	—	−1.6949	—	0.03455	—
13, 14	4.90	2665.81	+0.11	−72.549	−0.235	1.4286	−0.1468	34.223	−0.003	−1.6895	−0.0053	0.03456	−0.00203

Table II specifies the constants which define the several curves, while Table III presents the derived values of the Dunham coefficients, as far as they have been worked out. Table IV gives for the curves the computed values of Y_{lj}' and, in certain cases, of Y_{lj}'', to illustrate the rapidity of convergence of the W. B. K. process. Table V exhibits the divergences between the curves, gives values for curve 14, the best of these curves, and the differences from this of the other curves. The location of these curves with respect to each other involves some degree of arbitrariness. In practice one would use the observed energy level separations to determine the form of the potential curve; the absolute location of the curve would be adjusted to produce as satisfactory an agreement as possible between computed and observed term values. We have considered the curves to be so located that the lowest computed energy level coincides with lowest observed energy level, a process designed to give maximum accuracy of the curve in the general neighborhood of the minimum. Finally, Table VI exhibits the errors in E_v and in $r_v = (Rm/\mu B_v)^{\frac{1}{2}}$, the effective nuclear separation for the determination of the rotational terms of the vth vibrational state. Our method of adjusting the curves gives automatically zero error in E_0; to exhibit the differences in the curves near the minimum we give also the deviation of the minima of the curves from the minimum of curve 14, which we believe to be essentially correct.

A comparison of Tables V and VI affords a test of the correlations between errors in curves and errors in energies, as discussed in §4, by taking curve 14 as the standard of comparison. (Because of the smallness of the errors of the energies of this curve, Table VI gives essentially the deviations of the energies of the other curves from those of curve 14.) The turning points are roughly 1.6 and 2.2 for $v=0$, 1.45 and 2.5 for $v=1$, 1.35 and 2.8 for $v=2$, and 1.3 and 3.0 for $v=3$; the errors for a given v in Table VI should be correlated with those in Table V for the corresponding ranges in r. Fig. 2 shows the correlation graphically for two of the cruder curves.

We now discuss the individual curves, explaining their construction and estimating their defects. For the latter purpose we shall take curve 14 as a provisional standard, later attempting an estimate of the errors in this curve, as compared to the ideal curve for the state.

TABLE V. *Deviations of potential curves from curve* 14, (*given in first line*).*

CURVE	$r=1.3$	1.5	1.7	1.9	2.1	2.3	2.5	2.7	2.9
14	8487	2855	487	15	660	1958	3619	5461	7363
1–14	−891	−151	−4	+5	+15	+50	+91	+119	+119
2–14	−906	−154	−4	+5	+15	+52	+98	+131	+138
3–14	−433	−42	+9	+10	0	−26	−106	−258	—
4–14	+112	+109	−1	−31	−1	+56	+65	+2	−141
5–14	+32	+1	−1	+1	+1	−1	−10	−39	−87
6–14	−27	+2	+11	+1	−9	−10	−2	+8	+19
7–14	+1010	+52	+5	+5	+5	−8	−22	−65	−135
8–14	+78	+21	+5	+5	+5	0	+2	0	−5
9*a*–14	+3	+6	+6	+5	+5	+6	+5	−5	−30
9*b*–14	−2	+1	+1	0	0	+1	0	−10	−35
10–14	+5735	+39	−2	−2	−2	−4	−32	−83	−167
11–14	−13	0	−3	+1	+2	+3	+1	−2	−6
12–14	−50	0	0	0	0	+3	+50	+333	—
13–14	−7	0	0	0	0	0	+11	+122	+783

* Curves are adjusted to have the same lowest vibrational level. For curves 1 to 6, this can be calculated exactly. For curves 7, 8, and 9*a* the Hylleraas approximation has been used. 9*b* is the same curve as 9*a* relocated with the aid of the Dunham formulas, which have also been used for curves 10 to 14. Curve 14 is estimated to be correct within 1 cm^{-1} from $r=1.5$ to 2.5 inclusive, too low by about 2 cm^{-1} at 2.7, and by about 8 cm^{-1} at 2.9. At 1.3 its value is unreliable because of the steepness of the curve.

TABLE VI. *Errors in reproduction of energy levels by the potential curves.**

	Vibration						Rotation					
			Errors in E_v					Errors in $r_v\times 10^4$				
Curve	Method	Error at minimum	$v=1$	$v=2$	$v=3$	$v=4$	Method	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
1	1	5.3	−4.2	−17.6	−44.0		2	−63	−177	−269	−339	
2	1	5.2	−3.2	−14.4	−37.1		2	−65	−183	−281	−356	
3	1	10.0	−41.7	−130.1	−269.0		2	3	37	119	256	
4	1	−32.4	39.6	28.1	−38.8	−163.6	2	−1	−4	−7	−14	−30
5	1	0.5	−3.4	−14.9	−38.5	−77.0	2	0	12	41	91	155
6	1	3.6	−1.6	0.4	2.1	0.5	3	10	−8	−14	−7	10
7	5	4.9	2.9	5.9	6.3	3.2	2	6	66	206	447	
8	5	4.9	3.2	8.2	14.4	24.2	2	−1	−2	−1	−1	−6
9	5	4.8	0.8	0.1	−1.0	1.8						
	2	4.8	0.6	−1.3	−8.2	−21.2	2	−1	−2	−1	−1	−6
	3	0.0	−0.3	−5.0	−19.4	−49.1	3	1	4	20	59	127
10	2	5.0	0.3	2.2	8.0	21.5	2	6	69	216	470	
	3	−2.0	5.0	11.5	22.0	40.0						
11	3	−0.6	0.0	−1.8	−7.7	−21.2	3	−2	1	4	12	32
13	3	0.0	−0.1	−1.0	−5.4	−17.9	3	0	0	0	0	1
14	4	0.0	0.0	−0.1	−1.0	−3.4	4	0	0	2	6	18

* The approximation used in computing each set of entries is indicated in columns 2 and 8. 1 indicates use of an exact expression; 2, use of a trinomial expression in $v+\frac{1}{2}$; 3, use of all the terms given by Dunham; 4, use of Dunham's terms supplemented by results of numerical integrations; 5, use of the formula of Hylleraas.

Morse curves

Curve 1 is the Morse curve as generally constructed, reproducing experimental values of B_e, ω_e, and D, while curve 2 is designed to reproduce the experimental B_e, ω_e, $\omega_e x_e$. In the case of this particular state it happens that these two methods of construction give almost the same results, for the relation required by the Morse curve, $D=\omega_e^2/4\omega_e x_e$, is nearly satisfied by the experimental values. Usually a considerably greater difference will be found. The second method is preferable in determining the curve near the minimum. The errors in the computed E_v show that these curves tend to give excessive separations of classical turning-points, while the too-slow increase of r_v with v shows that they are too symmetrical about the minimum. Fig. 2 shows the net effect of these errors, the curves being much too low on the left and slightly too high on the right.

The Morse curve 3 was constructed in an attempt to improve the results by a better fitting of the rotational constants. It reproduces the observed α_e as well as B_e and ω_e; $\omega_e x_e$ then comes out much too large, so that the vibrational levels are very low. Fig. 2 shows that the result is an error which below $V=4000$ is approximately symmetrical; both sides of the curve are moved outward, with addition effects on E_v but compensating effects on r_v.

In constructing curve 4, which also gives the observed values of B_e and α_e, we concerned ourselves not with reproducing any vibrational constants, but with obtaining a good fit for the vibrational energy levels with $v\leqslant 4$. Both ω_e and $\omega_e x_e$ are then badly in error, but over the interesting range as a whole the energy levels and the potential curve itself are more satisfactory than for any other of the Morse curves. This is a good example of the advantages of direct fitting of energy levels over the reproduction of a limited number of spectroscopic constants; the flexibility of the Morse curve is, however, too limited to permit a really satisfactory fit.

Pöschl-Teller curves

Curve 5 is a Pöschl-Teller curve giving the observed ω_e, $\omega_e x_e$, B_e and α_e. As with the Morse function, practically the same curve is obtained if D is fixed instead of $\omega_e x_e$. (It is not possible to fix both D and $\omega_e x_e$ by sacrificing a rotational constant.) The errors in the energy levels indicate that the curve is quite good near the minimum, but that the classical turning points tend, with increasing v, to lie too far apart and too far to large r. Thus the curve must clearly lie too low on the right, as is verified by Table III, but the nature of the error on the left-hand side is not indicated by so simple an argument.

Curve 6 has been obtained by our method of energy level fitting, the energy levels used in its construction being those for $v \leqslant 4$. Since the vibrational levels of the P.-T. curve are exactly known, Y_{10} and Y_{20} could be chosen once for all to minimize the mean square errors in the computed E_v. Similar minimization of the errors in the B_v, by adjustment of Y_{01}' and Y_{11}', required the use of successive approximations, which converged rapidly. The computed E_v and B_v indicate that this curve has turning points too far apart at the bottom, (it must then be too shallow), too close together for $v=2$, 3, and too far apart above this; too far to the right for $v=0$, 4, and too far to the left in the intermediate region. In short, the errors of this curve are clearly small and of fluctuating sign, as also appears from Table IV. Since the sign of this error does fluctuate, it would of course be unjustified to assume that the magnitude of the errors in U is the same as that of the errors in E_v. In fact, the mean square error in the computed E_v is 1.2 cm^{-1}, while for $U(r)$ over the corresponding region it is about ten times as great. Comparison of this curve with curve 4 will indicate the great advantage of having one extra parameter to adjust by this method, though it is possible that the difference is unusually large for this state because of an especially appropriate character of the P.-T. curve.

Hylleraas curves

Curve 7 is a Hylleraas curve constructed as recommended by that author. According to his approximate formula for the vibrational levels these are excellently reproduced, the error remaining less than 10 cm^{-1} even up to $v=7$. The rotational terms are very bad, and indicate that beyond the range of $v=2$ the curve is as defective as the Morse curves 1 or 2, but in the opposite sense. This is caused by failure to control Y_{21} (the spectroscopic γ_e) which comes out large and with the wrong sign. (The same lack of control exists in a similar fitting of the Pöschl-Teller function, but it happens that the resulting error is there less serious.) Curve 8 represents an attempt to improve this curve by altering the value of the Hylleraas κ so as to get a satisfactory value of γ_e, while curve 9 was obtained by a general readjustment of constants to improve further the vibrational levels, as given by the Hylleraas approximation. The excellence of this result is, however, completely illusory; when E_v and r_v are computed for curve 9 from the more accurate formulas of Dunham it is found that the vibrational levels rapidly fall below the observed values as v rises, while r_v rises abruptly. Computation of the potential curve itself shows that it is little better than the Pöschl-Teller curve 5, except that it remains accurate over a somewhat larger range of r. We have not computed the exact levels of curves 7 and 8, but the magnitude of the errors in the Hylleraas approximation is evidently the same, since the errors in the computed potential curves, as compared to curve 14, are not of the character to be expected from the errors in E_v and r_v as given by that approximation.

Abandoning the Hylleraas approximate energy formula, we have determined curve 10 to give the experimental ω_e, $\omega_e x_e$, $\omega_e y_e$, D, B_e and α_e. The large size of the second order W. B. K. term Y_{10}'', and the inappropriate nature of the higher spectroscopic constants makes the result relatively poor.

Finally, abandoning preoccupation with the spectroscopic constants, we have determined curve 11 to give more satisfactory values for the energy levels, by a single application of the method of §4, with curve 9 as the starting point. The resulting curve is much the most satisfactory of the Hylleraas curves, and should be subject to further improvement by further application of this method.

We cannot recommend the Hylleraas curve as generally useful, since the curves to be described next give equal or greater flexibility and are more easily manipulated.

SERIES EXPANSION OF U

Curve 12 is a Dunham curve constructed with the coefficients a_0 to a_4 given by Sandeman, and designed to make the Y_{lj}' come out equal to the observed expansion coefficients as far as $\omega_e x_e$ and γ_e.[17] We have also determined a set of

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[17] Sandeman states that, for this set of a_n, Y_{10}'' has the very large value 16.5. This seems to be in error; we find the value -1.78, which is still much larger than the usual values.

a_n up to a_6 such that application of the full Dunham formulas gives Y_{lj} which, up to Y_{40}, and Y_{31}, are essentially equal to the corresponding constants in Sandeman's expansion. We have used these constants in determining curve 13, again setting equal to zero the a_n not explicitly determined. The difference of curves 12 and 13 thus illustrates the effect of failure to consider Y_{40}', Y_{31}', and the Y_{lj}''.

Finally, the extended Morse function, curve 14, has been determined, with the same set of a_n as for curve 13. These two curves agree in their first eight derivatives at their minima, but their different behavior as r becomes larger produces the differences exhibited in Table IV. Their energy levels are identical, so far as the formulas of Dunham will permit their computation; these values appear in Table VI as the levels for curve 13. A careful investigation of the higher vibrational levels, with results already stated in §3, served to determine more exactly the levels of curve 14 as shown in Table VI; the corrections for the higher levels are by no means negligible.

We may now undertake to estimate the errors in this curve in comparison with the "true" curve which gives the observed levels. Evidently this error is of the order 1 cm^{-1} for the range of $v=2$, for within this range the most important error is one of 0.0002 in r_2, corresponding to a depression of the order of 2 cm^{-1} at the outer turning point. Beyond this curve 14 becomes lower than the correct curve by a steadily increasing amount. Since this curve was taken as the standard in the preliminary estimation of the errors in the other curves, it follows that the entries in Table IV might now be corrected by subtracting the errors of curve 14. The only curve good enough to warrant this small correction is curve 6, which is evidently a better approximation for large values of r than is indicated by this table.

In order to check theoretical calculations the experimental potential curve must be located on the absolute energy scale, with zero energy that of the completely dispersed system. On this scale the energy of a normal H atom is -109678 cm^{-1}. Sandeman[18] computes a dissociation energy for H_2^+ of 21363 ± 5 cm^{-1}, a value checked experimentally, though with slightly less precision, by Beutler and Jünger.[19] Beutler and Jünger[20] also find for the ionization energy of $1s\sigma 2s\sigma\ ^3\Sigma_g$ H_2 the value 29344 ± 2 cm^{-1}. From these values one finds for the lowest energy level of this latter state the value -160385 ± 6 cm^{-1}. Using this result, and applying to curve 14 a correction of 2 cm^{-1} at $r=2.7$ and 8 cm^{-1} at $r=2.9$, we obtain the following most probable experimental values for the total and binding energies of this state:

$r=$	1.3	1.5	1.7	1.9	2.1	2.3	2.5	2.7	2.9
$-U$(cm^{-1})	153218	158850	161218	161690	161045	159747	158086	156242	154334
E(ev)	1.9885	2.6833	2.9754	3.0337	2.9540	2.7940	2.5891	2.3616	2.1262.

An appreciable uncertainty in these results, for points not too close to the minimum, arises from uncertainties in the values of the fundamental constants. U is accurately given as a function of $\xi=(r-r_e)/r_e$. The value of r_e, in cm, as deduced from B_e, depends on the values of h and μ. In atomic units its value depends on the quantity Rm/μ, which we have taken to be 119.371, corresponding to a ratio of 1838.6 for proton to electron mass. Recent discussions of the fundamental constants indicate that a slightly larger value of Rm/μ might be preferable. For comparison, we give a table of binding energies computed with $Rm/\mu=119.50$ (mass ratio 1836.6):

$r=$	1.3	1.5	1.7	1.9	2.1	2.3	2.5	2.7	2.9
E(ev) $=$	1.9853	2.6815	2.9747	3.0336	2.9546	2.7950	2.5904	2.3631	2.1278.

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[18] I. Sandeman, Proc. Roy. Soc., Edinburgh **55**, 72 (1935).

[19] H. Beutler and H.-O. Jünger, Zeits. f. Physik **101**, 304 (1936).

[20] H. Beutler and H.-O. Jünger, Zeits. f. Physik **101**, 285 (1936).