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Comparative Study of Empirical Internuclear Potential Functions*

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INTRODUCTION

A KNOWLEDGE of internuclear potential curves is of fundamental importance in a wide variety of fields ranging from gas kinetics to stellar structure. In particular, the recent increased interest in astrophysical problems has emphasized the need for accurate potential curves governing the interaction of two atoms in either their ground or excited states, i.e., the potential curves for the different electronic states of diatomic molecules. The interaction potential arises, for various nuclear separations, from the change in interaction of all the charged particles in the system from those existing at infinite separations of one or more of the atoms from the remainder of the system. For a diatomic system, the energy levels are determined from[1]

$$(\hat{H}_n+\hat{H}_e)\Psi=E\Psi, \tag{1}$$

where $\hat{H}_n$ and $\hat{H}_e$ depend, respectively, on nuclear coordinates alone, and electronic coordinates alone and are given by

$$\hat{H}_n=-\textstyle\sum_\alpha(h^2/8\pi^2M_\alpha)\nabla_\alpha^2+\hat{V}_{nn}, \tag{2}$$

$$\hat{H}_e=-\textstyle\sum_i (h^2/8\pi^2m)\nabla_i^2+\hat{V}_{ne}+\hat{V}_{ee}, \tag{3}$$

where $\hat{V}_{nn}$, $\hat{V}_{ne}$, and $\hat{V}_{ee}$ are the internuclear, nuclear-electron, and electron-electron-potential operators, respectively.

If the Born-Oppenheimer approximation is valid $\Psi=\psi_n\psi_e$ and

$$\hat{H}_e\psi_e=E_e\psi_e, \tag{4}$$

then,

$$(\hat{H}_n+E_e)\psi_n=E\psi_n. \tag{5}$$

Here, ψ_n depends only on the nuclear coordinates. E_e is the electronic energy which is a function of the internuclear distance r. According to Eq. (5), the potential-energy term appearing in the Hamiltonian for the nuclear motion is just the sum of E_e and V_{nn}. The problem of solving Eq. (4) for E_e is a highly complex one, incapable of exact solution at the present stage of mathematical advancement, except for the simple, triparticle systems H_2^+, etc. The difficulties are well exemplified by the calculations of Kolos and Roothaan[2] on the $X^1\Sigma_g^+$ and $B^1\Sigma_u^+$ states of the hydrogen molecule. To calculate E_e for the $X^1\Sigma_g^+$ state by a self-consistent-field procedure, 40- and 50-term wave functions were used. Excellent agreement with curves from experimental data was obtained at small displacements of the nuclei from the equilibrium position r_e. However, at bondlengths greater than 1.0 A, deviations occurred despite the complexity of the wave function used.[3] The reason, in this case, is that the wave functions are of the polynomial type which requires more and more terms, for increasing r, to approach the correct asymptotic form. Their results on the $B^1\Sigma_u^+$ state are not in as good agreement with the curve obtained from experimental data as in the case of the $X^1\Sigma_g^+$ state, but here only a 34-term wave function was used. Actually, the Kolos and Roothaan curves are in remarkably good agreement with the curves based on experimental data near $r=r_e$ and offer some hope that accurate calculated curves will soon be forthcoming for simple systems.

As the number of particles increases, however, the difficulties mount extremely quickly. At present, there does not seem to be much hope of obtaining accurate curves except for the simplest of systems. Furthermore, as the interacting atoms become more complicated, the number of electronic states arising from their interaction increases rapidly, thus compounding the difficulties.

Clearly, alternative procedures for obtaining potential curves are desirable, indeed essential at the present time. Potential curves for diatomic systems fall mainly into two categories, ones with appreciable minima (bound states) and ones which exhibit a very shallow minimum or none at all (repulsive states); we are concerned with the former. Three general methods exist for obtaining curves for the bound states of diatomic molecules. The first and perhaps most satis-

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factory of these is the calculation of the curve from the experimental energy levels using the method of Rydberg, Klein, and Rees (RKR).[4–7] This is a WKB method where one starts with the observed-energy levels E and from these calculates the maximum and minimum points of the vibration. Since this is a WKB method, one might expect this to be somewhat in error near r_e. However, the results near the minimum agree with the curve calculated by the Dunham procedure which is known to be accurate in this region.[7] Indeed, Jarmain[8] has shown that the two are equivalent for the lower-vibrational-energy levels. One major disadvantage of the RKR method is that the potential curve can be constructed only in the region for which sufficient spectroscopic data exist. For this reason, other reliable techniques must be found.

The second general method is due to Dunham.[9] He used the WKB method to show that the energy levels have the form

$$E_{vJ}=\sum_{l,j} Y_{lj}(v+\tfrac{1}{2})^l J^j(J+1)^j, \tag{6}$$

where l and j are summation indices and v and J are the vibrational and rotational numbers, respectively, and where the Y_{lj} are coefficients which can be determined from the experimental rotational and vibrational levels. Here, the energy zero is taken at the minimum of the potential curve. If the potential is assumed to be of the form

$$V=a_0\left(\frac{\Delta r}{r_e}\right)^2\left[1+a_1\left(\frac{\Delta r}{r_e}\right)+a_2\left(\frac{\Delta r}{r_e}\right)^2+a_3\left(\frac{\Delta r}{r_e}\right)^3+\cdots\right]$$
$$+B_eJ(J+1)\left[1-2\frac{\Delta r}{r_e}+3\left(\frac{\Delta r}{r_e}\right)^2-4\left(\frac{\Delta r}{r_e}\right)^3+\cdots\right], \tag{7}$$

where $\Delta r=r-r_e$, then the a_i's can be related to the Y_{lj}'s. Since the Y_{lj}'s are determined from the experimental data, the potential function based on this data can be determined from Eq. (7). The most serious drawback of the Dunham method is that it diverges as the energy approaches the dissociation limit and, hence, must be used with care at the higher-vibrational levels.

The third general method is based on empirical potential functions. The assumption is made that all bonding-potential curves can be fitted to a certain form of algebraic expression when the parameters in the expression are evaluated from the known spectroscopic constants. Numerous attempts to find suitable functions have been made. The parameters of these proposed functions can be related to the spectroscopic constants and also to the dissociation energy. For example, the vibrational frequency ω_e and the dissociation energy D_e are given by the classical expressions

$$V''(r_e)=k_e=4\pi^2c^2\omega_e^2\mu$$
$$V(r_e)-V(\infty)=D_e \tag{8}$$

and these enable one to determine two parameters in the assumed-potential expression. By solving the Schrödinger equation with the assumed form for $V(r)$, the other parameters in the expression can be related to the higher-order spectroscopic constants. The whole procedure of relating the parameters in the assumed-potential expression is greatly simplified by expanding the assumed potential and putting it in the form given by Eq. (7). Then, the parameters are given directly in terms of the Y_{lj}'s as determined by the Dunham method.[9] However, since the fit of all potential curves to a given algebraic expression must be considered as approximate, the only useful parameters are the harmonic and the first-order correction terms. This limits the number of paramters in the function to five for them to be determinate. Therefore, if the potential function contains fewer than five parameters, internal relationships among the spectroscopic constants exist.

The performance of a given function in correlation of these spectroscopic constants may be used as a first criterion for reliability of the function. Varshni[10] has examined a selection of the better known three-parameter functions on this basis, expressing the results graphically by plotting $G=(8\omega_ex_e/B_e)$ and $F=(\alpha_e\omega_e/6B_e^2)$ against $\Delta=(k_er_e^2/2D_e)$ and comparing with the experimental plots.

A far more stringent test of an empirical potential function lies in the comparison of the $V(r)$ vs r dependence with the curves for the different states of different molecules as determined from either the RKR or the Dunham method. The only published work known to the authors in which this has been done is the original work of Rydberg[4] and the work of Vanderslice *et al.* on the ground state of the hydrogen molecule.[7]

In view of the considerable importance of the empirical functions in supplementing curves obtained from the RKR and Dunham methods, and in view of the fact that for many highly excited states of diatomic molecules, it is the only way at present of obtaining anywhere near reliable potential curves, a systematic and thorough comparison of a number of the better-known and more widely used functions is believed to be useful. Two criteria exist for testing the validity of a given expression, as indicated in the foregoing. The first is the testing of internal correlations resulting from the use of less than five parameters in a function. Although Varshni[10] has carried out fairly extensive comparisons of this nature, a quantitative reassessment in terms of average percent deviation is felt to be a

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very useful addition to the problem. This is a strict test of the validity of the function close to the equilibrium configuration, but good results here do not necessarily mean that the function accurately represents the potential at small or large internuclear distances.

The second criterion is a comparison of the calculated curves with those given by the RKR method. Although the basic procedure, as enunciated by Rydberg,[4] was published in 1931, no extensive comparisons have been made. The quantity of experimental data now available is considerable, thus allowing for such comparisons. This is a more thorough and satisfying test of the long-range validity of the function.

The choice of ground states and excited states of diatomic molecules for which a test of this second criterion may be carried out is of necessity limited to molecules to which the RKR method has been applied. The following 19 examples are used in this comparative study. These are: the $X^1\Sigma_g^+$ state of H_2;[3] the $X^1\Sigma_g^+$ state of I_2;[11] the $X^1\Sigma_g^+$, $A^3\Sigma_u^+$, $a^1\Pi_g$, and $B^3\Pi_g$ states of N_2;[12] the $X^3\Sigma_g^-$, $B^3\Sigma_u^-$, and $A^3\Sigma_u^+$ states of O_2;[13] the $X^1\Sigma^+$, $d^3\Delta$, $A^1\Pi$, $e^3\Sigma^-$, and $a'^3\Sigma^+$ states of CO;[14] the $X^2\Pi_{\frac{1}{2}}$ and $B^2\Pi$ states of NO;[15] the $X^2\Pi_i$ and $A^2\Sigma^+$ states of OH;[16] and the $X^1\Sigma^+$ states of HF.[17]

EMPIRICAL FUNCTIONS FOR COMPARATIVE STUDY

Since Varshni[10] has given a discussion of the different empirical potential functions as well as of the criteria which should be satisfied by the functions, we emphasize only a few salient points.

Most of the proposed potential functions have been given in closed analytical form and make use of three parameters. Four- and five- parameter functions have also been proposed which usually are extensions of known three-parameter functions. All parameters must be evaluated in terms of known spectroscopic constants. Three-parameter functions can be evaluated by the quantities: equilibrium-bond length r_e, vibrational frequency for zero displacement of the nuclei ω_e, and bond-dissociation energy from the bottom of the potential curve D_e. The first two of these quantities are usually known if the state in question has been studied experimentally whereas the third D_e may or may not be well known, in which case a three-parameter function cannot be used to construct the potential curve unless a reasonably reliable method is available for predicting D_e from interrelations among the spectroscopic constants. This has been done with varying degrees of success for some of the proposed functions.

Five-parameter functions must be evaluated with the aid of two additional spectroscopic quantities. They usually are taken as the vibrational anharmonicity $\omega_e x_e$ and the vibrational rotational-coupling constant α_e. These quantities are usually not as well known for a given state as r_e and ω_e and, unless a state has been extensively studied spectroscopically, they may be unknown or known only with rather doubtful accuracy.

For three-parameter functions, conditions (8) along with

$$(dV/dr)_{r_e}=0 \tag{9}$$

are used with r_e, ω_e, and D_e to compute the three parameters. The higher derivatives $(d^3V/dr^3)_{r_e}$ and $(d^4V/dr^4)_{r_e}$ can then be used to predict or correlate the quantities $\omega_e x_e$ and α_e. For five-parameter functions, the higher derivatives must be used along with $\omega_e x_e$ and α_e to compute the parameters of the function.

In order to demonstrate the relation of the various spectroscopic constants used in describing the observed energy levels of a nonrigid, rotating, anharmonic oscillator to the parameters of any empirical function which may be expanded in a power series in $(r-r_e)$, it is sufficient to use the method of Dunham.[9] If B_e/ω_e is sufficiently small, which is the usual case, with the possible exception of hydrides, the Y_{lj}'s in Eq. (6) are related to the experimentally determined, molecular constants as follows:

$$\begin{array}{llll} Y_{10}=\omega_e & Y_{20}=-\omega_e x_e & Y_{30}=\omega_e y_e & Y_{40}=\omega_e z_e \\ Y_{01}=B_e & Y_{11}=-\alpha_e & Y_{21}=\gamma_e & . \\ Y_{02}=-D_e & Y_{12}=\beta_e & & \\ Y_{03}=H_e & & & \end{array} \tag{10}$$

Here, the experimentally determined, molecular levels are given by

$$\begin{aligned} E_{vJ}=&\,\omega_e(v+\tfrac{1}{2})-\omega_e x_e(v+\tfrac{1}{2})^2+\omega_e y_e(v+\tfrac{1}{2})^3 \\ &+\omega_e z_e(v+\tfrac{1}{2})^4+\cdots+B_vJ(J+1)-D_vJ^2(J+1)^2 \\ &+H_vJ^3(J+1)^3+\cdots, \end{aligned} \tag{11}$$

with $B_v=B_e-\alpha_e(v+\frac{1}{2})+\gamma_e(v+\frac{1}{2})^2$ and $B_e=h/8\pi^2\mu r_e^2$. Dunham's method shows that

$$\omega_e^2=4a_0B_e \quad \text{or} \quad D_e=a_0/\Delta \tag{12}$$

$$\omega_e x_e=(B_e/2)[3(a_2-5a_1^2/4)] \quad \text{or} \quad G=12(a_2-5a_1^2/4) \tag{13}$$

$$\omega_e y_e=(B_e^2/2\omega_e)[10a_4-35a_1a_3-17(a_2^2/2)+(225a_1^2a_2/4)-705a_1^4/32] \tag{14}$$

$$-\alpha_e=(B_e^2/\omega_e)[6(1+a_1)] \quad \text{or} \quad F=1+a_1 \tag{15}$$

$$\gamma_e=(6B_e^3/\omega_e^2)[5+10a_1-3a_2+5a_3-13a_1a_2+15(a_1^2+a_1^3)/2] \tag{16}$$

$$D_e=(4B_e^3/\omega_e^2), \tag{17}$$

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TABLE I. Summary of information on various empirical, potential-energy expressions.[a]

Name of function	Expression for V	Relations between parameters and spectroscopic constants	Predicted expression for α_e	Predicted expression for $\omega_e x_e$
Morse[18]	$D_e[1-e^{-ax}]^2$ $x=(r-r_e)$	$a=(k_e/2D_e)^{\frac{1}{2}}$	$(6B_e^2/\omega_e)(\Delta^{\frac{1}{2}}-1)$	$\omega_e^2/4D_e$
Hulburt-Hirschfelder[19,b]	$D_e[(1-e^{-ax})^2+ca^3x^3e^{-2ax}(1+abx)]$ $x=(r-r_e)$	$a=(k_e/2D_e)^{\frac{1}{2}}$ $b=2-\dfrac{1}{c}\left\{\dfrac{7}{12}-\dfrac{1}{a^2r_e^2}\left[\dfrac{5}{4}+\dfrac{5F}{2}+\dfrac{5F^2}{4}-\dfrac{G}{12}\right]\right\}$ $c=1-(1/ar_e)(1+F)$	...	...
Rosen-Morse[20]	$A\tanh(r/d)-C\,\mathrm{sech}^2(r/d)$	$\Delta=(r_e/d)^2[1+\tanh(r_e/d)]^2$ $A=-2C\tanh(r_e/d)$ $C=\dfrac{D_e}{[1-\tanh(r_e/d)]^2}$	$\dfrac{6B_e^2}{\omega_e}\left[\dfrac{2r_e}{d}\tanh\left(\dfrac{r_e}{d}\right)-1\right]$	$B_e\Delta[1-e^{-2r_e/d}+e^{-4r_e/d}]$
Rydberg[4]	$D_e[1-(1+dx)e^{-dx}]$ $x=(r-r_e)$	$d=(k_e/D_e)^{\frac{1}{2}}$	$(6B_e^2/\omega_e)[\frac{2}{3}(2\Delta)^{\frac{1}{2}}-1]$	$(11/12)B_e\Delta$
Pöschl-Teller[21]	$M\cosh^2(ar/2)$ $-N\,\mathrm{sech}^2(ar/2)$	$a=(k_e/4D_e)^{\frac{1}{2}}$ $N=D_e/[(1-y^2)^2]$ $M=Ny^4$ $y=\tanh(ar_e/2)$	$(6B_e^2/\omega_e)[\Delta^{\frac{1}{2}}\coth\Delta^{\frac{1}{2}}-1]$	$B_e\Delta$
Linnett[22]	a/r^m-be^{-nr} $(m=3)$	$\Delta=m(m+1-nr_e)nr_e/[2(m-nr_e)]$ $a=D_er_e^m[nr_e/(m-nr_e)]$ $b=mae^{nr_e}/nr_e^{m+1}$	$\dfrac{6B_e^2}{\omega_e}\left[\dfrac{(m+1)(m-1)-(nr_e)^2+3nr_e}{3(m+1-nr_e)}\right]$	$\dfrac{5B_e}{24}\left[\dfrac{20-(nr_e)^2}{4-nr_e}\right]$ $-\frac{1}{8}B_e[120-(nr_e)^3]/[4-nr_e]$
Frost-Musulin[23]	$e^{-ar}[c/r-b]$	$a=[(1+2\Delta)^{\frac{1}{2}}-1]/r_e$ $b=D_ee^{ar_e}[1+ar_e]$ $c=aD_er_e^2e^{ar_e}$	$\dfrac{2B_e^2}{\omega_e}\dfrac{(ar_e)[2(ar_e)+3]}{[(ar_e)+2]}$	$\dfrac{B_e\left\{\begin{array}{l}11(ar_e)^4+66(ar_e)^3\\ \quad+156(ar_e)^2+144(ar_e)+36\end{array}\right\}}{24[(ar_e)+2]^2}$
Varshni III[10]	$D_e\left\{1-\dfrac{r_e}{r}\exp[-\beta(r^2-r_e^2)]\right\}^2$	$\beta=(1/2r_e^2)[\Delta^{\frac{1}{2}}-1]$	$\dfrac{6B_e^2}{\omega_e\Delta^{\frac{1}{2}}}[\Delta-2\Delta^{\frac{1}{2}}+2]$	$\dfrac{B_e}{8}\left\{8\Delta-12\Delta^{\frac{1}{2}}+66-\dfrac{111}{\Delta^{\frac{1}{2}}}+\dfrac{73}{\Delta}\right\}$
Lippincott[24–28]	$D_e(1-e^{-x})\{1-abx^{\frac{1}{2}}\exp[-b(xr_e/r)^{\frac{1}{2}}]\}$ $b=1.065$	$x=n(r-r_e)^2/2r$ $n=2\Delta/r_e$ $a=(\frac{4}{5})(1-\Delta^{\frac{1}{2}}/b)$	$(6B_e^2/\omega_e)ab\Delta^{\frac{1}{2}}$	$\dfrac{B_e}{8}\left\{\begin{array}{l}3+12ab\Delta^{\frac{1}{2}}+6\Delta\\ \quad+15a^2b^2\Delta-12ab^2\Delta\end{array}\right\}$

[a] The following definitions[10] are used in the table: $\Delta=k_er_e^2/2D_e$ $F=\alpha_e\omega_e/6B_e^2$ $G=8\omega_ex_e/B_e$.

[b] The reviewer has pointed out to us that the expression for the constant b given in the original Hulburt-Hirschfelder paper is in error. The correct one, given in this table, was used for the final calculations reported in this paper. [See H. M. Hulburt and J. O. Hirschfelder, J. Chem. Phys. **35**, 1901 (L), (1961).]

TABLE II. Molecular constants used in calculations.[a]

Molecule	State	ω_e (cm^{-1})	r_e (A)	B_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	α_e (cm^{-1})	D_e (ev)
H_2	$X^1\Sigma_g^+$	4400.39	0.74173	60.8407	120.815	3.0177	4.7467
I_2	$X^1\Sigma_g^+$	214.518	2.668	0.03734	0.6127	1.208×10^{-4}	1.5571
N_2	$X^1\Sigma_g^+$	2358.07	1.0976	1.9987	14.188	0.0171	9.902
	$A^3\Sigma_u^+$	1460.60	1.2867	1.4545	13.851	0.01798	3.690
	$a^1\Pi_g$	1693.7	1.2197	1.6181	13.825	0.0183	6.07
	$B^3\Pi_g$	1735.42	1.2128	1.6375	15.198	0.01794	4.90
O_2	$X^3\Sigma_g^-$	1580.36	1.20740	1.44566	12.0730	0.01579	5.2129
	$B^3\Sigma_u^-$	700.36	1.604	0.819	8.0023	0.011	1.005
	$A^3\Sigma_u^+$	801.0	1.5183	0.9142	13.81	0.0165	0.8239
CO	$X^1\Sigma^+$	2169.829	1.12822	1.9312	13.295	0.0175	11.245
	$d^3\Delta$	1137.79	1.3770	1.296	7.624	0.0171	3.516
	$A^1\Pi$	1515.61	1.2351	1.6116	17.2505	0.02229	3.175
	$e^3\Sigma^-$	1093.99	1.3933	1.2663	9.578	0.0179	3.147
	$a'^3\Sigma^+$	1230.65	1.3518	1.3453	11.0130	0.01872	4.324
NO	$X^2\Pi_{\frac{1}{2}}$	1904.03	1.1590	1.6809	13.97	0.0174	6.609
	$B^2\Pi$	1036.96	1.4176	1.1226	7.603	0.0121	3.29
OH	$X^2\Pi_i$	3734.09	0.9705	18.867	82.665	0.708	4.624
	$A^2\Sigma^+$	3203.28	1.0117	17.358	113.85	0.7868	2.53
HF	$X^1\Sigma^+$	4137.25	0.91717	20.946	88.726	0.7888	6.114

[a] These constants are consistent with the data used in the calculation of the experimental-potential curves by the RKR method. The references to the original data are given in references (7), (11)–(17).

where, following Varshni,[10] we define

$$F=\alpha_e\omega_e/6B_e^2,\quad G=8\omega_e x_e/B_e \tag{18}$$

and $\Delta=k_e r_e^2/2D_e$. Additional relations are available relating higher-order terms.

By expanding any proposed function in a power series of the form of (7), one has a convenient method of relating the parameters of the function to the known, spectroscopic constants. Also, it is convenient to use Eqs. (12) to (17) to evaluate any additional spectroscopic quantities not used in determining the parameters.

We have chosen nine empirical functions for this comparative study of internuclear potentials. Each function is evaluated for its ability to reproduce the potential curve as determined by the RKR method and for its ability to predict $\omega_e x_e$ and α_e or other spectroscopic quantities such as bond-dissociation energy. After careful consideration of all proposed functions known to us, we have selected the following for consideration: Morse[18]; Hulburt-Hirschfelder[19]; Rosen-Morse[20]; Rydberg[4]; Pöschl-Teller[21]; Linnett[22]; Frost-Musulin[23]; Varshni[10]; and Lippincott.[24–28] Several factors affected this selection, including: known performance, form of the function, ability to correlate spectroscopic quantities, number of parameters, etc. The selection covers a sufficiently wide range of types so as to make an effective comparative study of empirical potential functions.

Table I summarizes the necessary information on these potential functions. The relations between the parameters and the spectroscopic constants were obtained from Eqs. (8) and (9). The predicted expressions for α_e and $\omega_e x_e$ for each potential function were obtained from Eqs. (12) to (17). The results in Table I agree with those of Varshni[10] except for the Linnett and Lippincott functions.[29]

Varshni[10] has proposed a number of functions for consideration as empirical internuclear potentials. We have used his III function in the comparison study here since it appears to be the best over-all function of those he proposed.[10]

The spectroscopic data needed for the evaluation of the parameters of the potential curves are given in Table II.

RESULTS

The results of this comparative study are shown in Tables III to XXIV. Tables III to XXI show the comparison between the RKR and various empirical potential curves for all the molecular states considered. Tables XXII and XXIII give a comparison between the calculated and observed values of $\omega_e x_e$ and α_e for the various functions. Table XXIV gives a summary of the results showing the average percent errors from the experimental values for $\omega_e x_e$ and α_e and the average percent error for the quantity $(|V-V_{\mathrm{RKR}}|)/D_e$ for

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TABLE III. Results of potential-curve calculations for $X^1\Sigma_g^+$ state of H_2.[a]

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
0.4109	4.729	3.868	4.652	3.680	4.854	6.918	5.787	3.189	4.187	4.946
0.4319	3.880	3.243	3.823	3.097	3.950	4.745	4.629	2.721	3.498	4.038
0.4597	2.935	2.533	2.913	2.435	2.982	3.930	3.421	2.172	2.716	3.054
0.5088	1.730	1.558	1.724	1.508	1.745	2.154	1.938	1.384	1.648	1.790
0.6337	0.269	0.259	0.268	0.256	0.269	0.291	0.279	0.248	0.264	0.272
0.8833	0.269	0.275	0.270	0.279	0.269	0.250	0.261	0.287	0.273	0.264
1.2186	1.730	1.734	1.724	1.790	1.687	1.450	1.608	1.869	1.757	1.608
1.5148	2.935	2.870	2.902	2.975	2.815	2.395	2.721	3.084	2.959	2.667
1.8524	3.880	3.715	3.782	3.838	3.672	3.183	3.628	3.924	3.846	3.500
2.3748	4.522	4.358	4.413	4.454	4.339	3.931	4.371	4.489	4.467	4.205
2.2835	4.729	4.679	4.690	4.712	4.676	4.491	4.712	4.714	4.714	4.626
4.23	4.745	4.736	4.737	4.743	4.735	4.673	4.745	4.743	4.743	4.722
6.35	4.747	4.747	4.747	4.747	4.747	4.744	4.747	4.747	4.747	4.747

[a] The energies given in Tables III–XXI are in ev.

TABLE IV. Results of potential-curve calculations for $X^1\Sigma_g^+$ state of I_2.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
2.288	1.500–1.556	1.637	1.521	1.548	1.634	1.285	1.458	1.603	1.451	1.593
2.292	1.493	1.589	1.475	1.504	1.587	1.251	1.417	1.561	1.412	1.545
2.309	1.245	1.399	1.297	1.328	1.398	1.114	1.256	1.372	1.255	1.363
2.336	0.977	1.131	1.048	1.080	1.130	0.919	1.027	1.107	1.029	1.105
2.423	0.465	0.517	0.482	0.500	0.517	0.446	0.483	0.503	0.487	0.507
3.056	0.465	0.411	0.452	0.422	0.411	0.506	0.436	0.404	0.445	0.417
3.389	0.977	0.848	0.951	0.879	0.848	1.204	0.914	0.840	0.945	0.866
3.671	1.245	1.111	1.231	1.151	1.111	1.732	1.194	1.104	1.216	1.135
4.448	1.493	1.445	1.501	1.475	1.445	2.598	1.502	1.438	1.474	1.464
6.522	1.551	1.555	1.555	1.556	1.555	2.602	1.557	1.55	1.555	1.556
8.814	1.556	1.557	1.557	1.557	1.557	2.106	1.557	1.55	1.557	1.557

TABLE V. Results of potential-curve calculations for $X^1\Sigma_g^+$ state of N_2.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
0.896	5.021	5.128	4.925	4.926	5.166	5.181	4.801	4.950	4.854	5.207
0.919	3.865	3.764	3.624	3.634	3.784	3.791	3.551	3.673	3.597	3.809
0.942	2.618	2.673	2.582	2.595	2.685	2.684	2.543	2.618	2.576	2.704
0.983	1.280	1.290	1.256	1.263	1.294	1.289	1.244	1.272	1.258	1.302
1.027	0.435	0.433	0.426	0.427	0.434	0.431	0.424	0.432	0.426	0.429
1.185	0.435	0.434	0.443	0.439	0.435	0.436	0.445	0.432	0.444	0.430
1.261	1.280	1.252	1.297	1.277	1.251	1.267	1.305	1.267	1.303	1.245
1.358	2.618	2.510	2.639	2.580	2.507	2.573	2.662	2.559	2.678	2.503
1.447	3.865	3.675	3.893	3.795	3.671	3.811	3.941	3.740	3.988	3.668
1.528	5.021	4.656	4.949	4.820	4.651	4.883	5.025	4.742	5.102	4.653

TABLE VI. Results of potential-curve calculations for the $A^3\Sigma_u^+$ state of N_2.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
1.046	2.257	3.181	2.968	3.023	3.194	2.973	2.878	3.066	2.910	3.178
1.089	1.564	1.886	1.772	1.813	1.892	1.780	1.741	1.838	1.771	1.884
1.145	0.780	0.822	0.783	0.800	0.824	0.784	0.778	0.804	0.791	0.821
1.203	0.268	0.243	0.236	0.239	0.244	0.235	0.236	0.233	0.238	0.242
1.405	0.268	0.281	0.291	0.285	0.280	0.291	0.291	0.286	0.290	0.279
1.503	0.780	0.733	0.778	0.752	0.733	0.784	0.775	0.745	0.779	0.736
1.633	1.564	1.379	1.486	1.424	1.378	1.533	1.483	1.399	1.507	1.389
1.756	2.257	1.924	2.082	1.994	1.923	2.210	2.086	1.950	2.129	1.942

TABLE VII. Results of potential-curve calculations for $a^1\Pi_g$ state of N_2.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
1.013	2.686	2.69	2.70	2.59	2.70	2.69	2.52	2.61	2.55	2.72
1.036	2.016	2.00	2.00	1.93	2.00	1.99	1.89	1.95	1.91	2.02
1.077	1.103	1.08	1.08	1.06	1.09	1.08	1.04	1.07	1.05	1.09
1.139	0.311	0.30	0.29	0.29	0.30	0.30	0.29	0.30	0.29	0.30
1.325	0.311	0.32	0.32	0.32	0.32	0.32	0.33	0.33	0.33	0.32
1.445	1.103	1.10	1.11	1.13	1.10	1.13	1.16	1.13	1.16	1.10
1.564	2.016	1.99	2.01	2.05	1.99	2.07	2.13	2.03	2.15	1.99
1.655	2.686	2.63	2.67	2.72	2.63	2.77	2.84	2.69	2.88	2.63

TABLE VIII. Results of potential-curve calculations for $B^3\Pi_g$ state of N_2.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
0.983	3.500	4.05	3.65	3.85	4.07	3.84	3.67	3.89	3.72	4.06
1.006	2.738	3.05	2.78	2.92	3.06	2.91	2.80	2.94	2.85	3.05
1.037	1.880	2.01	1.85	1.94	2.01	1.92	1.87	1.95	1.90	2.00
1.082	0.932	0.97	0.92	0.95	0.97	0.94	0.92	0.95	0.94	0.97
1.132	0.319	0.32	0.31	0.31	0.32	0.32	0.31	0.32	0.31	0.32
1.316	0.319	0.31	0.32	0.32	0.31	0.32	0.32	0.32	0.32	0.31
1.409	0.932	0.88	0.93	0.90	0.88	0.93	0.93	0.90	0.93	0.88
1.531	1.880	1.71	1.84	1.77	1.71	1.87	1.84	1.74	1.87	1.72
1.644	2.738	2.42	2.61	2.51	2.42	2.73	2.62	2.46	2.67	2.44
1.760	3.500	3.02	3.25	3.14	3.02	3.49	3.28	3.06	3.34	3.05

TABLE IX. Results of potential-curve calculations for $X^3\Sigma_g^-$ state of O_2.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
0.979	3.551	3.623	3.590	3.461	3.642	3.570	3.330	3.483	3.371	3.656
1.022	2.063	2.108	2.076	2.034	2.114	2.085	1.972	2.037	2.004	2.121
1.067	1.034	1.063	1.046	1.037	1.066	1.067	1.013	1.037	1.028	1.068
1.158	0.098	0.108	0.101	0.102	0.102	0.119	0.101	0.094	0.102	0.104
1.262	0.098	0.095	0.096	0.096	0.094	0.110	0.095	0.094	0.096	0.095
1.422	1.034	0.983	1.021	1.007	0.982	1.035	1.036	0.994	1.039	0.984
1.556	2.063	1.900	2.001	1.961	1.898	2.040	2.040	1.929	2.067	1.905
1.662	2.844	2.561	2.711	2.652	2.559	2.800	2.771	2.600	2.820	2.573
1.768	3.551	3.125	3.310	3.240	3.123	3.476	3.392	3.171	3.447	3.143

TABLE X. Results of potential-curve calculations for $B^3\Sigma_u^-$ state of O_2.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
1.334	0.956	1.132	0.942	1.069	1.133	0.946	1.003	1.129	1.005	1.110
1.356	0.749	0.895	0.745	0.850	0.894	0.759	0.802	0.893	0.808	0.879
1.405	0.441	0.499	0.423	0.480	0.498	0.436	0.459	0.503	0.465	0.491
1.531	0.043	0.047	0.044	0.046	0.047	0.046	0.046	0.053	0.046	0.046
1.683	0.043	0.037	0.039	0.037	0.037	0.039	0.037	0.041	0.037	0.036
1.962	0.441	0.382	0.460	0.395	0.382	0.467	0.411	0.389	0.421	0.387
2.232	0.749	0.666	0.798	0.691	0.666	0.908	0.720	0.674	0.735	0.679
2.865	0.956	0.938	0.995	0.956	0.938	1.439	0.975	0.945	0.957	1.005

all points considered for all states of all molecules for each function, along with the same quantity for values of $r>r_e$.

Some functions show an average performance which is distinctly superior to others. The five-parameter Hulburt-Hirschfelder gives an average error of about 1.5% in $(|V-V_{\mathrm{RKR}}|)/D_e$, while the better three-parameter functions give average errors of 2% to 3% in this same quantity. However, no one function is best for all molecular states considered, nor can we predict *a priori* which function will give the more correct potential for a restricted range of r. Furthermore, it is easy to see from Tables III to XXI that no one function gives consistent positive or negative deviations from the experimental curves for a given value of r/r_e.

The empirical potentials give better average

TABLE XI. Results of potential-curve calculations for $A^3\Sigma_u^+$ state of O_2.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
1.300	0.783	0.985	0.824	0.929	0.987	0.751	0.872	0.972	0.863	0.954
1.318	0.629	0.775	0.650	0.735	0.777	0.604	0.695	0.763	0.692	0.753
1.350	0.409	0.485	0.413	0.465	0.487	0.394	0.445	0.479	0.446	0.474
1.410	0.145	0.158	0.141	0.154	0.158	0.139	0.150	0.153	0.151	0.156
1.668	0.145	0.130	0.146	0.133	0.131	0.153	0.136	0.130	0.138	0.132
1.823	0.409	0.341	0.404	0.353	0.341	0.462	0.366	0.337	0.378	0.348
1.984	0.629	0.518	0.612	0.538	0.518	0.790	0.559	0.513	0.575	0.530
2.247	0.783	0.690	0.770	0.711	0.690	1.206	0.732	0.688	0.728	0.704

TABLE XII. Results of potential-curve calculations for $X^1\Sigma^+$ state of CO.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
0.901	5.428	5.283	5.480	5.086	5.357	5.611	5.059	5.048	5.052	5.439
0.923	4.211	4.081	4.211	3.945	4.127	4.291	3.921	3.930	3.927	4.181
0.952	2.878	2.802	2.873	2.723	2.827	2.913	2.706	2.718	2.716	2.856
0.997	1.430	1.392	1.416	1.364	1.401	1.429	1.356	1.369	1.362	1.411
1.054	0.400	0.389	0.392	0.384	0.390	0.393	0.383	0.392	0.384	0.395
1.220	0.400	0.407	0.404	0.411	0.405	0.402	0.414	0.413	0.413	0.408
1.322	1.430	1.452	1.437	1.482	1.448	1.431	1.505	1.481	1.507	1.440
1.438	2.878	2.916	2.881	2.998	2.907	2.883	3.074	2.986	3.096	2.889
1.544	4.211	4.258	4.207	4.398	4.246	4.227	4.539	4.372	4.595	4.218
1.649	5.428	5.475	5.416	5.671	5.461	5.469	5.880	5.627	5.967	5.424

TABLE XIII. Results of potential-curve calculations for the $d^3\Delta$ state of CO.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
1.097	2.367	2.411	2.715	2.305	2.430	2.443	2.239	2.308	2.265	2.452
1.119	2.000	1.944	2.141	1.865	1.956	1.962	1.815	1.869	1.840	1.973
1.151	1.475	1.385	1.484	1.336	1.391	1.392	1.304	1.343	1.325	1.400
1.204	0.744	0.718	0.744	0.699	0.720	0.720	0.686	0.705	0.697	0.722
1.277	0.209	0.203	0.205	0.201	0.204	0.203	0.198	0.204	0.201	0.204
1.506	0.209	0.207	0.210	0.210	0.207	0.209	0.213	0.213	0.211	0.207
1.657	0.744	0.722	0.754	0.740	0.720	0.738	0.761	0.738	0.764	0.719
1.837	1.475	1.391	1.497	1.437	1.389	1.450	1.484	1.422	1.514	1.388
1.991	2.000	1.893	2.064	1.962	1.891	2.006	2.049	1.934	2.082	1.894
2.122	2.367	2.246	2.455	2.328	2.244	2.411	2.435	2.299	2.470	2.249

TABLE XIV. Results of potential-curve calculations for $A^1\Pi$ state of CO.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
1.003	2.742	3.276	2.939	3.101	3.285	2.952	2.927	3.227	2.950	3.257
1.021	2.275	2.625	2.369	2.497	2.630	2.384	2.370	2.593	2.399	2.608
1.050	1.591	1.782	1.627	1.709	1.784	1.636	1.635	1.764	1.662	1.773
1.085	0.967	1.045	0.970	1.012	1.045	0.972	0.977	1.041	0.994	1.043
1.148	0.276	0.288	0.276	0.283	0.289	0.275	0.277	0.286	0.280	0.289
1.348	0.276	0.265	0.277	0.269	0.266	0.279	0.275	0.258	0.274	0.266
1.484	0.967	0.887	0.966	0.913	0.888	0.988	0.946	0.884	0.957	0.895
1.599	1.591	1.412	1.537	1.461	1.412	1.642	1.525	1.415	1.558	1.428
1.744	2.275	1.957	2.124	2.029	1.956	2.383	2.123	1.967	2.165	1.982
1.867	2.742	2.303	2.475	2.385	2.303	2.894	2.490	2.314	2.515	2.333

percentage deviations from the RKR curves for $r>r_e$, as shown in the fourth row of Table XXIII where the better functions give an average error between 1 and 2% in dissociation energy. This is not unexpected since, for $r>r_e$, a small change in r gives a large change in V. There are not many states for which data are available for a comparison of the function for large r, the region of importance in the calculations of macroscopic properties that depend on collision phenomena like the transport properties. Although there are not many examples in Tables III to XXI where the RKR curves are available for $r\gg r_e$, the indications are that the

TABLE XV. Results of potential-curve calculations for $e^3\Sigma^-$ state of CO.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
1.124	2.014	2.031	2.172	1.944	2.046	2.031	1.882	1.956	1.902	2.059
1.147	1.616	1.609	1.697	1.546	1.618	1.604	1.501	1.559	1.520	1.625
1.176	1.182	1.169	1.216	1.130	1.174	1.163	1.100	1.138	1.116	1.179
1.217	0.710	0.699	0.715	0.681	0.701	0.694	0.666	0.681	0.675	0.705
1.292	0.201	0.194	0.195	0.191	0.194	0.194	0.189	0.189	0.191	0.195
1.527	0.201	0.203	0.205	0.206	0.203	0.205	0.209	0.195	0.208	0.204
1.681	0.710	0.688	0.706	0.706	0.687	0.709	0.730	0.689	0.730	0.688
1.806	1.182	1.114	1.158	1.150	1.113	1.167	1.194	1.124	1.208	1.114
1.924	1.616	1.486	1.557	1.539	1.485	1.582	1.606	1.505	1.631	1.489
2.042	2.014	1.810	1.905	1.877	1.809	1.954	1.963	1.834	1.994	1.815

TABLE XVI. Results of potential-curve calculations for $a'^3\Sigma^+$ state of CO.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
1.075	2.907	2.692	3.044	2.578	2.720	2.775	2.523	2.574	2.534	2.749
1.094	2.397	2.236	2.494	2.149	2.255	2.295	2.104	2.147	2.120	2.279
1.119	1.829	1.723	1.890	1.663	1.736	1.759	1.630	1.663	1.647	1.751
1.164	1.071	1.013	1.060	0.985	1.019	1.027	0.969	0.986	0.980	1.025
1.257	0.226	0.210	0.216	0.207	0.211	0.213	0.206	0.208	0.207	0.211
1.479	0.226	0.238	0.234	0.241	0.238	0.238	0.244	0.236	0.243	0.238
1.681	1.071	1.078	1.056	1.108	1.076	1.093	1.141	1.095	1.147	1.074
1.846	1.829	1.805	1.778	1.867	1.802	1.854	1.939	1.839	1.965	1.798
1.981	2.397	2.326	2.305	2.411	2.323	2.419	2.515	2.371	2.554	2.322
2.122	2.907	2.780	2.770	2.882	2.777	2.926	3.011	2.831	3.048	2.778

TABLE XVII. Results of potential-curve calculations for the $X^2\Pi_{\frac{1}{2}}$ state of NO.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
0.929	4.582	5.116	5.031	4.876	5.149	5.018	4.689	4.907	4.734	5.166
0.949	3.774	4.015	3.937	3.847	4.035	3.934	3.712	3.868	3.767	4.049
0.982	2.485	2.586	2.530	2.496	2.596	2.535	2.422	2.505	2.392	2.599
1.026	1.246	1.282	1.257	1.251	1.286	1.260	1.223	1.258	1.242	1.289
1.113	0.118	0.120	0.119	0.119	0.118	0.117	0.118	0.111	0.118	0.121
1.210	0.118	0.113	0.114	0.114	0.111	0.112	0.115	0.113	0.112	0.112
1.360	1.246	1.188	1.232	1.217	1.187	1.233	1.251	1.198	1.252	1.189
1.486	2.485	2.319	2.440	2.394	2.316	2.469	2.488	2.340	2.518	2.324
1.623	3.774	3.427	3.626	3.552	3.424	3.743	3.713	3.472	3.776	3.442
1.725	4.582	4.109	4.342	4.260	4.106	4.563	4.459	4.156	4.525	4.131

TABLE XVIII. Results of potential-curve calculations for the $B^2\Pi$ state of NO.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
1.130	2.184	2.32	2.22	2.21	2.33	2.33	2.15	2.22	2.17	2.35
1.188	1.258	1.29	1.24	1.25	1.30	1.29	1.22	1.25	1.23	1.31
1.239	0.681	0.70	0.67	0.68	0.70	0.70	0.66	0.68	0.67	0.70
1.356	0.064	0.064	0.063	0.064	0.065	0.064	0.063	0.064	0.063	0.063
1.488	0.064	0.063	0.064	0.064	0.063	0.064	0.064	0.064	0.064	0.062
1.690	0.681	0.63	0.67	0.65	0.63	0.65	0.67	0.64	0.67	0.63
1.831	1.258	1.12	1.21	1.16	1.12	1.17	1.20	1.14	1.21	1.12
1.962	1.793	1.54	1.67	1.60	1.54	1.63	1.66	1.57	1.69	1.54
2.068	2.184	1.84	2.00	1.91	1.84	1.97	1.99	1.88	2.03	1.84

percentage errors in the interaction energy $V-D_e$ will be large in this region and that the various functions will retain, for the most part, the same relative performance.

The average percent errors for α_e and $\omega_e x_e$ shown in Table XXIV indicate that a good fit with the RKR curves may sometimes mean a satisfactory prediction of α_e and $\omega_e x_e$, but this is not general for all functions. For example, this seems to hold for the Linnett and Lippincott functions and to a lesser extent with the Rydberg function, but does not hold for the Varshni III function which gives good correlation with the RKR

TABLE XIX. Results of potential-curve calculations for $X^2\Pi_i$ state of OH.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
0.702	3.478	3.348	3.550	3.194	3.479	3.931	3.352	3.065	3.182	3.579
0.731	2.580	2.477	2.590	2.377	2.553	2.831	2.469	2.299	2.379	2.618
0.777	1.495	1.442	1.482	1.397	1.473	1.589	1.432	1.364	1.403	1.501
0.831	0.672	0.657	0.666	0.643	0.666	0.699	0.651	0.633	0.646	0.674
1.179	0.672	0.668	0.674	0.682	0.664	0.641	0.685	0.682	0.691	0.657
1.329	1.495	1.452	1.482	1.497	1.444	1.379	1.518	1.500	1.541	1.423
1.538	2.580	2.449	2.523	2.538	2.438	2.332	2.601	2.537	2.649	2.398
1.760	3.478	3.235	3.337	3.351	3.224	3.115	3.455	3.337	3.493	3.179

TABLE XX. Results of potential-curve calculations for $A^2\Sigma^+$ state of OH.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
0.752	2.394	2.50	2.19	2.37	2.55	2.70	2.35	2.33	2.31	2.60
0.777	1.797	1.90	1.69	1.81	1.93	2.02	1.79	1.78	1.78	1.96
0.809	1.233	1.29	1.18	1.24	1.30	1.35	1.23	1.23	1.23	1.32
0.863	0.565	0.60	0.56	0.58	0.59	0.61	0.57	0.57	0.58	0.61
1.244	0.565	0.54	0.56	0.55	0.54	0.54	0.56	0.55	0.57	0.53
1.428	1.233	1.13	1.19	1.17	1.13	1.14	1.22	1.16	1.23	1.13
1.614	1.797	1.61	1.68	1.67	1.61	1.66	1.74	1.65	1.76	1.61
2.038	2.394	2.21	2.25	2.27	2.21	2.34	2.34	2.24	2.32	2.21

TABLE XXI. Results of potential-curve calculations for the $X^1\Sigma^+$ state of HF.

r (A)	RKR (ev)	Morse	Hulburt-Hirschfelder	Rydberg	Pöschl-Teller	Linnett	Varshni	Rosen-Morse	Lippincott	Frost-Musulin
0.623	5.987	5.190	6.015	4.935	5.530	6.578	5.471	4.616	4.930	5.724
0.639	5.079	4.462	5.104	4.258	4.724	5.539	4.667	4.004	4.267	4.879
0.662	3.951	3.549	3.988	3.404	3.722	4.285	3.678	3.225	3.423	3.838
0.716	2.092	1.938	2.100	1.877	1.999	2.210	1.974	1.804	1.893	2.045
0.786	0.745	0.699	0.729	0.685	0.710	0.751	0.703	0.666	0.690	0.721
1.115	0.745	0.772	0.755	0.788	0.766	0.730	0.783	0.795	0.794	0.755
1.317	2.092	2.116	2.074	2.184	2.099	1.962	2.188	2.208	2.240	2.055
1.633	3.951	3.873	3.848	4.015	3.852	3.609	4.086	4.033	4.167	3.767
1.922	5.079	4.870	4.876	5.030	4.855	4.618	5.154	5.026	5.180	4.770
2.555	5.987	5.796	5.811	5.894	5.791	5.695	5.982	5.870	5.935	5.749

TABLE XXII. Comparison of observed values of $\omega_e x_e$ with calculated values for various functions.

Molecule	State	$\omega_e x_e$ (observed)	Morse	Rosen-Morse	Rydberg	Pöschl-Teller	Linnett	Frost-Musulin	Varshni	Lippincott
H_2	$X^1\Sigma_g^+$	120.815	126.545	84.5915	116.00	126.545	197.73	148.78	178.49	117.71
I_2	$X^1\Sigma_g^+$	0.6127	0.9165	0.9039	0.8402	0.9165	0.41521	0.87153	0.84863	0.7016
N_2	$X^1\Sigma^+$	14.188	17.4126	15.8476	15.9616	17.4126	15.6394	17.389	17.748	13.810
	$A^3\Sigma_u^+$	13.851	17.9278	16.9588	16.4339	17.9278	13.2889	17.527	17.595	13.994
	$a^1\Pi_g$	13.825	14.6494	13.3998	13.4287	14.6494	12.9074	14.591	14.864	11.595
	$B^3\Pi_g$	15.198	19.0633	17.8997	17.4748	19.0633	14.626	18.690	18.814	14.913
O_2	$X^3\Sigma_g^-$	12.0730	14.8517	13.7959	13.6141	14.8517	12.240	14.676	14.850	11.682
	$B^3\Sigma_u^-$	8.0023	15.1264	14.7357	13.8659	15.1264	8.5264	14.475	14.362	11.653
	$A^3\Sigma_u^+$	13.81	24.1387	23.861	22.1272	24.1387	10.310	18.293	22.476	18.453
CO	$X^1\Sigma^+$	13.295	12.9777	11.3698	11.8963	12.9777	13.099	13.227	13.684	10.458
	$d^3\Delta$	7.624	11.4141	10.4383	10.4630	11.4141	10.060	11.369	11.582	9.0343
	$A^1\Pi$	17.2505	22.4280	21.4432	20.5591	22.4280	15.393	21.762	21.758	17.429
	$e^3\Sigma^-$	9.578	11.7890	10.8218	10.8066	11.7890	10.240	11.654	11.922	9.3178
	$a'^3\Sigma^+$	11.0130	10.8575	9.7597	9.9527	10.8575	10.115	10.904	11.172	8.6483
NO	$X^2\Pi_{\frac{1}{2}}$	13.97	17.0042	15.7364	15.5872	17.0042	14.242	16.827	17.059	13.394
	$B^2\Pi$	7.603	10.1253	9.3063	9.2816	10.1253	8.7464	10.057	10.277	7.9991
OH	$X^2\Pi_i$	82.665	93.4369	77.545	85.6508	93.4369	105.76	98.429	103.22	77.162
	$A^2\Sigma^+$	113.85	125.642	111.419	115.172	125.642	122.92	101.81	131.39	100.75
HF	$X^1\Sigma^+$	88.726	86.8172	69.418	79.5827	86.8172	104.49	91.293	98.993	72.974

TABLE XXIII. Comparison of observed values of α_e with calculated values for various functions.

Molecule	State	α_e (observed)	Morse	Rosen-Morse	Rydberg	Pöschl-Teller	Linnett	Frost-Musulin	Varshni	Lippincott
H_2	$X^1\Sigma_g^+$	3.0177	2.2319	0.9074	1.8156	3.0936	5.4483	3.5831	4.1481	2.7053
I_2	$X^1\Sigma_g^+$	0.0001208	0.000154	0.00015	0.000143	0.000154	0.000092	0.001482	0.000131	0.0001334
N_2	$X^1\Sigma_g^+$	0.0171	0.01983	0.01846	0.01812	0.02000	0.01939	0.02020	0.01656	0.01743
	$A^3\Sigma_u^+$	0.01798	0.02182	0.02099	0.02007	0.02187	0.01827	0.02161	0.01808	0.01904
	$a^1\Pi_g$	0.0183	0.01863	0.01742	0.01703	0.01876	0.01791	0.01890	0.01552	0.01635
	$B^3\Pi_g$	0.01794	0.02236	0.02141	0.02055	0.02243	0.01922	0.02222	0.01852	0.01953
O_2	$X^3\Sigma_g^-$	0.01579	0.01749	0.01658	0.01604	0.01758	0.01591	0.01756	0.01451	0.01532
	$B^3\Sigma_u^-$	0.011	0.01894	0.01863	0.01753	0.01896	0.01308	0.01835	0.01587	0.01644
	$A^3\Sigma_u^+$	0.0165	0.02590	0.02572	0.02406	0.02591	0.01496	0.02485	0.02208	0.0224
CO	$X^1\Sigma^+$	0.0175	0.01642	0.01471	0.01489	0.01672	0.01796	0.01724	0.01406	0.01452
	$d^3\Delta$	0.0170	0.01685	0.01575	0.01540	0.01697	0.015286	0.01709	0.01403	0.01479
	$A^1\Pi$	0.02229	0.02807	0.02723	0.02588	0.02811	0.02222	0.02760	0.02330	0.02445
	$e^3\Sigma^-$	0.0179	0.01803	0.01692	0.01650	0.01815	0.01713	0.01825	0.01501	0.01582
	$a'^3\Sigma^+$	0.01872	0.01624	0.01497	0.01481	0.01641	0.01641	0.01667	0.01363	0.01429
NO	$X^2\Pi_{\frac{1}{2}}$	0.01781	0.01976	0.01867	0.01810	0.01986	0.01821	0.01987	0.01640	0.01731
	$B^2\Pi$	0.0116	0.013851	0.01300	0.01267	0.01394	0.01309	0.01400	0.01152	0.01215
OH	$X^2\Pi_i$	0.708	0.70089	0.5881	0.6281	0.7310	0.8806	0.7781	0.6429	0.6269
	$A^2\Sigma^+$	0.7868	0.9539	0.8657	0.8671	0.9681	1.01068	0.9920	0.8091	0.8422
HF	$X^1\Sigma^+$	0.7888	0.6590	0.5226	0.5850	0.7040	1.10725	0.7501	0.6478	0.5946

TABLE XXIV. Average error (%) for the quantities $\omega_e x_e$, α_e, $[|V_{\text{RKR}}-V|/D_e]_{\underset{r}{\text{all}}}$, and $[|V_{\text{RKR}}-V|/D_e]_{r>r_e}$ for various potential functions.

	Morse	Hulburt-Hirschfelder	Rosen-Morse	Rydberg	Pöschl-Teller	Linnett	Frost-Musulin	Varshni	Lippincott
$\omega_e x_e$	26.93	···	21.24	19.71	26.93	14.94	24.29	28.94	12.18
α_e	19.67	···	22.33	17.45	18.47	15.55	23.55	15.57	13.80
$[\|V_{\text{RKR}}-V\|/D_e]_{\underset{r}{\text{all}}}$	3.68	1.51	3.71	2.94	3.48	4.18	3.41	2.28	2.17
$[\|V_{\text{RKR}}-V\|/D_e]_{r>r_e}$	3.20	1.44	2.80	2.27	3.28	5.07	3.30	1.68	1.44

curves but is the poorest of all functions in predicting $\omega_e x_e$. This latter function would then be a poor one to predict dissociation values using r_e, ω_e, and $\omega_e x_e$. On the other hand, a study of Tables III to XXI shows that a function which predicts good values of $\omega_e x_e$ and α_e does not necessarily show good agreement with the RKR results. This is particularly true of the Linnett function.

We can summarize as follows. The Hulburt-Hirschfelder curve, being a five-parameter function, gives the best average results and in general gives the best or near the best fit of the potential for all the cases studies. However, for values of $r > r_e$, the Lippincott function gives equally good results. The Morse-Rosen-Morse and the Pöschl-Teller give very similar results. The Linnett curve ($m=3$) gives good predictions for $\omega_e x_e$ and α_e for many states, and, in general, gives a good representation of the RKR curves for these same states. Nevertheless, its average performance is the worst and in many cases it predicts maxima in a potential curve where none exist or are expected to exist. The Frost-Musulin potential does not give any appreciable improvement over the Morse curve, whereas the Rydberg potential is a distinct improvement. The Varshni III and Lippincott functions, the best of the three-parameter functions in fitting the RKR results, both give good predictions of α_e. On the other hand, the Lippincott function gives fairly reliable predictions of $\omega_e x_e$ (or D_e from $\omega_e x_e$), while the Varshni III function does not.

DISCUSSION

It is desirable to investigate the possibility that an empirical function can be proposed which will yield curves for any state of any molecule to an accuracy of less than 1% in bond-dissociation energy. There seem to be two justifiable approaches to this problem. One is to consider the expressions for E obtained from quantum-mechanical calculations of potential curves for various diatomic molecules. If these expressions were similar for the various states of different molecules, then presumably one could arrive at suitable potential forms which would have some basis in fact. Unfortunately, in order to obtain reliable values of E_e for even the simplest systems, one has to use 40- and 50-term wave functions[2] which yield very complicated expressions for E_e. There does not seem to be any chance of obtaining a suitable potential form from this approach.

A second approach is to consider the relatively simple expression for the vibrational- and rotational-energy levels of a diatomic molecule, Eq. (6). It is well known[30]

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[30] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).

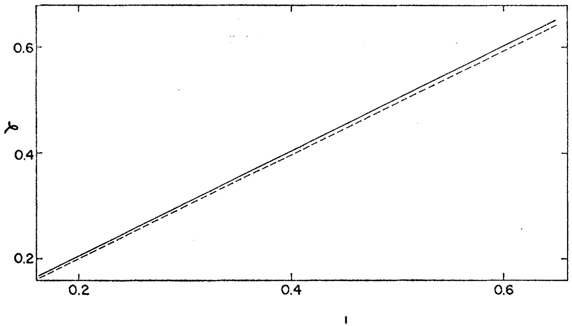

FIG. 1. $\gamma = \tanh[(\omega_e x_e/B_e)^{\frac12}\,(r_2-r_1)/2r_e]$ plotted against $(4\omega_e x_e V/\omega_e^2)^{\frac12}$. The solid line corresponds to the $X^1\Sigma_g^+$ state of N_2; the dashed line corresponds to the $a'\,{}^3\Sigma^+$ state of CO.

that, for many molecules, the first few terms in this equation are sufficient to fit the observed data within reasonable limits. The equation then reduces to the simple form

$$E_{vJ}=\omega_e(v+\tfrac12)-\omega_e x_e(v+\tfrac12)^2+B_e J(J+1)-\alpha_e J(J+1)(v+\tfrac12). \quad (19)$$

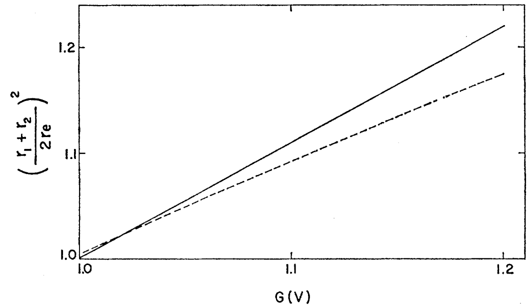

FIG. 2. $[(r_1+r_2)/2r_e]^2$ vs $G(V)$. The solid line corresponds to the $X^1\Sigma_g^+$ state of N_2; the dashed line corresponds to the $a'\,{}^3\Sigma^+$ state of CO.

In such a case, Rees[6] has shown that the potential curve can be obtained from the expressions

$$2f=(r_2-r_1)=(B_e/\omega_e x_e)^{\frac12}\ln W \quad (20)$$

$$2g=(1/r_1-1/r_2)=[1/B_e(\omega_e x_e)^3]^{\frac12}(\omega_e/r_e)\times\left[\alpha_e(4\omega_e x_e V/\omega_e^2)^{\frac12}+\left(2\frac{\omega_e x_e}{\omega_e}B_e-\alpha_e\right)\ln W\right] \quad (21)$$

$$W=(1-4\omega_e x_e V/\omega_e^2)^{\frac12}/[1-(4\omega_e x_e V/\omega_e^2)^{\frac12}]. \quad (22)$$

Here, r_1 and r_2 are minimum and maximum points of the vibration. If ω_e, $\omega_e x_e$, B_e, α_e are known, then r_1 and r_2 can be obtained for any V from the expression (20) and the following

$$(r_1+r_2)/2=(f/g+f^2)^{\frac12}. \quad (23)$$

Presumably, one could use Eqs. (20) and (23) as a basis for an empirical potential curve for "well-behaved" molecular states whose energy levels are given by Eq. (19). First, let us put (20) in a more convenient form. By expanding the logarithms of the numerator and denominator of W, it is easy to show that $\ln W=\tanh^{-1}(4\omega_e x_e V/\omega_e^2)$, and, hence,

$$(4\omega_e x_e V/\omega_e^2)^{\frac12}=\tanh(\omega_e x_e/B_e)^{\frac12}(r_2-r_1)/2r_e. \quad (24)$$

Equation (23), which gives the average value of r, cannot be written in simpler form. It is possible to sidestep this problem by taking B_v, which is equal[30] to $B_e r_e^2/r^2$, to be a measure of $[(r_1+r_2)/2]^{-2}$. If this is so, then,

$$[(r_1+r_2)/2]^2=B_e r_e^2/B_v=B_e r_e^2/[B_e-\alpha_e(v+\tfrac12)]. \quad (25)$$

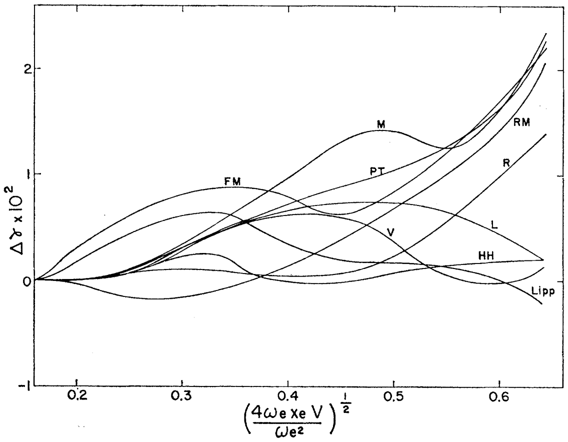

FIG. 3. $\gamma-\gamma_{\text{RKR}}$ vs $(4\omega_e x_e V/\omega_e^2)^{\frac12}$ for the various potential functions. The meaning of the symbols is as follows:

M = Morse
FM = Frost-Musulin
RM = Rosen-Morse
PT = Pöschl-Teller
R = Rydberg.
L = Linnett
HH = Hulburt-Hirschfelder
V = Varshni
Lipp = Lippincott

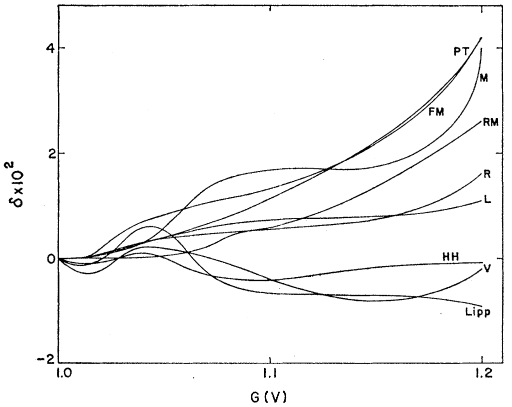

FIG. 4. $\delta=[(r_1+r_2)/2r_e]^2-[(r_1+r_2)/2r_e]^2_{\text{RKR}}$ vs $G(V)$ for the various potential functions. Symbols are as in Fig. 3.

This can be written in terms of ω_e, $\omega_e x_e$ and V to get

$$[(r_1+r_2)/2r_e]^2=1/[1-(\alpha_e\omega_e/2B_e\omega_e x_e) + \{(\alpha_e\omega_e/2B_e\omega_e x_e)^2-\alpha_e^2 V/B_e^2\omega_e x_e\}^{\frac{1}{2}}]=G(V). \quad (26)$$

Hence, for a molecule whose energy levels are given by Eq. (19), plots of

$$(4\omega_e x_e V/\omega_e^2)^{\frac{1}{2}} \quad \text{vs} \quad \tanh(\omega_e x_e/B_e)^{\frac{1}{2}}(r_2-r_1)/2r_e$$

and

$$[(r_1+r_2)/2r_e]^2 \quad \text{vs} \quad G(V)$$

should be straight lines with a slope of unity. Figures 1 and 2 show such plots. The solid lines are the results for the ground state of N_2 whose energy levels can be reasonably expressed by an expression of the form (19). The slopes, although close to unity, are not quite 1 since the ω_e, $\omega_e x_e$, B_e, and α_e used were determined from data at the lower-vibrational levels and not from the complete range of data.

It is now possible to compare the deviations of the proposed empirical potential functions from the experimental curves in a different manner. In Figs. 3 and 4 are plotted for each empirical function the differences of $\tanh(\omega_e x_e/B_e)^{\frac{1}{2}}(r_2-r_1)/2r_e$ and $[(r_1+r_2)/2r_e]^2$ from the experimental values for the $X^1\Sigma_g^+$ state of N_2 as a function of $(4\omega_e x_e V/\omega_e^2)^{\frac{1}{2}}$ and $G(V)$, respectively. In general, the various functions show the same relative deviations from the width of the potential bowl and the midpoint of the vibration as they show for errors in the quantities $|V-V_{\mathrm{RKR}}|$, $\omega_e x_e$, and α_e. All of the proposed empirical functions considered predict too wide a bowl for the potential curve. The empirical curves generally give too large a value for the midpoint of the vibrations. The exceptions to this last point are the Varshni, Hulburt-Hirschfelder, and Lippincott functions. The Hulburt-Hirschfelder potential curve gives the best predictions of bowl width and midpoint of vibration. This is in agreement with the fact that this potential gives the best reproduction of the RKR curves. The Varshni and Lippincott functions predict too large a bowl and too small a value for the midpoint. The deviations are relatively small, and the net result appears to be that these errors cancel somewhat so that these two functions give the next best average performance. For all others, the predicted bowl is too large and the midpoint is shifted to larger values, leading to poorer average performance.

The above conclusions are based, of course, only on the $X^1\Sigma_g^+$ state of N_2. However similar results should follow for any state with energy levels represented by Eq. (19). It would seem that the least one could expect from any empirical function proposed in the future would be reliable predictions for "well-behaved" states like the ground states of N_2, O_2, I_2, and H_2.

It may be possible to generate reliable potential curves by using equations similar to (24) and (26). Since these are in reduced units, all well-behaved molecular states should give nearly the same plots as the ground states of N_2 shown in Figs. 1 and 2. As a check, the $a'^3\Sigma^+$ state of CO was chosen at random and similar plots were made. These are shown as the dashed lines in the figures. As one can see, particularly from Fig. 2, large errors could be made in the calculations of the potential curve for the $a'^3\Sigma^+$ state of CO if the solid lines were chosen as the standard curves.

In summary then, the comparison of empirical potential functions given here indicates that the better 3-parameter functions can be expected to give potential curves with an average error of 2 to 3% in $|V-V_{\mathrm{RKR}}|/D_e$, whereas the better 5-parameter functions should give average error of from 1 to 2%. It does not seem likely that any substantial improvement (errors of less than 1%) can be made by suggesting new functions which have no theoretical or experimental basis. The task of giving a satisfactory theoretical or experimental foundation for any empirical function appears difficult indeed.