

A new four-parameter empirical potential energy function for diatomic molecules

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Abstract. A new empirical four-parameter function is proposed for the construction of potential curves of 15 stable states of diatomic molecules. The parameters are evaluated in terms of experimentally known spectroscopic constants. On comparing its performance with other functions, the proposed function is found to be simple and reliable for a wide range of molecules.

Keywords. Empirical model; potential function; diatomic molecule.

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1. Introduction

The simple physical picture of the molecular system leads to a curve with a minimum at equilibrium internuclear distance, a sharp rise towards infinity as the nuclei are brought together and a less sharp rise towards the dissociation limit as the separation is increased. A good deal of information about the structure of the molecule is summarized in its potential energy curves, where the potential energy minima determine the bond lengths, the second derivatives of the potential energy with respect to distance give the force constants and these determine the vibrational and rotational levels of the molecules. Anharmonicity constants depend on higher derivatives of the potential energy curves.

Empirical potential method is the most widely used method to represent the potential curves where functions are suggested so that all stable potential curves can be fitted to certain algebraic expressions. The criteria that a good potential function must satisfy are: (a) It should come asymptotically to a finite value as $r \rightarrow \infty$; (b) it should have minima at $r = r_e$; (c) it should become infinite at $r = 0$.

According to this, these potential functions can be broadly divided into three classes:

- (i) Purely exponential potential: e.g., Morse function [1].

- (ii) Combination of power-law potential and the exponential potential: e.g., Hulburt–Hirschfelder potential function [2].
- (iii) The combination of the inverse power-law potential and the exponential potential: e.g., Linnett potential [3].

A number of three- to five-parameter functions are used in potential curve calculations of stable diatomic molecules (Fayyazuddin–Rafi [4] and references therein).

The most general form of a diatomic potential function $U(r)$, in terms of the displacement $(r - r_e)$ from equilibrium, is given by

$$U(r) = U(r_e) + (r - r_e) \left. \frac{dU}{dr} \right|_{r_e} + \frac{(r - r_e)^2}{2!} \left. \frac{d^2U}{dr^2} \right|_{r_e} + \frac{(r - r_e)^3}{3!} \left. \frac{d^3U}{dr^3} \right|_{r_e} + \dots \quad (1.1)$$

To evaluate the parameters in three-parameter function, we apply the following relations:

$$U_\infty - U(r_e) = D_e, \quad (1.2)$$

$$\left. \frac{dU}{dr} \right|_{r_e} = 0, \quad (1.3)$$

$$\left. \frac{d^2U}{dr^2} \right|_{r_e} = k_e. \quad (1.4)$$

In four- and five-parameter functions these conditions are extended further with

$$\left. \frac{d^3U}{dr^3} \right|_{r_e} = X k_e, \quad (1.5)$$

$$\left. \frac{d^4U}{dr^4} \right|_{r_e} = Y k_e, \quad (1.6)$$

where X and Y are related to α_e and $\omega_e x_e$, respectively, by the relations

$$X r_e = -3 \left[\frac{\omega_e \alpha_e}{6 B_e^2} + 1 \right], \quad (1.7)$$

$$Y r_e^2 = \frac{5}{3} X^2 r_e^2 - 8 \frac{\omega_e x_e}{B_e}. \quad (1.8)$$

For further calculations, we use the Sutherland parameter Δ , which is defined as

$$\Delta = \frac{k_e r_e^2}{2 D_e}. \quad (1.9)$$

All these details help us to work out potential functions such that the conditions (1.2)–(1.6) are obeyed. We propose a new four-parameter empirical potential function.

2. The proposed function

The proposed function is

$$U(x) = D_e [e^{-2ax} f(x) - 2e^{-ax}] + D_e, \quad (2.1)$$

where

$$f(x) = \frac{1}{2} [\tanh(bx) + e^{-bx} + \operatorname{sech}(bx)]. \quad (2.2)$$

We can write eq. (2.1) as

$$U(x) = D_e \left[1 - 2e^{-ax} + \frac{1}{2} e^{-2ax} \left(\frac{e^{bx} - e^{-bx}}{e^{bx} + e^{-bx}} + e^{-bx} + \frac{2}{e^{bx} + e^{-bx}} \right) \right], \quad (2.3)$$

where $x = r - r_e$, r being the internuclear distance, r_e the equilibrium bond length and $b = \beta a$.

For $r = r_e$, $x = 0$ and so the second and third derivatives with respect to x , i.e. $U''(0)$ and $U'''(0)$ are found as

$$U''(0) = 2D_e a^2, \quad (2.4)$$

$$U'''(0) = -6D_e a^3 \left[1 + \frac{1}{4} \beta^3 \right]. \quad (2.5)$$

Since eq. (1.4) defines $U''(0) = k_e$, eq. (2.4) can be written as

$$\begin{aligned} 2D_e a^2 &= k_e, \\ a^2 r_e^2 &= \frac{k_e r_e^2}{2D_e}, \\ a r_e &= \Delta^{1/2}, \end{aligned} \quad (2.6)$$

where

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

Further, eqs (1.5) and (2.5) yield

$$\begin{aligned} k_e X &= -6D_e a^3 \left[1 + \frac{1}{4} \beta^3 \right] \\ X r_e &= -\frac{6D_e a^3 r_e}{k_e} \left[1 + \frac{1}{4} \beta^3 \right] \end{aligned} \quad (2.7)$$

$$= -3\Delta^{1/2} \left[1 + \frac{1}{4} \beta^3 \right]. \quad (2.8)$$

Table 1. Molecular constants used in the calculation of the potential energy curves.

Molecule	State (cm ⁻¹)	ω_e (cm ⁻¹)	r_e (Å)	B_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	α_e (cm ⁻¹)	D_e (cm ⁻¹)	Δ	F	Ref.
H ₂	X ¹ Σ _g ⁺	4401.2	0.7415	60.847	120.6	3.0513	38292.9	2.0821	0.6045	[9]
LiH	X ¹ Σ ⁺	1405.64	1.5955	7.5134	22.68	0.2154	20287.7	3.2415	0.8931	[10]
NaH	X ¹ Σ ⁺	1171.7	1.8874	4.9033	19.523	0.1371	15900	4.4092	1.1135	[11]
KH	X ¹ Σ ⁺	986.65	2.2401	3.4189	15.844	0.0944	14772.7	4.8248	1.3279	[12]
CsH	X ¹ Σ ⁺	891.25	2.493	2.709	12.816	0.067	14791.2	4.9634	1.3551	[13]
K ₂	X ¹ Σ ⁺	92.3994	3.9244	0.0562	0.328	0.0002	4440	8.5691	0.9752	[14]
Na ₂	C ¹ Π _u	116.43	3.5427	0.1166	0.665	0.0001	5531.1	5.2513	0.2171	[15]
Rn ₂	X ¹ Σ _g ⁺	57.78	4.2099	0.0224	0.139	0.00005	3950	9.4458	0.9596	[16]
CO	X ¹ Σ ⁺	2169.8	1.1283	1.9313	13.291	0.0175	90529	6.7421	1.6973	[17]
ICl	X ¹ Σ ⁺	384.27	2.3209	0.1141	1.492	0.0005	17557.6	184452	2.6155	[18]
ICl	A ³ Π	211.03	2.6851	0.0853	2.121	0.0007	3814.8	342683	3.5966	[18]
XeO	d ¹ Σ ⁺	156.82	2.8523	0.1456	9.868	0.0055	693	60.9973	6.8097	[19]
I ₂	XO _g ⁺	214.52	2.6664	0.0374	0.615	0.0001	12547.3	24.5713	2.9132	[20]
Cs ₂	X ¹ Σ _g ⁺	42.02	4.648	0.0127	0.082	0.00002	3649.5	10.3161	0.8684	[21]
RbH	X ¹ Σ ⁺	937.1	2.3668	3.0195	14.278	0.0707	14580	4.9895	1.2113	[22]

In terms of constant F we have eq (2.8) as

$$F + 1 = \Delta^{1/2} \left[1 + \frac{1}{4}\beta^2 \right],$$

where

$$F = - \left(\frac{Xr_e}{3} + 1 \right).$$

We define $b = \beta a$. a is evaluated from eq. (2.6) and the value of β is obtained from eq. (2.8). The value of b is thus calculated for each r value of a molecular state. The potential curve calculations are thus made from the proposed function (eq. (2.3)).

3. Potential curve calculations

We have made potential curve calculation of 15 molecular states of diatomic molecules from the proposed function given in eq. (2.1). The parameters of the function are evaluated in terms of the experimentally determined spectroscopic constants as described in §2. The constants used in the potential curve calculations are given in table 1. Three other four-parameter potential functions of the same type as that of the proposed one are used in making potential curve calculations so as to make comparison with the proposed function. We have also added the Morse potential function which is a widely referred function in literature for our comparative study. An example of this comparison is given for the two molecular states in tables 2 and 3.

Steele *et al* [8] suggest that calculation of the average per cent error be made for the quantity $\frac{|U-U_{\text{RKR}}|}{D_e} \Delta_r$ for comparative study of the potential functions. Here

Table 2. $X^1\Sigma_g^+$ state of H_2 .

r (Å)	RKR (cm^{-1})	Ref. [1] (cm^{-1})	Ref. [5] (cm^{-1})	Ref. [6] (cm^{-1})	Ref. [7] (cm^{-1})	Proposed (cm^{-1})
3.003	37998.90	37372.47	36724.41	49736.4	37528.66	37357.34
1.992	33330.88	31910.56	30394.60	42259.5	31857.04	31778.29
1.523	23684.58	23184.11	21790.21	30055.2	22826.35	22849.06
1.229	13960.51	14075.73	13266.49	1741.3	13709.65	13709.09
0.882	2179.68	2212.63	2147.38	2395.1	2160.57	2158.03
0.633	2179.68	2120.52	2158.84	1960.44	2173.75	2166.94
0.509	13960.51	12687.33	13447.34	10814.6	14084.78	13698.12
0.451	23684.58	20664.69	22315.89	17096.9	24172.11	22937.80
0.425	33330.88	28017.92	30688.25	22726.9	34371.73	31775.36
0.411	37998.90	31385.99	34578.82	25268.1	39357.38	35915.24

Table 3. $X^1\Sigma^+$ state of LiH.

r (Å)	RKR (cm^{-1})	Ref. [1] (cm^{-1})	Ref. [5] (cm^{-1})	Ref. [6] (cm^{-1})	Ref. [7] (cm^{-1})	Proposed (cm^{-1})
5.205	20169.84	19600.70	19473.15	26095.03	19819.51	19600.52
3.411	16635.24	15385.35	15087.69	20325.24	15542.95	15338.82
2.866	12366.42	1175.49	11493.41	15244.9	11799.75	11675.87
2.376	7056.58	6952.84	6803.63	8588.79	6921.62	6873.96
1.778	697.88	701.98	697.11	750.11	698.46	697.79
1.446	697.88	688.89	695.96	651.55	697.36	696.53
1.193	7056.58	6688.88	6920.63	5755.68	7066.79	6966.85
1.099	12366.24	11442.65	11971.9	9531.08	12422.06	12098.15
1.042	16635.24	15266.43	16092.2	12482.6	16922.78	16307.09
1.005	20169.84	18195.34	19278.5	14707.3	20488.99	19574.62

Δ_r is the range of r values in the potential well. We use the same method and calculate the average per cent error for the 15 molecular states from the proposed function and the functions of refs [1,5–7] as given in table 4. The results show that no single function can be regarded to be the best for all the molecular states. The proposed function yields the least per cent error in six molecular states whereas the function of Rafi *et al* [7] shows the least error for other six states. The Morse function is better for the three states. Functions of Fayyazuddin *et al* [5] and Rafi *et al* [6] are not up to the mark when compared on this criterion.

To conclude with, it is found that no one potential energy function behaves good for all stable states of diatomic molecules. New functions are, therefore, introduced in literature now and then. The proposed function is an attempt in this direction and it can be regarded as a suitable four-parameter function where RKR and quantum mechanical methods cannot be applied.

Table 4. Average error (%) $\frac{|U-U_{\text{RKR}}|}{D_e} \Delta_r$.

Molecule	State	Δ_r (Å)	Ref. [1]	Ref. [5]	Ref. [6]	Ref. [7]	Proposed
H ₂	X ¹ Σ _g ⁺	2.592	5.182	3.864	6.545	1.590	2.080
LiH	X ¹ Σ ⁺	4.205	3.486	2.631	4.041	1.389	1.982
NaH	X ¹ Σ ⁺	1.617	0.897	0.850	0.912	0.507	0.859
KH	X ¹ Σ ⁺	5.455	2.076	3.845	4.089	4.349	4.039
CsH	X ¹ Σ ⁺	2.659	1.126	1.940	1.969	1.971	1.896
K ₂	X ¹ Σ ⁺	3.505	10.451	4.122	3.857	10.747	1.567
Na ₂	C ¹ Π _u	1.683	1.766	3.798	4.221	3.700	3.776
Rb ₂	X ¹ Σ _g ⁺	2.773	8.390	3.062	2.489	6.248	0.784
CO	X ¹ Σ ⁺	0.849	0.618	0.245	0.627	0.499	0.048
ICl	X ¹ Σ ⁺	0.591	1.039	0.359	0.056	0.015	0.213
ICl	A ³ Π	3.892	8.230	4.224	7.855	7.107	0.688
XeO	d ¹ Σ ⁺	2.182	6.320	6.297	6.227	4.896	6.297
I ₂	XO _g ⁺	6.809	7.669	5.332	5.730	4.035	1.607
Cs ₂	X ¹ Σ _g ⁺	8.040	16.679	6.893	11.113	59.741	0.801
RbH	X ¹ Σ ⁺	1.988	1.285	2.583	1.231	0.792	1.340

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