Correlation among parameters of the extended-Rydberg potential energy function

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This paper reports a remarkable correlation among parameters of extended-Rydberg potential function by recasting the Morse potential in the form of extended-Rydberg function via the application of infinite series expansion to the exponential terms of the Morse function. By using linear regression, a reasonable band that encompasses 90% of the diatomic combination given by Huxley and Murrell [J. Chem. Soc. Faraday Trans. II 79 (1983) 323] is furnished in a plotted characteristic map.

KEY WORDS: extended-Rydberg, interatomic potential, parametric characteristic map

AMS subject classification: 41A58, 62J05, 70F05, 92E99

1. Introduction

In recent years relationships between parameters of various interatomic potential functions have been developed [1–15], mainly to understand the extent of relatedness amongst these potential functions and for preliminary development of a potential function converter [16,17]. The understanding of relationships between various potential functions is justified by the numerous computational chemistry softwares that employ different combinations of 2-body, 3-body, 4-body and non-bonded functions [18–35], as well as the numerous potential functions used in condensed matter physics [36]. In a departure from previous attempts in relating parameters from different potential functions [1–17], we herein develop relationship among parameters from within a single potential function, which are those of the extended-Rydberg potential.

2. Analysis

The original Rydberg [37] potential is given in the form

$$U_{\mathrm{Ryd}} = -D\left\{1 + a\rho\right\}\exp\left(a\rho\right), \tag{1}$$

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where

$$\rho = r - R \tag{2}$$

with D, r, and R referring to the magnitude of the minimum well-depth, the interatomic distance and the equilibrium interatomic distance, respectively. Here the parameter a influences the shape of the potential energy curve. Although the original Rydberg potential has been adopted in describing the 2-body energy of cubic crystals [38,39], diamond structure [40], silicon microstructure [41], 17–19-atom metal clusters [42], and employed in computer program [43], with

$$\rho = \frac{r - R}{R}, \tag{3}$$

the additional parameters incorporated in the extended-Rydberg potential

$$U_{ER} = -D \left\{ \sum_{i=0}^{n} a_i \rho^i \right\} \exp(-a_1 \rho), \tag{4}$$

where $n = 3$ and $a_0 = 1$ allow greater flexibility [44,45]. In the extended-Rydberg potential, the symbol ρ is described by equation (2). There is, however, no fixed limit to the number of terms in the power series. For example Yang et al. [46] adopted the extended-Rydberg potential with $n = 4$ when analyzing H–H bond in hydrogen molecule. In this paper, we limit our scope to $n = 3$ in view of the numerous parametric data available from Huxley and Murrell [45].

Since the bond dissociation energy, D, and the equilibrium bond length, R, are highly dependent on the combination of diatoms, the only meaningful parametric correlation that can be made is confined to a_1, a_2, and a_3. To do so, we recall the Morse potential function [47]

$$U_M = D \left\{ \exp(-2\alpha\rho) - 2\exp(-\alpha\rho) \right\}, \tag{5}$$

where ρ is defined by equation (2). The parameter α influences the shape of the potential energy curve. Here the Morse potential is selected due to the proven closeness between the original Morse and original Rydberg potential curves [10], as well as that between the Generalized Morse and the extended-Rydberg potential curves [11]. To pave a way for eliminating the bond dissociation energy and the equilibrium bond length, equation (5) is rewritten in an alternate, but nevertheless equivalent, form:

$$U_M = -D \left\{ \exp[(a_1 - 2\alpha)\rho] - 2\exp[(a_1 - \alpha)\rho] \right\} \exp(-a_1 \rho). \tag{6}$$

Substituting

$$\exp[(a_1 - x\alpha)] = \sum_{i=0}^{\infty} \frac{(a_1 - x\alpha)^i \rho^i}{i!} \tag{7}$$

for $x = 1, 2$ into equation (6) and expanding up to $i = 3$, we arrive at

$$U_{\mathrm{M}} = -D \left\{ 1 + a_1 \rho + \left(\frac{1}{2} a_1^2 - \alpha^2 \right) \rho^2 + \left(\frac{1}{6} a_1^3 - a_1 \alpha^2 + \alpha^3 \right) \rho^3 \right\} \exp(-a_1 \rho). \quad (8)$$

Comparison of terms between equations (4) and (8) gives

$$a_2 = \frac{1}{2} a_1^2 - \alpha^2 \quad (9)$$

and

$$a_3 = \frac{1}{6} a_1^3 - a_1 \alpha^2 + \alpha^3. \quad (10)$$

Hence elimination of α in equations (9) and (10) gives

$$a_3 = \frac{1}{6} a_1^3 - g(a_1, a_2) \left(a_1 - \sqrt{g(a_1, a_2)} \right), \quad (11a)$$

where

$$g(a_1, a_2) = \frac{1}{2} a_1^2 - a_2. \quad (11b)$$

3. Results and discussion

To assess the validity of equation (11), which describes the correlation among the parameters a_1, a_2, and a_3, a graph of

$$f(a_1, a_2) = \frac{1}{6} a_1^3 - g(a_1, a_2) \left(a_1 - \sqrt{g(a_1, a_2)} \right) \quad (12)$$

was plotted against a_3. Figure 1 shows the data points of $f(a_1, a_2)$ versus a_3 from all 71 sets of parameters $a_i (i = 1, 2, 3)$ given by Huxley and Murrell [45] (see table 1).

The two parallel lines represent the upper and lower shift of a best-fit linear band that covers 90% of the data points. We observe three major trends.

(a) the data points lie on a linear narrow gap;

(b) the data points are most condensed near the origin, and decreases in density away from the origin;

(c) the slope of $f(a_1, a_2)$ versus a_3 implies

$$a_3 \approx 0.8 f(a_1, a_2). \quad (13)$$

To obtain a better view, the almost overlapping data points near the origin need to be spaced further apart whilst the data points far away from the origin can

Table 1

Parameters of a_1, a_2 and a_3 by Huxley and Murrell [45], used in the present illustration.

Diatoms	a_1 (Å^{-1})	a_2 (Å^{-2})	a_3 (Å^{-3})
AlAl	2.634	1.536	0.038
AlCl	2.150	1.052	0.824
AlF	2.479	1.172	1.484
AlH	2.316	1.084	0.576
AlO	2.409	−0.418	1.106
AlS	2.634	0.827	0.466
BB	3.581	2.787	0.752
BCl	2.457	1.067	1.012
BeCl	3.100	2.475	1.417
BeF	2.948	1.586	1.509
BeH	4.278	5.873	3.858
BeO	2.828	0.477	1.029
BeS	2.128	−0.308	0.220
BF	3.200	1.930	2.926
BH	2.935	1.638	0.983
BN	4.487	5.580	6.391
BO	4.253	3.967	2.368
BS	3.526	2.768	1.327
CC	5.026	6.630	3.787
CCl	3.463	2.360	1.000
CF	3.557	2.303	2.672
CH	3.836	3.511	2.268
ClCl	4.478	6.022	3.749
ClF	4.137	3.311	0.213
ClH	3.698	3.349	1.999
ClLi	1.700	0.533	0.496
ClNa	1.316	0.630	0.372
ClO	5.142	7.971	6.116
ClSi	2.880	2.021	1.140
CN	5.312	7.663	5.369
CO	3.897	2.305	1.898
CP	4.487	5.506	3.156
CS	3.445	2.370	1.238
FF	6.538	12.521	11.717
FH	4.216	3.965	3.835
FLi	2.196	1.102	1.151
FMg	1.854	−0.341	0.854
FN	4.895	6.571	5.197
FNa	2.006	0.987	0.957
FO	7.228	18.759	22.835
FP	3.521	2.863	1.835
FS	5.040	7.564	5.072
FSi	3.008	1.807	1.605

Table 1 *(Continued)*

Diatoms	a_1 (Å^{-1})	a_2 (Å^{-2})	a_3 (Å^{-3})
HH	3.961	4.064	3.574
HLi	2.173	1.088	0.447
HMg	3.815	4.499	2.455
HN	4.482	4.971	3.397
HNa	2.154	1.071	0.365
HO	4.507	4.884	3.795
HP	3.645	3.470	1.771
HS	3.284	1.837	0.494
HSi	3.058	2.335	1.188
LiLi	1.919	1.077	0.232
LiNa	1.846	0.993	0.237
MgMg	2.043	1.005	0.526
MgO	1.909	−0.509	0.686
MgS	1.780	−0.358	0.339
NaNa	2.067	1.384	0.365
NN	5.396	7.328	4.988
NO	5.398	7.041	4.823
NP	4.491	5.165	2.882
NS	4.926	6.677	4.539
NSi	3.732	2.975	1.460
OO	6.080	11.477	11.003
OP	4.275	4.399	2.717
OS	4.748	6.504	5.228
OSi	3.208	1.685	1.217
PP	3.920	4.266	2.246
SiSi	2.957	2.300	0.962
SS	3.954	4.312	2.332
SSi	2.773	1.462	0.647

be condensed. Figure 2 shows an alternative representation of figure 1 with natural logarithm imposed on both axes. Since $\ln[x] < 0$ for $0 < x < 1$, data of $\ln[1 + f(a_1, a_2)]$ and $\ln[1 + a_3]$ were plotted instead of $\ln[f(a_1, a_2)]$ and $\ln[a_3]$ in order to give positive value. With reference to table 1 and figure 2, only the AlAl, AlF, BB, BF, CF, ClF, and FLi do not fall into the band.

4. Conclusion

By expressing the Morse potential in the form of extended-Rydberg potential, a correlation amongst parameters of the latter potential function has been obtained. Whilst the number of the polynomial terms – and hence the $a_i (i = 1, 2, 3, \dots)$ parameters – are helpful in enabling better fitting of the interatomic energy curve, it was herein shown that only the first two parameters, $a_i (i = 1, 2)$ are the most critical. This can be inferred from the fact that an approximate
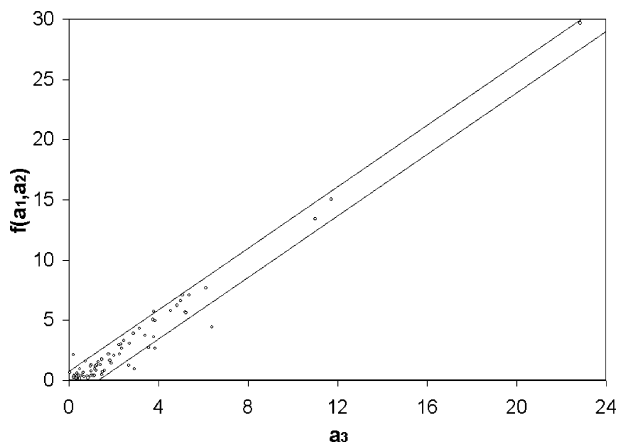
Figure 1. Plot of $f(a_1, a_2)$ versus a_3 shows a reasonable correlation, with the narrow gap covering 90% of the data given by Huxley and Murrell [45].
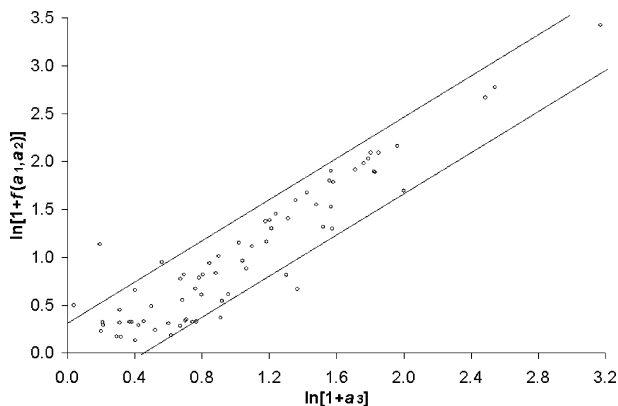

Figure 2. Uncluttered view of the correlation between $f(a_1, a_2)$ and a_3.

parameter of a_3 can be estimated from both a_1 and a_2. It follows that the connection obtained herein among a_1, a_2 and a_3 is an additional characteristic of the interatomic potential energy.

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