

Application of Extended-Rydberg parameters for extracting the 2-body portion of Kaxiras–Pandey function

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A set of relationship is developed herein between parameters of the Extended-Rydberg and the 2-body portion of the Kaxiras–Pandey potential energy functions. Unlike previous method which relied on multi-derivatives, the approach herein adopts the series expansion approach in order to recast the 2-body part of the Kaxiras–Pandey potential into a form similar to the Extended-Rydberg function. Results plotted for eight pairs of diatoms reveal good correlation. The improved agreement, as evident from a narrower gap between two sets of potential functions, may well be attributed to the removal of simplifying assumptions that were invoked in the previous method. The present relationship, together with other recently developed parametric relations, will be used for the development of an interatomic potential function converter.

KEY WORDS: interatomic energy, potential function, series expansion

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1. Introduction

Without doubt, the interatomic potential functions developed early last century have since been adopted in chemistry and physics communities. For example, the Lennard–Jones potential [1] has been adopted in computational chemistry softwares (e.g. [2–4]) for describing van der Waals interaction, and the 2-body portion of the Pearson–Takai–Halicioglu–Tiller potential function [5] for silicon. The original Morse potential [6] has been adopted in computational chemistry softwares for describing covalent bonds (e.g.[7,8]) and van der Waals energy [9], whilst a more generalized form of the Morse potential was adopted by Biswas and Hamann [10] for their description of 2-body energy in silicon structure. Likewise, the Buckingham potential [11] was employed by computational chemistry softwares (e.g. [12–14]) to quantify van der Waals energy, as well as by Bauer et al. [15] for describing 2-body energy portion in FCC metals. The original Rydberg

potential [16] has been used in the 2-body portion of condensed matter [17–21], while an extended version was used for diatoms [22]. With the numerous examples of potential functions used in both chemical and condensed matter computations, there is no doubt that a potential function parameterized for a particular X–X interaction for condensed matter can be applied for chemical computation and vice versa. Following that, it has become much more cost effective to convert parameters of a widely parameterized potential to parameters of a different and less parameterized potential, instead of performing experiments for the latter. As a result, a prototype potential function converter has been developed [23] and initial test reveal its accuracy, which uses a limited number of simple potential functions used by the chemical community.

In regard to the potential functions of interest to the condensed matter community, several potential function relationships have been established [24–34]. Recently, a relationship between the original Rydberg potential (or 2-body portion of Murrell–Mottram potential) and the 2-body portion of Kaxiras–Pandey [35] potential has been developed [36], whereby the former has three parameters (D, R, a) whilst the latter has four ($A_1, A_2, \alpha_1, \alpha_2$). However the Rydberg potential considered was the original, not the extended, version. This results in a fairly large gap between the two potential functions upon plotting. For the relationship between the Extended-Rydberg the 2-body portion of Kaxiras–Pandey potentials, it is expected that a good description of the latter can be obtained based on the former, which has five parameters (D, R, a_1, a_2, a_3). By equating the zeroth, first and second derivatives of these two functions at the equilibrium bond distance, a reasonable relationship was obtained between them [37]. However, two major simplifying assumptions were made, namely: (i) the Extended-Rydberg and the 2-body Kaxiras–Pandey potentials were indirectly related via a Generalized Morse potential function, and that (ii) the ratio (α_1/α_2) was set as 2. The assumptions were made due to the analytical complexities that arose therein. In this paper, the two simplifying assumptions are removed by adopting a different analytical approach. Instead of the multiple derivatives approach (e.g. [25–34,36,37]), we employ the series expansion approach, which was previously found to be suitable when dealing with potential functions that exhibit polynomial forms [38,39]. A major benefit in the establishment between the Extended-Rydberg and the 2-body portion of Kaxiras–Pandey potentials is the availability of more than 70 combinations of diatom parameters which can be converted for use in the Kaxiras–Pandey function, as well as the reliability of converting a potential with a larger number of parameters (five for Extended-Rydberg) to a potential with a lower number of parameters (four for 2-body portion of Kaxiras–Pandey).

2. Analysis

Consider the form of the Extended-Rydberg function

$$U_{\text{ER}} = -D \left\{ \sum_{i=1}^3 a_i \rho^i \right\} \exp(-a_1 \rho), \quad (1)$$

where D is the magnitude of the minimum well-depth, $a_0 = 1$ and $\rho = r - R$, with r and R being the instantaneous and the equilibrium interatomic distance. Hence the 2-body portion of Kaxiras–Pandey function

$$U_{\text{KP}} = A_1 \exp(-\alpha_1 r^2) - A_2 \exp(-\alpha_2 r^2), \quad (2)$$

whereby subscripts 1 and 2 refer to the repulsive and attractive terms respectively, is herein rewritten as

$$U_{\text{KP}} = \left\{ \sum_{i=1}^2 (-1)^{i-1} B_i \exp \left[- \left(\alpha_i \rho^2 + (2\alpha_i R - a_1) \rho \right) \right] \right\} \exp(-a_1 \rho), \quad (3)$$

in which

$$B_i = A_i \exp(-\alpha_i R^2) \quad (4)$$

for $i = 1, 2$. Since $(\partial U_{\text{KP}}/\partial r)_{r=R} = 0$ and $(U_{\text{KP}})_{r=R} = -D$ by definition, then

$$\alpha_1 B_1 = \alpha_2 B_2 \quad (5)$$

and

$$D = (j - i) \frac{\alpha_i - \alpha_j}{\alpha_j} B_i \quad (6)$$

for $i, j = 1, 2$. Substituting equations (5) and (6) into equation (3), we have

$$U_{\text{KP}} = D \left\{ \sum_{i=1}^2 C_i \exp \left[- \left(\alpha_i \rho^2 + (2\alpha_i R - a_1) \rho \right) \right] \right\} \exp(-a_1 \rho), \quad (7)$$

where

$$C_i = \frac{\alpha_j}{\alpha_i - \alpha_j} \quad (8)$$

for $i, j = 1, 2$. At this juncture, the 2-body portion of Kaxiras–Pandey potential has been described in terms of the minimum well-depth magnitude, D , and the exponential term, $\exp(-a_1 \rho)$. Hence comparison can be made if the summed terms in equation (7) can be expressed in terms of increasing order of ρ , akin to

the summative terms shown in equation (1). Imposing the Taylor series expansion up to the third order, we obtain

$$\exp \left[- \left(\alpha_i \rho^2 + (2\alpha_i R - a_1) \rho \right) \right] = \sum_{k=0}^3 b_k \rho^k, \tag{9}$$

where

$$b_0 = 1 \tag{9a}$$

$$b_1 = a_1 - 2 (\alpha_i R) \tag{9b}$$

$$b_2 = \frac{1}{2} a_1^2 - 2a_1 (\alpha_i R) + 2 (\alpha_i R)^2 \tag{9c}$$

$$b_3 = \frac{1}{6} a_1^3 - a_1 \alpha_i + (2\alpha_i^2 - a_1^2 \alpha_i) R + 2a_1 (\alpha_i R)^2 - \frac{4}{3} (\alpha_i R)^3. \tag{9d}$$

Substituting equation (9) into equation (7), we have

$$U_{KP} = -D \left\{ \sum_{i=1}^3 c_i \rho^i \right\} \exp (-a_1 \rho), \tag{10}$$

where

$$c_0 = 1 \tag{10a}$$

$$c_1 = a_1 \tag{10b}$$

$$c_2 = \frac{1}{2} a_1^2 - 2\alpha_1 \alpha_2 R^2 \tag{10c}$$

$$c_3 = \frac{1}{6} a_1^3 - 2\alpha_1 \alpha_2 R \left[(1 + a_1 R) - \frac{2}{3} (\alpha_1 + \alpha_2) R^2 \right]. \tag{10d}$$

Comparison of equations (1) and (10) for equal powers of ρ , i.e. $a_i = c_i$, gives two trivial relations ($i = 0, 1$) and two useful relations $i = (2, 3)$. The latter gives

$$\begin{Bmatrix} a_2 \\ a_3 \end{Bmatrix} = \begin{bmatrix} 1 & 1 \\ (a_1/3) & (a_1 + R^{-1}) - 2 (\alpha_1 + \alpha_2) R/3 \end{bmatrix} \begin{Bmatrix} a_1^2/2 \\ -2\alpha_1 \alpha_2 R^2 \end{Bmatrix}. \tag{11}$$

Solving equation (11) simultaneously for α_1 and α_2 , and bearing in mind that $\alpha_1 > \alpha_2$ to maintain sign consistency for equations (7) and (8) whereby

$$C_1 > 0 > C_2, \tag{12}$$

then

$$\begin{Bmatrix} \alpha_1 \\ \alpha_2 \end{Bmatrix} = \frac{f(a_1, a_2, a_3)}{2} \begin{Bmatrix} 1 \\ 1 \end{Bmatrix} + \frac{1}{2} \sqrt{[f(a_1, a_2, a_3)]^2 - \left(\frac{a_1^2 - 2a_2}{R^2} \right)} \begin{Bmatrix} +1 \\ -1 \end{Bmatrix}, \tag{13}$$

where

$$f(a_1, a_2, a_3) = \frac{1}{2R} \left[3 \left(a_1 + \frac{1}{R} \right) - \frac{a_1^3 - 6a_3}{a_1^2 - 2a_2} \right]. \quad (14)$$

For completeness' sake, it follows from equations (4) and (6) that

$$\begin{Bmatrix} A_1 \\ A_2 \end{Bmatrix} = \frac{D}{\alpha_1 - \alpha_2} \begin{Bmatrix} \alpha_2 \exp(\alpha_1 R^2) \\ \alpha_1 \exp(\alpha_2 R^2) \end{Bmatrix}, \quad (15)$$

whereby the indices α_1 and α_2 can be calculated from Extended-Rydberg parameters using equation (14). Hence equations (13) and (15) describe the 2-body Kaxiras–Pandey indices (α_1, α_2) and coefficients (A_1, A_2) in terms of Extended-Rydberg parameters (D, R, a_1, a_2, a_3) .

3. Results and discussion

In order to verify the relationships developed, theoretical curves of Extended-Rydberg and the 2-body portion of Kaxiras–Pandey interatomic energy have to be plotted and compared. The Extended-Rydberg curve can be plotted based on its parameters given by Huxley and Murrell [22]. Using these Extended-Rydberg parameters, the parameters of the 2-body portion of Kaxiras–Pandey function can be calculated using equations (13)–(15). For presentation purposes, we plot two groups of diatomic curves: (i) the first group exhibits an almost consistent increment of D , (ii) the second group shows an almost consistent increment of R . Hence curves of interatomic energy based on increasing D , i.e. NaNa, BeCl, CN and CO, were plotted against non-dimensionalized bond length, r/R , as shown in figure 1 (see table 1). Here, the continuous curves were plotted using Extended-Rydberg function while the open circles refer to the 2-body Kaxiras–Pandey function. Curves of non-dimensionalized interatomic energy, U/D , were plotted against the bond length, r , based on increasing R , i.e. HH, HNa, LiNa and MgMg, as shown in figure 2 (see table 2). In this figure, the thick curves were plotted using the 2-body Kaxiras–Pandey function while the thin curves correspond to Extended-Rydberg function. We observe that (i) both sets of functional curves coincide at and near the equilibrium, and that (ii) 2-body portion of Kaxiras–Pandey function slightly underestimates the Extended-Rydberg curve only at large diatomic separation. Observation (i) verifies the validity of the developed relationship. Observation (ii) reveals a narrower gap between these two potential functions for both HH and MgMg diatoms using the series expansion method than the multi-derivative method [37].

4. Conclusions

A refined relationship between the Extended-Rydberg and the 2-body Kaxiras–Pandey potential functions has been developed in this paper. A key

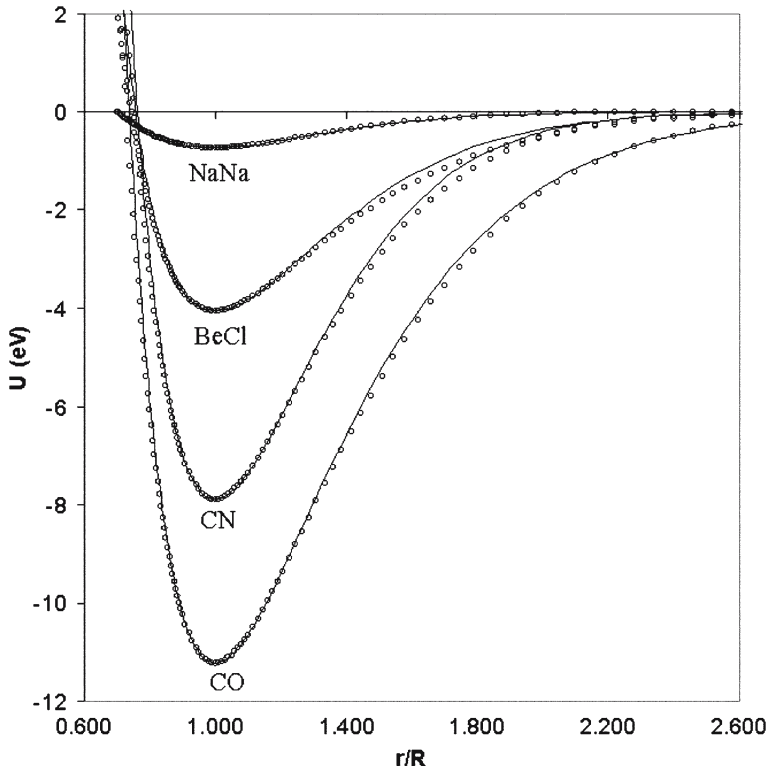


Figure 1. Plots of NaNa, BeCl, CN and CO potential curves using Extended-Rydberg function (continuous curves) and 2-body portion of Kaxiras–Pandey function (open circles) based on the former’s parameters.

Table 1
Extended-Rydberg parameters for NaNa, BeCl, CN and CO and equivalent Kaxiras–Pandey parameters using developed relationship.

Diatoms	$D(eV)$	$R(\text{\AA})$	$a_1(\text{\AA}^{-1})$	$a_2(\text{\AA}^{-2})$	$a_3(\text{\AA}^{-3})$	$\alpha_1(\text{\AA}^{-2})$	$\alpha_2(\text{\AA}^{-2})$
NaNa	0.730	3.0789	2.067	1.384	0.365	0.327085	0.121304
BeCl	4.052	1.7971	3.100	2.475	1.417	1.547845	0.233053
CN	7.888	1.1718	5.312	7.663	5.369	3.282067	0.715128
CO	11.226	1.1283	3.897	2.305	1.898	3.811648	0.544910

improvement herein is the removal of two simplifying assumptions that were adopted previously [37]. Although the larger number of Extended-Rydberg parameters than those of 2-body Kaxiras–Pandey indicate that one can only obtain latter from the former but not vice versa, a recent relationship whereby $a_3 \approx a_3(a_1, a_2)$ shows that D, R, a_1, a_2 can be obtained from $\alpha_1, \alpha_2, A_1, A_2$ while a_3 may then be estimated from a_1 and a_2 [40]. The practical significance of this

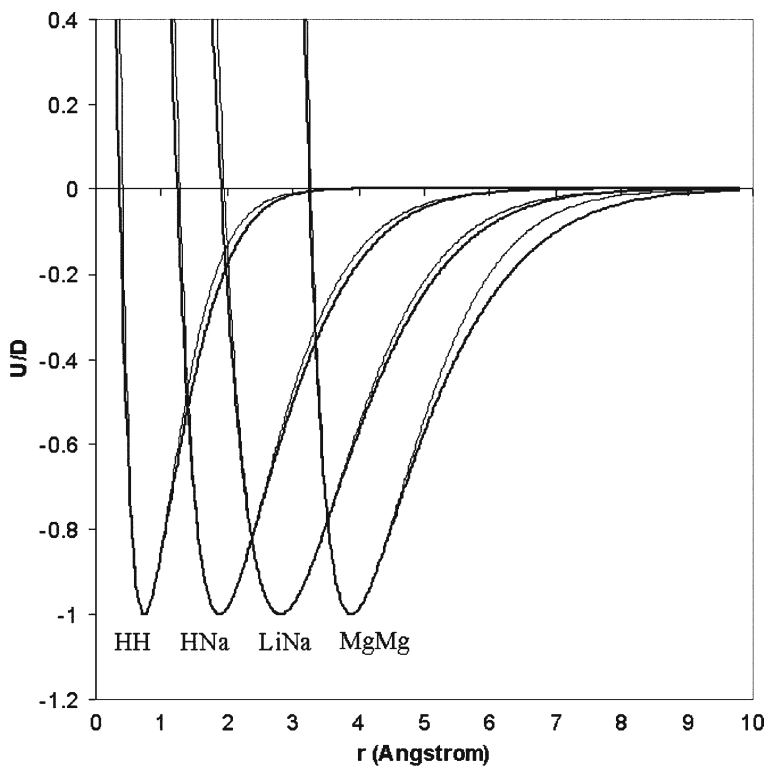


Figure 2. Plots of HH, HNa, LiNa and MgMg potential curves using Extended-Rydberg function (thin curves) and 2-body portion of Kaxiras–Pandey function (thick curves) based on the former’s parameters.

Table 2
Extended-Rydberg parameters for HH, HNa, LiNa and MgMg and equivalent Kaxiras–Pandey parameters using developed relationship.

Diatoms	$D(eV)$	$R(\text{\AA})$	$a_1(\text{\AA}^{-1})$	$a_2(\text{\AA}^{-2})$	$a_3(\text{\AA}^{-3})$	$\alpha_1(\text{\AA}^{-2})$	$\alpha_2(\text{\AA}^{-2})$
HH	4.747	0.7414	3.961	4.064	3.574	6.590820	0.521801
HNa	1.952	1.8874	2.154	1.071	0.365	1.153254	0.151995
LiNa	0.916	2.8100	1.846	0.993	0.237	0.470333	0.095705
MgMg	0.053	3.8905	2.043	1.005	0.526	0.495673	0.072104

developed relationship is the enormous combinations of diatomic parameters in the Extended-Rydberg functions [22] which can be conveniently converted to the Kaxiras–Pandey parameters whose function is used for computational simulation of many-body condensed matter systems.

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