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Scaling Factors between the 2-Body Energy of the Bauer-Maysenholder-Seeger and the Kaxiras-Pandey Potential Functions

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Abstract

A relationship between the two-body portion of the Bauer-Maysenholder-Seeger (BMS) and the Kaxiras-Pandey (KP) potential functions is established by means of a scaling factor to bridge parameters of these two potentials. The scaling factor was obtained by equating, at the equilibrium bond length, the 2-body portion derivatives of BMS and KP from the zeroth up to the third orders. The scaling factor based on derivatives up to the second order gives excellent agreement for bond extension but limited validity for bond-compression. The scaling factor based on derivatives up to the third order gives good correlation for both bond-compression and bond-extension.

1 Introduction

Although the quantum mechanical approach is known to be exact, the practicality of empirical potential energy functions in many-body systems remain relevant due to their ease of usage especially in the computation of

large scale and dynamical cases. With the availability of numerous potential functions for many-body systems (e.g. Erkoc [1] reviewed 38 potential functions), there is a need to understand how these potential functions differ from one another, how can they be related, and to which extent are their relatedness. One way to understand how these potential functions are related is to analytically connect their parameters. As such, graphical plots of two or more potential functions based on one set of potential function parameters reveals any discrepancy and the extent of their relatedness. Parametric relationships are also helpful when available or preferred parametric data and adopted potential function in software are based on different sets of potentials. Recently, parametric relationships have been developed amongst potential functions used in bond-torsion [2], bond-bending [3], bond-stretching [4,5] and van der Waals [6-8] interactions, thereby resulting in a molecular potential function converter [9,10], which takes advantage of series expansions [11]. Most of the developed relationships are, however, limited to the case of near equilibrium. Likewise, Stoneham et al. [12] performed a comparison of eight valence-force potentials, which are useful only for describing small distortions from equilibrium. Balamane et al. [13] gave a good review on six potential functions, but no analytical relationships were established amongst the considered potentials. In this paper, a set of analytical relationship is developed for relating parameters from the 2-body interaction portion of the Bauer-Maysenholder-Seeger (BMS) [14] and the Kaxiras-Pandey (KP) [15] potential functions by means of a scaling factor akin to previous works by Lim [6,8,16-21].

2 Analysis

One common characteristic of the BMS and the KP potential function that paves a way for relating the parameters is the fact that both of them quantify a system's energy as a summation of 2-body and 3-body interactions

$$\Phi_{Total} = \phi_{2-body} + \phi_{3-body} = \sum_{i<j} U_{ij} = \sum_{i<j<k} W_{ijk} \,. \tag{1}$$

In addition, the 2-body portion for both potentials consists of two distinct parts, namely a repulsive term and an attractive term:

$$U_{ij} = U_{ij}^{repul} + U_{ij}^{attr} \,. \tag{2}$$

Specifically, the 2-body portion of the BMS and KP potentials are

$$U_{BMS} = A\exp\left(-\frac{r}{\rho}\right) - \frac{B}{r^n} \tag{3}$$

and

$$U_{KP} = A_1 \exp\left(-\alpha_1 r^2\right) - A_2 \exp\left(-\alpha_2 r^2\right) \tag{4}$$

respectively, where r is the interatomic distance. Equating the derivatives at the equilibrium bond length R,

$$\left(\frac{\partial^m U_{BMS}}{\partial r^m}\right)_{r=R} = \left(\frac{\partial^m U_{KP}}{\partial r^m}\right)_{r=R} \tag{5}$$

from the zeroth to the third orders ($m = 0,1,2,3$), we have

$$\begin{bmatrix} \xi^0 & 1 \\ \xi^1 & n \\ \xi^2 & n(n+1) \\ \xi^3 & n(n+1)(n+2) \end{bmatrix} \begin{Bmatrix} A\exp(-\xi) \\ -\left(\frac{B}{R^n}\right) \end{Bmatrix} = \begin{bmatrix} 1 & 1 \\ \psi_1 & \psi_2 \\ \psi_1(\psi_1 - 1) & \psi_2(\psi_2 - 1) \\ {\psi_1}^2(\psi_1 - 3) & {\psi_2}^2(\psi_2 - 3) \end{bmatrix} \begin{Bmatrix} A_1 \exp\left(-\frac{\psi_1}{2}\right) \\ -A_2 \exp\left(-\frac{\psi_2}{2}\right) \end{Bmatrix} \tag{6}$$

where the scaling factors, ξ, ψ_1 and ψ_2 are defined as

$$\xi = \frac{R}{\rho} \tag{7a}$$

and

$$\psi_i = 2\alpha_i R^2 \quad ; \quad (i = 1,2) \,. \tag{7b}$$

Since the minimum well-depth is defined at $r = R$, equating the second row of Eq.(6) as zero gives

$$\frac{B}{R^n} = \frac{\xi}{n} A \exp(-\xi) \tag{8}$$

and

$$\alpha_1 A_1 \exp\left(-\alpha_1 R^2\right) = \alpha_2 A_2 \exp\left(-\alpha_2 R^2\right). \tag{9}$$

Substituting Eqs.(8) and (9) into the first and third rows of Eq.(6) enables the terms $A\exp(-\xi)$ and $A_1 \exp(-\alpha_1 R^2)$ to be eliminated such that we obtain the BMS scaling function.

$$\xi = \frac{n+1}{2} + \frac{2}{n}\alpha_1\alpha_2 R^4 \pm \frac{1}{2}\sqrt{\left(n+1+\frac{4}{n}\alpha_1\alpha_2 R^4\right)^2 - 16\alpha_1\alpha_2 R^4}\,. \tag{10}$$

The BMS function expresses the BMS scaling factor in terms of KP parameters. Alternatively, substituting Eqs.(8) and (9) into the third and fourth rows of Eq.(6) and solving similarly leads to another BMS scaling function

$$\xi = (\alpha_1 + \alpha_2)R^2 - \frac{3}{2} \pm \frac{1}{2}\sqrt{\left[2(\alpha_1+\alpha_2)R^2 - 3\right]^2 - 4(n+1)\left[2(\alpha_1+\alpha_2)R^2 - n - 5\right]}\quad . \tag{11}$$

As such, the scaling functions described by Eqs.(10) and (11) correspond to orders up to $m = 2$ and $m = 3$ respectively. Considering Eq.(8) and the first row of Eq.(6) , the 2-body portion of the BMS potential as described by Eq.(3) can be rewritten in the loose form

$$U_{BMS} = D_{KP}\left[\frac{n}{\xi - n}\exp\left(\xi\left(1-\frac{r}{R}\right)\right) - \frac{\xi}{\xi - n}\left(\frac{R}{r}\right)^n\right] \tag{12a}$$

with the following magnitude of the minimum well-depth

$$D_{KP} = \frac{\alpha_1 - \alpha_2}{\alpha_2} A_1 \exp\left(-\alpha_1 R^2\right) = \frac{\alpha_1 - \alpha_2}{\alpha_1} A_2 \exp\left(-\alpha_2 R^2\right) \tag{12b}$$

and the scaling function, ξ, in terms of KP parameters and the equilibrium bond length. The loose form displayed in Eq.(12) is analogous to the loose form of Exponential-6 potential

$$U_{X6} = D_{LJ}\left(\frac{n}{\xi - n}\right)\exp\left[\xi\left(1-\frac{r}{R}\right)\right] - D_{LJ}\left(\frac{\xi}{\xi - n}\right)\left(\frac{R}{r}\right)^n \tag{13}$$

in terms of the Lennard-Jones parameters (D_{LJ}, R) where $n = 6$, with scaling factors 13.772 and 12.0 for near equilibrium and long range respectively [6,22-25]. Since the equilibrium bond length is not reflected in both the original form of BMS and KP potentials, it is hence not a parameter for these two functions. We extract from Eq.(9) to obtain the equilibrium bond length

$$R = \sqrt{\frac{1}{\alpha_1 - \alpha_2}\ln\left(\frac{\alpha_1 A_1}{\alpha_2 A_2}\right)}. \tag{14}$$

On the other hand, solving for the KP scaling factors using Eqs.(8), (9), and the first, third and fourth rows of Eq.(6), gives the KP scaling function,

$$\psi_{1,2} = \frac{1}{2}\left[3 + \frac{(R/\rho)^2 - (n+1)(n+2)}{(R/\rho) - (n+1)}\right] \pm \frac{1}{2}\sqrt{\left[3 + \frac{(R/\rho)^2 - (n+1)(n+2)}{(R/\rho) - (n+1)}\right]^2 - \frac{4(R/\rho)n\left((R/\rho) - (n+1)\right)}{(R/\rho) - n}} \tag{15}$$

which describes the KP scaling factor in terms of BMS parameters. With reference to Eq.(9) and the first row of Eq.(6), the 2-body portion of KP as shown in Eq.(4) can be rewritten as

$$U_{KP} = D_{BMS}\left[\frac{\psi_2}{\psi_1 - \psi_2}\exp\left(\frac{\psi_1}{2}\left(1-\frac{r^2}{R^2}\right)\right) - \frac{\psi_1}{\psi_1 - \psi_2}\exp\left(\frac{\psi_2}{2}\left(1-\frac{r^2}{R^2}\right)\right)\right] \tag{16}$$

with the magnitude of the minimum well-depth

$$D_{BMS} = \frac{(R/\rho) - n}{n} A\exp\left(-\frac{R}{\rho}\right) = \frac{(R/\rho) - n}{(R/\rho)}\left(\frac{B}{R^n}\right) \tag{17}$$

and the scaling functions, $\psi_i\,(i=1,2)$, in BMS parameters and the equilibrium bond length. A summary of parametric relationships for the 2-body portion of BMS and KP potentials is listed in Table 1.

Table 1: Parametric relationships between the 2-body portions of BMS and KP potentials

Potentials (2-body portion)	**Parametric relationships**
U_{BMS} $=U_{BMS}(A,B,\rho,n,r)$	$A\left(\frac{(R/\rho)-n}{n}\right)\exp\left(-\frac{R}{\rho}\right)=A_1\left(\frac{\alpha_1-\alpha_2}{\alpha_2}\right)\exp\left(-\alpha_1 R^2\right)$ $B\left(\frac{(R/\rho)-n}{(R/\rho)}\right)R^{-n}=A_2\left(\frac{\alpha_1-\alpha_2}{\alpha_1}\right)\exp\left(-\alpha_2 R^2\right)$ $\xi\rho\equiv R\equiv\sqrt{\frac{\psi_i}{2\alpha_i}}\quad;\quad(i=1,2)$ where $R=\sqrt{\frac{1}{\alpha_1-\alpha_2}\ln\left(\frac{\alpha_1 A_1}{\alpha_2 A_2}\right)}$ and ξ is given in the upper solutions of Eqs.(10) or (11) based on the second or third order derivatives respectively, whilst ψ_1 and ψ_2 are given in the upper and lower solutions of Eq.(15) respectively based on the second and third orders.
U_{KP} $=U_{KP}(A_1,A_2,\alpha_1,\alpha_2,r)$	

3 Results and discussion

For the purpose of illustration, we choose $n=6$ as this is a value most consistently adopted in a number of pair potentials (see Table 2). Applying the KP parameters $(A_1,A_2,\alpha_1,\alpha_2)$ as listed in Table 3 [15] and $n=6$ for Eq.(14) gives $R=2.401657\,\mathrm{\AA}$. Substituting these values into Eqs.(10) and (11), we have the upper solutions for the scaling factors as $\xi=7.805016$ and $\xi=8.094231$ respectively. The corresponding lower solutions are not valid since they are lower than $n=6$, which changes the sign of the repulsive and

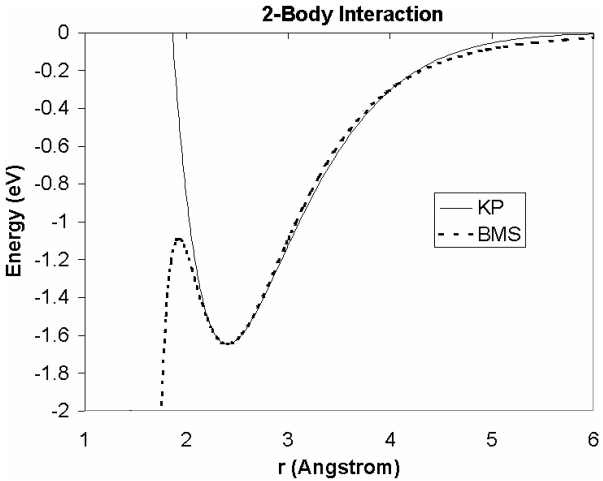
Table 2: Examples whereby $n \cong 6$

Potential functions	**2-body portion**	**References**
Buckingham potential	$U_{X6} = A_{X6}\exp(-Cr) - \frac{B_{X6}}{r^6}$	[26]
Lennard-Jones and the 2-body portion of Pearson-Takai-Halicioglu-Tiller potential function	$U_{LJ} = D_{LJ}\left[\left(\frac{R}{r}\right)^{12} - 2\left(\frac{R}{r}\right)^{6}\right]$	[27,28]
Erkoc's potential for FCC	$U_{Erkoc} = \varepsilon\left[\frac{n}{m-n}\left(\frac{R}{r}\right)^{m} - \frac{m}{m-n}\left(\frac{R}{r}\right)^{n}\right]\exp(\alpha r^*)$ where $n = 5$ for Pd, $n = 7$ for Kr, but a majority with $n = 6$ for Xe, Al, Cu and Pb.	[29]

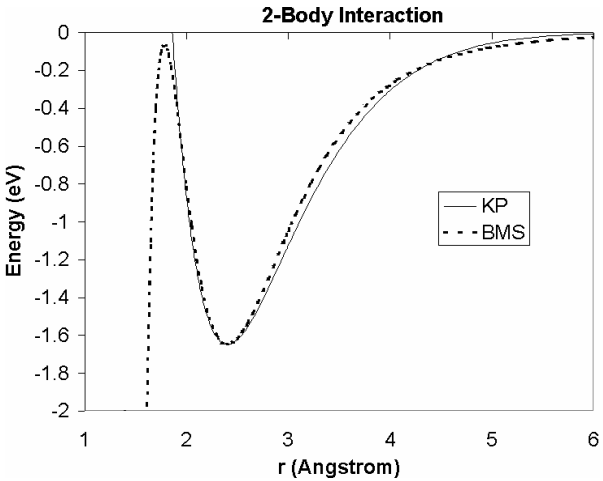
Table 3: Kaxiras-Pandey parameters for silicon

Parameters	**Value**
A_1	57.316072 eV
A_2	6.4373054 eV
α_1	0.8233523 Å^{-2}
α_2	0.19061589 Å^{-2}

attractive terms. Hence the BMS curves, based upon KP parameters, were plotted using $\xi = 7.805016$ and $\xi = 8.094231$ in Figures 1(a) and 1(b) respectively. The KP 2-body energy is also plotted for comparison. We observe that adopting derivatives up to $m = 2$ gives very good approximation except for bond compression, as shown in Figure 1(a). On the other hand, considering $m = 3$, as depicted in Figure 1(b), extends the applicability of the present parametric relationship to a further extent of bond compression with a minor penalty in the accuracy for bond extension. In practical consideration, Eq.(10) is suggested for bond-stretching whilst Eq.(11) is recommended when



(a)



(b)

Figure 1: Two-body curve of BMS potential based on KP parameters [15] and $n = 6$ considering derivatives up to the (a) second order $\xi = 7.805016$, and (b) third order $\xi = 8.094231$.

both bond-stretching and bond-compression are modeled. Both sets of scaling factors, however, give equally accurate description for small distortion about the equilibrium due to the imposition of equal curvature at the minimum well-depth. No illustration is made herein for the case of comparing the KP potential using BMS parameters with the purely BMS potential due to the lack of BMS parametric data. However, with the use of up to $m = 3$ for obtaining both ψ_1 and ψ_2 simultaneously, the parametric relationship in this case is comparable to that described in Eq.(11).

4 Conclusions and recommendation

By equating the derivatives of the 2-body portions of the BMS and KP potential functions, a set of parametric relationships has been established. Two scaling factors were extracted by equating derivatives from the zeroth order up to second and third orders at the equilibrium bond length. The former is highly suitable for bond-stretching whilst the latter is generally applicable for both compression and stretching of bonds. With the parametric relationship between the 2-body portion of BMS and KP obtained, it is hereby suggested that parametric relationship be obtained for the 3-body portion of these two potential functions.

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