

Linnett potential energy curves using Morse parameters

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(Received March 25, 2008)

Abstract

The Linnett potential's fulfillment of all three necessary requirements of a potential energy function places it as a viable alternative to the Morse function. Unlike the Morse function, the Linnett function gives infinite energy when $r = 0$. Since Morse parameters are readily available, we propose the use of Morse parameters for conversion into Linnett potential energy. Three methods are proposed herein – long range, short range, and mid range approaches. The short range (or local approach) has been found to be suitable for $r < 1.2R$ while the mid range approach (or global approach) was found to be suitable for $r > 1.2R$. The long range (or asymptotic approach) was found not to be suitable.

1. Introduction

The use of Morse function [1]

$$U_M = D\{\exp[-2\alpha(r-R)] - 2\exp[-\alpha(r-R)]\} \quad (1)$$

for describing the potential energy of bonds has been extensive in molecular mechanics softwares (e.g. [2-5]) and also in condensed matter computation in the general form [6]

$$U_M^{GEN} = A_1 \exp(-\lambda_1 R) + A_2 \exp(-\lambda_2 R) \quad (2)$$

In spite of its pervasiveness, the Morse function fulfills only two out of three necessary requirements of a potential energy function, i.e. it becomes asymptotically to a finite value as $r \rightarrow \infty$, and it has a minimum at $r = R$. However the Morse function “fails” the third necessary requirement in that it is not infinite at $r = 0$ [7] although it is sufficiently “high” for very small r .

Even though the “false” behavior corresponds to the energy range above the dissociation limit where there are no bound vibrational states, this drawback poses a serious consequence on the properties computed using the Morse curve for modeling intramolecular energy during molecular collision. For such cases, the bonds are highly compressed momentarily to above the dissociation energy. This disadvantage was overcome by Linnett’s [8-9] potential function

$$U_L = \frac{A}{r^m} - B \exp(-Cr). \quad (3)$$

It is easily seen that Linnett’s potential function interchanges the functional forms of the attractive term with the repulsive terms from the Buckingham’s potential function [10,11]

$$U_B = A \exp(-Br) - \frac{C}{r^n}. \quad (4)$$

As a result, the Linnett function enables all the three requirements to be fulfilled. Furthermore, Linnett’s attractive term resembles Morse’s attractive term, thereby providing no doubt as to the former’s suitability for quantifying bond stretching energy.

In this paper, we propose the use of Linnett potential function as a good alternative to the Morse function for large change in bond length. Due to the vast availability of Morse parameters, we herein convert Morse parameters into Linnett parameters using three different approaches. Finally, a recommendation is made upon comparing all the conversion methods considered herein.

2. Analysis

It has recently been shown that the generalized versions of Morse [1], Linnett [8,9], Buckingham [10,11] and Lennard-Jones [12-14] potential functions can be represented by [15]

$$\frac{U_F}{D} = \frac{n^x \xi_2^{1-x}}{m^y \xi_1^{1-y} - n^x \xi_2^{1-x}} \left(\frac{R}{r}\right)^{my} \exp\left[\xi_1 \left(1 - \frac{r}{R}\right)(1-y)\right] - \frac{m^y \xi_1^{1-y}}{m^y \xi_1^{1-y} - n^x \xi_2^{1-x}} \left(\frac{R}{r}\right)^{nx} \exp\left[\xi_2 \left(1 - \frac{r}{R}\right)(1-x)\right] \quad (5)$$

whereby substitution of $(x,y) = (0,0)$, $(0,1)$, $(1,0)$ and $(1,1)$ reduces it to the generalized Morse, Linnett, Buckingham and Lennard-Jones potentials respectively. On the basis of Eq.(5), the Linnett function can be written in an alternative form to Eq.(3) as

$$U_L = D \left[\left(\frac{R}{r}\right)^m - 2 \exp\left(-\frac{n}{R}(r-R)\right) \right] \quad (6)$$

We further recall that in the case van der Waals potential energy curves, the Exponential-6 potential function, which is a specific Buckingham potential with $n = 6$,

$$U_{X6} = A \exp(-Br) - \frac{C}{r^6} \quad (7)$$

was expressed in a loose form

$$U_{X6} = D \left\{ \frac{6}{\xi - 6} \exp\left[\xi \left(1 - \frac{r}{R}\right)\right] - \frac{\xi}{\xi - 6} \left(\frac{R}{r}\right)^6 \right\} \quad (8)$$

such that substitution of $\xi = 12$ gives the same long range attraction as the Lennard-Jones (12-6) form while substituting $\xi = 13.772$ gives equal curvature with that of Lennard-Jones (12-6) at the minimum well-depth so that a short range relation was obtained [3,4]. This analogy, substitution of

$$n = \alpha R \tag{9}$$

into Eq.(6) would give it the same long range attraction as the Morse form. In order to give a short range relation we let

$$\left(\frac{\partial^2 U_M}{\partial r^2} \right)_{r=R} = \left(\frac{\partial^2 U_L}{\partial r^2} \right)_{r=R} \tag{10}$$

such that

$$n = -\frac{1}{2} \pm \frac{1}{2} \sqrt{1 + 4\alpha^2 R^2} . \tag{11}$$

The imposition of equal curvatures has been shown to be successful for relating parameters between different potential functions, normally within the range $0.9 \leq (r/R) \leq 1.2$ [16-21]. Since it is required for $n > 0$, then the physically admissible value for n is the upper solution

$$n = \frac{1}{2} \left[1 + \sqrt{1 + (2\alpha R)^2} \right]. \tag{12}$$

Recently it has been shown that good parameter relations for mid range can be obtained by imposing equal energy integral within the range $1 \leq (r/R) \leq \infty$ [22-24]. Hence equating

$$\int_R^\infty U_M dr = \int_R^\infty U_L dr \tag{13}$$

and selecting the upper solution for n gives

$$n = \frac{1}{2} \left[\left(\frac{1}{2} + \alpha R \right) + \sqrt{\left(\frac{1}{2} + \alpha R \right)^2 - \frac{8}{3} \alpha R} \right]. \tag{14}$$

3. Results and Discussion

To test the validity of the converted Linnett parameters, we use the Morse parameters furnished by Girifalco and Weizer [25]. In order to compare the potential energy curves in non-dimensionalized planes, the interatomic energy U and bond length r are plotted in terms of non-dimensionalized ratios U/D and r/R . As a result, the parameter D for the 16 metals considered by Girifalco and Weizer is omitted in Table 1.

Table 1. The long, short and mid range Linnett parameter n based on Morse parameters (α, R) by Girifalco and Weizer [25].

Metal	α (Å ⁻¹)	R (Å)	αR	n (long range)	n (short range)	n (mid range)
Mo	1.5079	2.976	4.48751	4.48751	4.01528	4.29018
Pb	1.1836	3.733	4.41838	4.41838	3.94658	4.22045
Cr	1.5721	2.754	4.32956	4.32956	3.85834	4.13082
W	1.4116	3.032	4.27997	4.27997	3.80908	4.08076
Ag	1.369	3.115	4.26444	4.26444	3.79365	4.06507
Fe	1.3885	2.845	3.95028	3.95028	3.4818	3.74755
Ni	1.4199	2.78	3.94732	3.94732	3.47886	3.74456
Cu	1.3588	2.866	3.89432	3.89432	3.42629	3.69091
Al	1.1646	3.253	3.78844	3.78844	3.3213	3.58369
Sr	0.73776	4.988	3.67995	3.67995	3.21376	3.4737
Ca	0.80535	4.569	3.67964	3.67964	3.21346	3.47339
Ba	0.65698	5.373	3.52995	3.52995	3.06519	3.32143
K	0.49767	6.369	3.16966	3.16966	2.70885	2.95443
Na	0.58993	5.336	3.14787	3.14787	2.68733	2.93216
Cs	0.41569	7.557	3.14137	3.14137	2.68091	2.92551
Rb	0.42981	7.207	3.09764	3.09764	2.63773	2.88079

Based on the data of α and R for the 16 metals, the Linnett parameter as described by Eqs.(9), (12) and (14) was calculated and furnished in Table 1 and n (long range), n (short range) and n (mid range) respectively. Of the 16 metals, four were selected for illustration on the basis of almost equal spacing of αR , i.e. molybdenum (Mo), iron (Fe), barium (Ba) and rubidium (Rb). In figures 1 to 3, the discrete points denoted by white circles, black circles, white triangles and black triangles refer to the plotted Morse potential energy curves

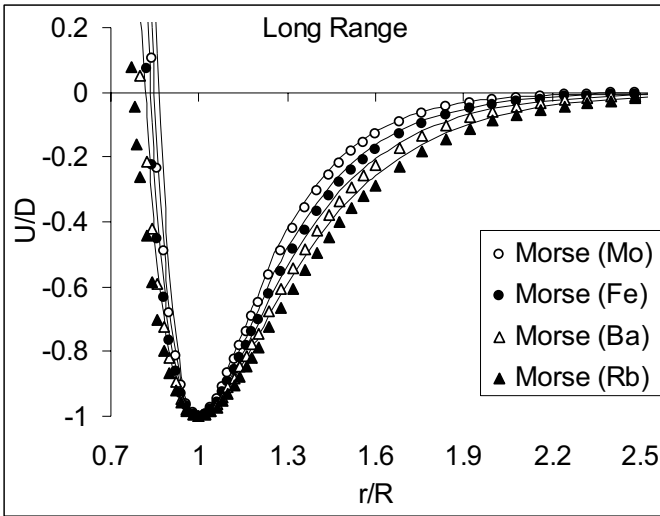
of Mo, Fe, Ba and Rb respectively. The smooth continuous curves in Figs.1, 2 and 3 correspond to the Linnett potential energy curve with the parameter n based on Eqs.(9), (12) and (14) respectively. Parts (a) of these figures show the overall plots while parts (b) focus at near the minimum well-depth.

It is easily seen in Fig.1(a) that the long range parameter conversion gives overestimated Linnett curves. These curves appear to coincide with the corresponding Morse data points at large bond stretching, i.e. for $r > 1.9R$. However, the long range parameter conversion is not satisfactory for small bond-stretching. This can be inferred from the Linnett curves of Fe, Ba and Rb, which coincide with the Morse data points of Mo, Fe and Ba, respectively. See Fig.1(b).

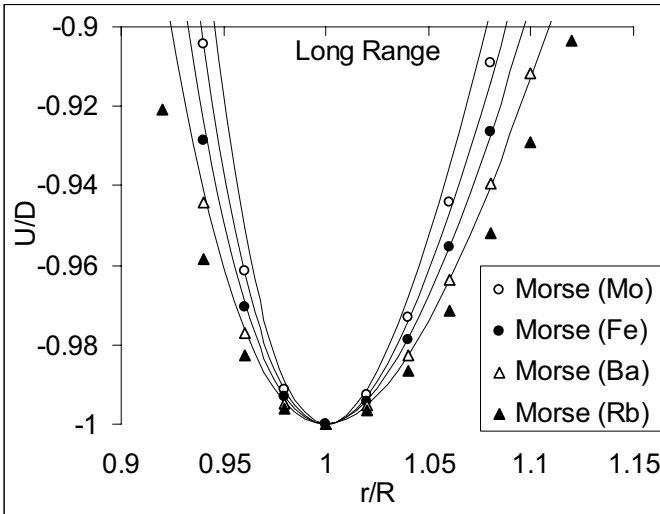
Unlike the long range conversion, the short range conversion tends to give underestimated Linnett curves, as shown in Fig.2(a). The Linnett curves agree well with their corresponding Morse data points near the minimum well-depth, as can be seen in Fig.2(b). This is attributed to the imposition of equal curvatures at the minimum well-depth.

For the case of mid range parameter conversion, the Linnett curves correlate very well with their corresponding Morse data points, as evident from Fig.3(a). However the Linnett curves slightly overestimates their corresponding Morse data points, as evident from Fig.3(b). It is also worth noting that at large bond stretching, the mid range parameter conversion gives better agreement with the Morse energy than the Linnett curves based on long range conversion. The mid range conversion gives better agreement because it takes into consideration both the repulsive and attractive terms, unlike the long range conversion. The long range parameter conversion may well be the most appropriate for extremely large bond stretching beyond the range considered in Figs. 1 to 3, but any accuracy at such large bond stretching would be of no practical value.

In all the three figures, the Linnett curves overestimate the Morse data points for bond compression. This should be viewed in a positive light in that such overestimation is accompanied with the requirement for infinite interatomic energy at $r = 0$ [7].

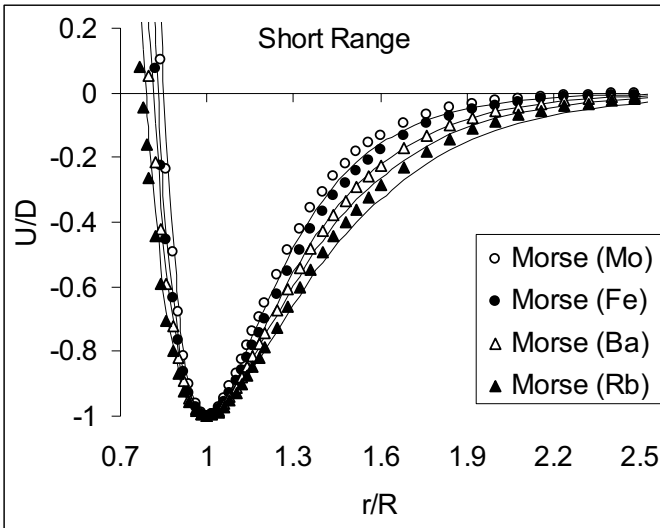


(a)

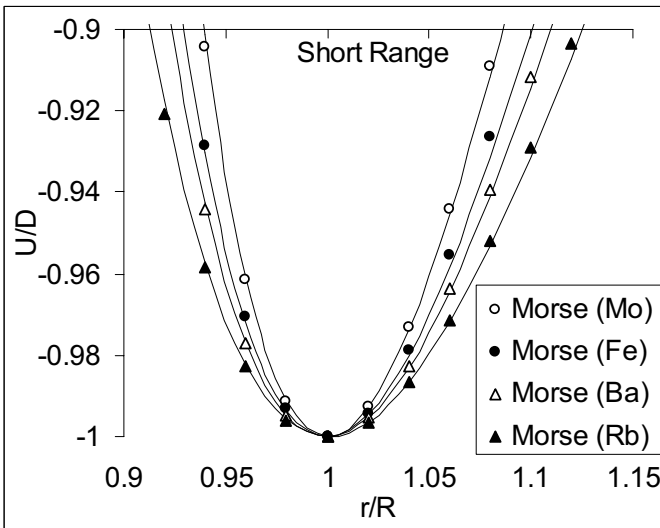


(b)

Fig.1. Plots of Morse potential energy (data points) and the converted Linnett potential energy (curves) using Eq.(9) for long range approach: (a) overview, and (b) near equilibrium.

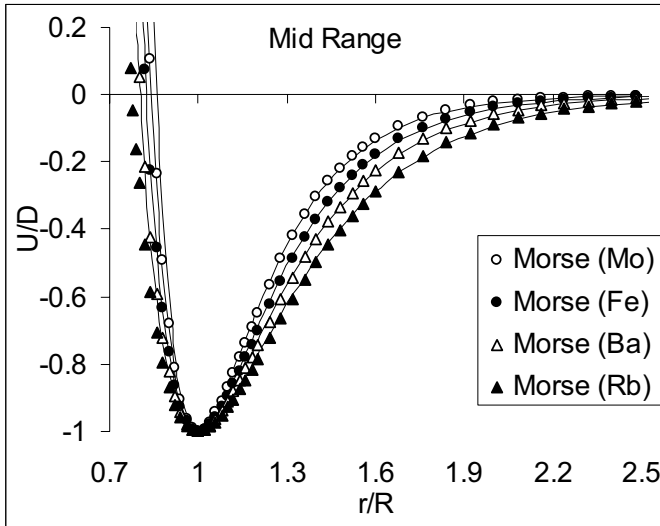


(a)

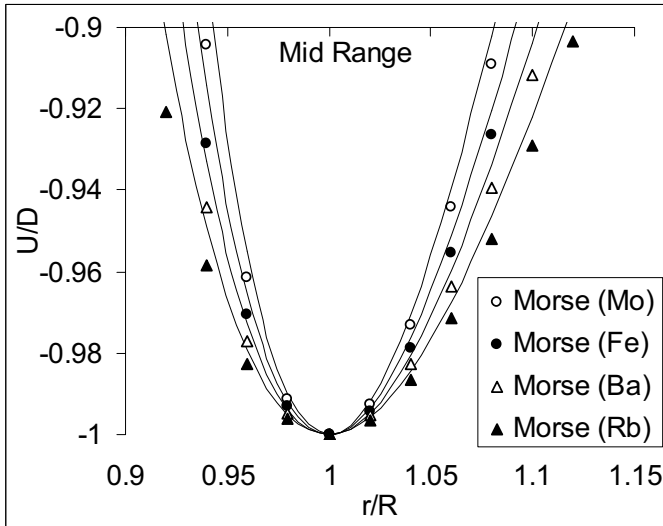


(b)

Fig.2. Plots of Morse potential energy (data points) and the converted Linnert potential energy (curves) using Eq.(12) for short range approach: (a) overview, and (b) near equilibrium.



(a)



(b)

Fig.3. Plots of Morse potential energy (data points) and the converted Linnett potential energy (curves) using Eq.(14) for mid range approach: (a) overview, and (b) near equilibrium.

4. Conclusions

The Linnett potential function is appropriate for describing the interatomic energy for bonds due to its adherence to all the three necessary requirements for an interatomic potential energy function. In view of the lack of Linnett parameters, it is more economical to obtain the Linnett potential function from Morse parameters, which is widely available. Three conversion methods were identified. The long range approach is convenient but not recommended because it is the least accurate among the three methods. The short range approach is based on second derivative equality imposition to give equal curvature at the minimum well-depth – thereby enabling very accurate Linnett energy for small change in bond length. The mid range approach is based on integral equality imposition to give equal energy integral from equilibrium to dissociation – thereby enabling very accurate Linnett energy for mid to large bond stretching. Plotted results reveal that for large change in bond length, the Linnett potential function is a viable option and that the Morse parameters can be converted to the former's parameters for convenience. The parameter conversion based on short range should be switched to mid range when the bond length reaches $r=1.2R$. Although costly and/or more time consuming, it is recommended that the extraction of Linnett parameters be made from original spectroscopic or *ab initio* data, which yield more accurate results. It is further suggested that a relationship between Linnett function be established with recently developed potential functions (e.g. [26-30]).

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