

Improved long range relationship between parameters of the Morse and Rydberg potential functions

Teik-Cheng Lim

Received: 20 March 2007 / Accepted: 13 July 2007 / Published online: 25 August 2007
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Abstract Information on parameter relationships between different interatomic potential energy functions is useful when there is a functional mismatch between preferred parameters from one potential function and the adoption of another potential function in computational chemistry softwares. Previous attempts in relating parameters of different potential functions focus on equating the potential curves' curvatures at the minimum well-depth, which are not accurate for large bond-stretching. In this paper, the long range error is minimized by imposing equal energy integral from equilibrium bond length to bond dissociation. Plotted results for the long range parameter relationship between the Morse and Rydberg potential energy functions reveal excellent agreement for long range interaction.

Keywords Bond-stretching · Long range · Parameter relations · Morse · Rydberg

1 Introduction

Knowledge on the relationship between interatomic potential energy functions is useful when a need arises to convert parameters from a preferred potential function into parameters of potential functions adopted in computational chemistry softwares. So far, relationships between parameters from different potential energy functions were developed either by the multi-derivative approach or the series expansion approach [1–7]. For both methods, the connected parameters across different potential functions lead to equal curvature at the equilibrium bond length. Although this criterion is valid for infinitesimal change in bond length, the error becomes more evident for large

T.-C. Lim (✉)

School of Science and Technology, SIM University (UniSIM), 535A Clementi Road, S 599490,
Singapore, Republic of Singapore
e-mail: alan_tc_lim@yahoo.com

bond stretching. An attempt to provide long range relationship between the Morse parameter [8] and the Rydberg [9, 10], which was adopted as the 2-body portion of the Murrell–Mottram potential, did not provide satisfactory result [11]. In this paper, a novel philosophy is put forward whereby the criterion for equal curvature at minimum well-depth is relaxed to pave a way for another criterion to be implemented.

2 Analysis

The potential energy functions by Morse and Rydberg are given as

$$U_M = D \left(e^{-2\alpha(r-R)} - 2e^{-\alpha(r-R)} \right) \quad (1)$$

and

$$U_{Ryd} = -D(1 + a\rho) e^{-a\rho}. \quad (2)$$

Respectively, where D and r are the magnitude of the minimum well-depth and the bond length respectively. The equilibrium bond length is denoted by R . The parameters α and a control the shape of the potential energy curves. There are two definitions adopted for ρ , i.e. either

$$\rho = \frac{r - R}{R} \quad (3)$$

or

$$\rho = r - R. \quad (4)$$

If ρ is defined by Eq. 3 as in the case of the 2-body portion of the Murrell–Mottram function used in many-body condensed matter systems, then the parameter a is dimensionless [12–17]. In this paper, we define ρ as described by Eq. 4 in order to align it to the Murrell–Sorbie function [18–20], thereby incurring an inverse length dimension to parameter a . This dimension corresponds to that of α .

It is easily seen that both functions give

$$(U_M)_{r=R} = (U_{Ryd})_{r=R} = -D \quad (5)$$

and

$$\left(\frac{\partial U_M}{\partial r} \right)_{r=R} = \left(\frac{\partial U_{Ryd}}{\partial r} \right)_{r=R} = 0 \quad (6)$$

at the minimum well-depth. Imposing

$$\left(\frac{\partial^2 U_M}{\partial r^2} \right)_{r=R} = \left(\frac{\partial^2 U_{Ryd}}{\partial r^2} \right)_{r=R} \quad (7)$$

Fig. 1 Similarity and dissimilarity between the short and long range approaches

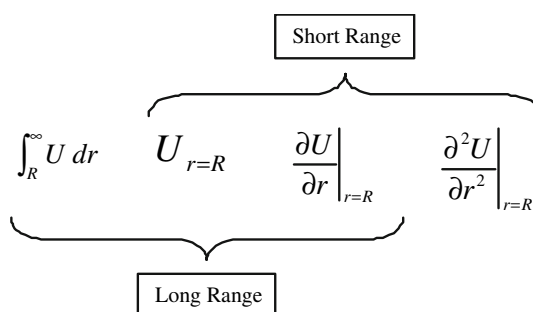


Table 1 Morse parameters for molybdenum and rubidium, and their corresponding converted Rydberg parameters

Diatom	Morse parameter αR [21]	Rydberg parameter aR (short range)	Rydberg parameter aR (long range)
Molybdenum	4.48751	6.346298	5.983347
Rubidium	3.097641	4.380726	4.130188

gives the short range relation as

$$\frac{a}{\alpha} = \sqrt{2}. \quad (8)$$

In an opposed manner, we let the integral of both potential functions be equal for the range $R \leq r \leq \infty$, i.e.

$$\int_R^\infty U_M dr = \int_0^\infty U_{Ryd} d\rho \quad (9)$$

to yield

$$\frac{a}{\alpha} = \frac{4}{3}. \quad (10)$$

Figure 1 summarizes the similarity and dissimilarity between both the short and long range parameter relationships.

3 Results and discussion

In order to verify the long range parameter relationship, the non-dimensional interatomic potential energy (U/D) curves were plotted against the non-dimensional bond length (r/R). Table 1 lists the Morse parameters of molybdenum and rubidium based on data from Girifalco and Wiezer [21], and the Rydberg parameters based on

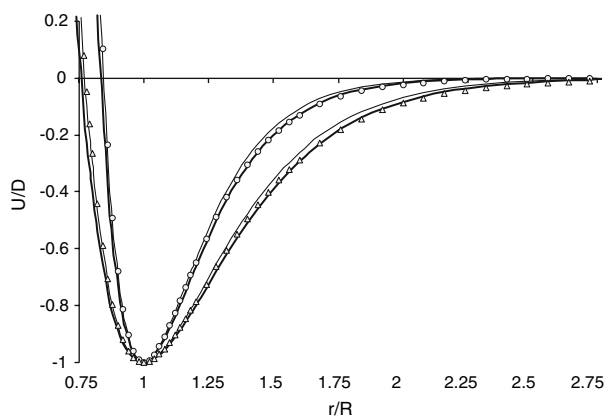


Fig. 2 Morse potential energy curves for Molybdenum (circles) and Rubidium (triangles) with their corresponding Rydberg curves based on short range (thin curves) and long range (thick curves) relationships

conversion from the short and long range relations. Rewriting Eqs. 1 and 2 as

$$\frac{U_M}{D} = e^{2\alpha(1-\frac{r}{R})} - 2e^{\alpha(1-\frac{r}{R})} \quad (11)$$

and

$$\frac{U_{Ryd}}{D} = \left[aR \left(1 - \frac{r}{R} \right) - 1 \right] e^{aR(1-\frac{r}{R})} \quad (12)$$

respectively, the potential energy curves for molybdenum and rubidium were plotted as shown in Fig. 2. This illustration reveals that the short range relation is highly advantageous for small bond stretching but its superiority is surpassed by the long range relations for intermediate and large bond stretching. For clarity, non-dimensional error was plotted against the non-dimensional bond length, as depicted in Fig. 3.

It can be seen in Fig. 2, and especially more so in Fig. 3, that there is a crossover of both potential functions for $R < r < \infty$ when the long range relation was imposed, but not so for the case of short range relation. This cross-over was made possible through the implementation of Eq. 9, which enforces equal area above both energy curves from the equilibrium bond length to bond dissociation. Hence the overall error for the range $R \leq r \leq \infty$ is zero. As a result of this cross-over, the long range parameter relation provides a lower extent of error, or a more accurate parameter conversion, for the case of large bond-stretching.

4 Conclusions

In a departure from previous approaches for obtaining parameter relations among different interatomic potential energy functions, this paper relaxes the requirement for equal curvature at the well-depth. This requirement is replaced by the imposition of equal energy integral within $R \leq r \leq \infty$ so as to reduce the overall error for that range

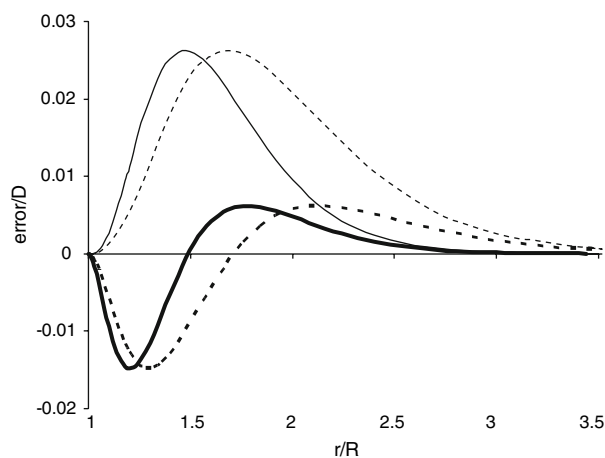


Fig. 3 Error distribution of obtained Rydberg curves by short range (thin curves) and long range (thick curves) with reference to the Morse curves of molybdenum (continuous lines) and rubidium (dashed lines)

to zero. Illustration for the case of Morse and Rydberg over long range exhibit immense improvement compared to earlier result [11]. It is herein recommended that further investigation on the suitability of the integral approach is performed for other combinations of potential functions before a long range parameter converter is embarked on.

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