

Extracting the long range Rydberg parameter from the Generalized Morse potential energy function

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Abstract

An integral method is adopted herein in order to extract the Rydberg parameter from those of the generalized Morse potential energy function. By imposing equal area above the potential energy curves from equilibrium to dissociation, the parameter relationship is suitable for the case of large bond-stretching. This integral approach is significantly different from the double or higher derivative and the series expansion approach, which gives acceptable parameter relations only for the case of small bond-stretching. The obtained relations enable parameters of the more flexible function, the generalized Morse potential, to be converted into those of the Rydberg parameters for application in 2-body interaction of multi-body systems.

1. Introduction

Unlike the bridging parameter which describes the difference between various potential energy functions [1-4], parameter relationships among different potential energy functions are useful for converting parameters from a preferred potential energy function into parameters of another function, which is adopted in some molecular mechanics and chemical physics softwares. Earlier attempts of obtaining the parameter relationships

have been largely confined to the philosophy of imposing equal curvature at the minimum well depth of the potential energy curves [5-10]. Although these relations are valid for small bond-stretching, the error between both potential curves become more pronounced for the bond length range within $1.2R < r < 2.4R$.

In this paper, the imposition of equal curvature at the minimum well-depth is removed to make way for a criterion more appropriate in large bond-stretching. Specifically, integral of both functions are taken from the equilibrium state to dissociated state. Thereafter, both integrals are equated so that the areas above both potential energy curves are equal for $R \leq r \leq \infty$. Hence the error is effectively minimized. See Fig.1.

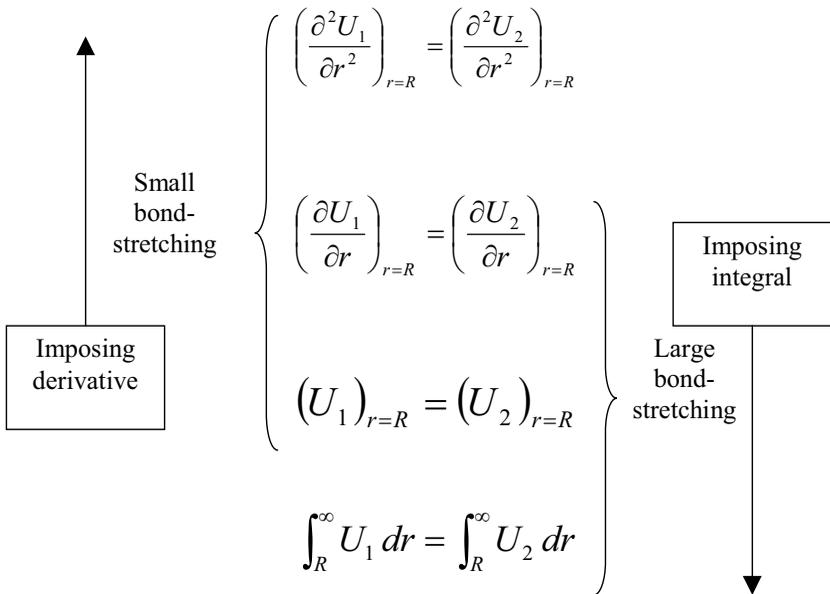


Fig. 1. Similarity and dissimilarity between the parameter relations for small and large bond stretching.

In this paper, we show the advantage of the integral approach over the derivative approach for obtaining the Rydberg parameter using those of the Generalized Morse potential energy function.

2. Analysis

The Rydberg potential energy function [11,12] is given as

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

where D is the dissociation energy while the parameter a controls the shape of the potential energy curve. The variable ρ is defined either as

$$\rho = r - R \quad (2)$$

or as

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

where r is the bond length upon stretching while R is the bond length at equilibrium. These 2 definitions result in inverse length dimension or no dimension for a . In this paper, we select the definition described by Eq.(2). As a consequence of its good fit for covalent bonds, the Rydberg parameter has been adopted as the stretching energy between bonded atoms in many-body condensed matter systems [13-18] and also extended to more parameters [19-24]. Of equal importance in covalent bond energy description is the Morse potential function [25]

$$U_M = D(e^{-2\alpha(r-R)} - 2e^{-\alpha(r-R)}) \quad (4)$$

where α is a parameter that influences the potential energy curve at large bond stretching. A more generalized Morse function was introduced by Biswas and Hamann [26]

$$U_{GM} = A_1 \exp(-\lambda_1 r) + A_2 \exp(-\lambda_2 r) \quad (5)$$

for describing the 2-body energy in condensed matter. Here A_i and λ_i control the potential energy curve's magnitude and shape respectively, while subscripts $i=1$ and $i=2$ correspond to the repulsive and attractive terms respectively. One can see that there are 4 parameters in the original generalized Morse function $(A_1, A_2, \lambda_1, \lambda_2)$ and in its equivalent form $(D, R, \lambda_1, \lambda_2)$, but only 3 parameters exist in the Rydberg function

(D, R, a) , thereby implying the higher flexibility of the generalized Morse function for curve-fitting, especially for long range interaction. This forms the justification for converting the generalized Morse parameters into those of Rydberg function for large bond-stretching in softwares (e.g. [13-18]).

Since the dimensions of λ_1 and λ_2 are reciprocal to the length dimension, we have selected Eq.(2) as the definition of ρ in order to set a common unit for a , λ_1 and λ_2 . Imposing

$$(U_{GM})_{r=R} = -D \quad (6)$$

and

$$\left(\frac{\partial U_{GM}}{\partial r} \right)_{r=R} = 0, \quad (7)$$

the generalized Morse function can be recasted as

$$\frac{U_{GM}}{D} = \frac{\lambda_2}{\lambda_1 - \lambda_2} \exp\left[\lambda_1 R \left(1 - \frac{r}{R}\right)\right] - \frac{\lambda_1}{\lambda_1 - \lambda_2} \exp\left[\lambda_2 R \left(1 - \frac{r}{R}\right)\right]. \quad (8)$$

In this form the generalized Morse function is described by the dissociation energy D and the equilibrium bond length R , to make it more comparable to the Rydberg potential function. When both functions are expressed in non-dimensionalized energy (U/D), the number of parameters on the right hand sides of Eqs.(1) and (8) are less by one. This simplification paves a way for the proceeding analysis.

The Rydberg function integral

$$\frac{1}{D} \int_R^\infty U_{Ryd} dr = - \int_0^\infty (1 + a\rho) e^{-a\rho} d\rho \quad (9)$$

can be obtained via performing integration by parts

$$\int_0^\infty (1 + a\rho) e^{-a\rho} d\rho = - \left(\frac{1}{a} + \rho \right) e^{-a\rho} \Big|_0^\infty + \int_0^\infty e^{-a\rho} d\rho \quad (10)$$

to give

$$\frac{1}{D} \int_R^\infty U_{Ryd} dr = - \frac{2}{a}. \quad (11)$$

Writing Eq.(8) as

$$\frac{U_{GM}}{D} = \frac{\lambda_2}{\lambda_1 - \lambda_2} \exp(-\lambda_1 \rho) - \frac{\lambda_1}{\lambda_1 - \lambda_2} \exp(-\lambda_2 \rho) \quad (12)$$

enables convenient integration to give

$$\frac{1}{D} \int_R^\infty U_{GM} dr = -\frac{\lambda_1 + \lambda_2}{\lambda_1 \lambda_2}. \quad (13)$$

The negative signs in Eqs.(11) and (13) are due to the area being under the horizontal axis.

Clearly,

$$a = 2 \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}. \quad (14)$$

To appreciate the large bond-stretching relationship, we obtain the small bond-stretching through equating the curves at the minimum well-depth. Hence equating

$$\left(\frac{\partial^2 U_{Ryd}}{\partial r^2} \right)_{r=R} = \left(\frac{\partial^2 U_{GM}}{\partial r^2} \right)_{r=R} \quad (15)$$

gives

$$a = \sqrt{\lambda_1 \lambda_2}. \quad (16)$$

3. Results and Discussion

To exhibit the advantage of the parameter relationship for long range, i.e. Eq.(14), over the short range approach, i.e. Eq.(16), for large bond-stretching, we compare the generalized Morse curve with the Rydberg curve obtained using the short and long bond-stretching assumptions. Based on the generalized Morse parameter furnished by Biswas and Hamann [26] whereby $\lambda_1 = 3.946668 \text{ \AA}^{-1}$ and $\lambda_2 = 1.191187 \text{ \AA}^{-1}$ for the 2-body interaction of silicon, we plot the generalized Morse curve using Eq.(8). The equilibrium bond length $R = 2.773872 \text{ \AA}$ was obtained by solving Eq.(7). The Rydberg shape parameter was obtained as $a = 1.830032 \text{ \AA}^{-1}$ using Eq.(14) and $a = 2.16823 \text{ \AA}^{-1}$ using Eq.(16) for large and small bond-stretching respectively, so that the potential energy curve can be plotted using

$$\frac{U_{Ryd}}{D} = \left[aR \left(1 - \frac{r}{R} \right) - 1 \right] e^{aR \left(1 - \frac{r}{R} \right)}. \quad (17)$$

Equations (8) and (17) enable the potential energy curves to be plotted as non-dimensionalized bond energy against non-dimensionalized bond length, as shown in Fig. 2.

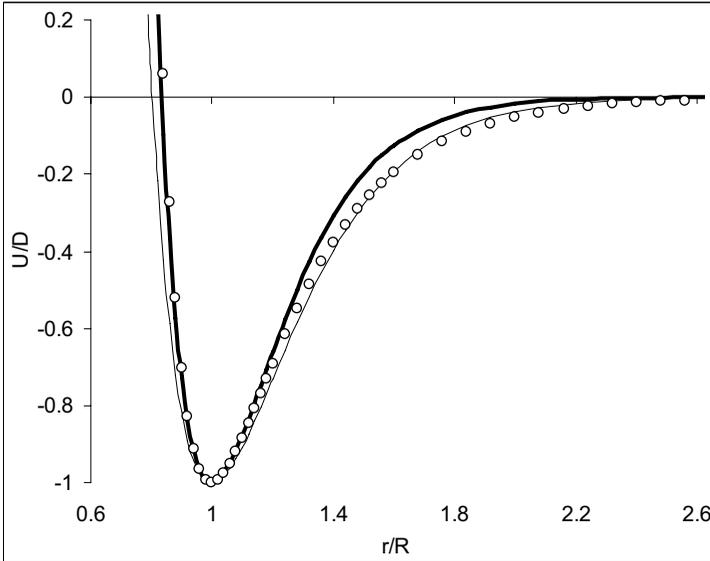


Fig.2. The generalized Morse energy (circles) using Biswas-Hamann parameters [26] and the Rydberg approximation using the second derivative (bold curve) and the integral (fine curve) approaches.

It can be seen that the parameter relation by second derivative approach, Eq.(16), gives good agreement for bond compression and small bond stretching. However, this approximation clearly overestimates the generalized Morse energy at larger internuclear distance. Although the Rydberg approximation by the integral approach underestimates the generalized Morse energy for bond compression and small bond stretching, it gives a better agreement with the latter for larger internuclear distance.

To clearly show the advantage of the integral approach over the second derivative approach for large deformation, we calculate the error as

$$error = U_{Ryd} - U_{GM} \tag{18}$$

and plotted in non-dimensionalized terms, as depicted in Fig.3.

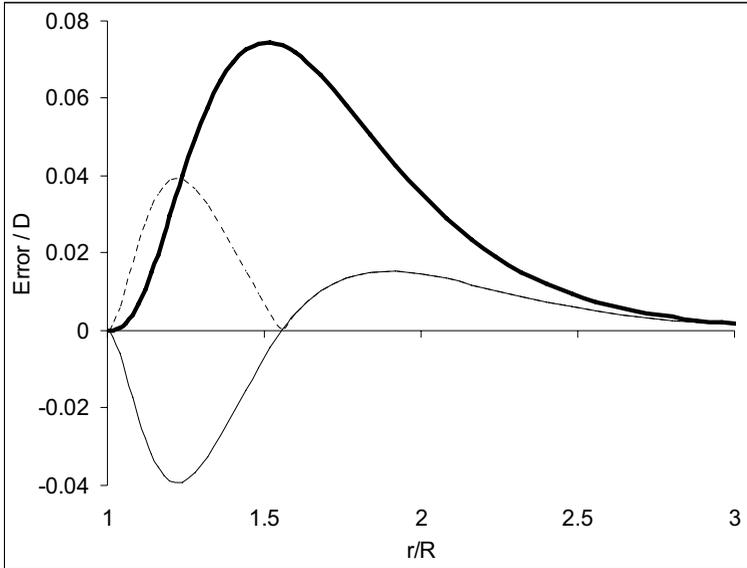


Fig.3. Error due to second derivative approach (bold curve) compared to the integral approach (fine curve). The negative portion is flipped up as dotted curve for comparison with the bold curve.

It shows that the short range Rydberg approximation overestimates the generalized Morse curve regardless of the extent of bond stretching. The higher slope at the inflexion point for the short range Rydberg approximation shows that the Rydberg function gives a more solid-like long-range description.

By replacing the imposition of equal curvature at the minimum well-depth with equal integral over the entire stretching range, a better long range approximation is achieved at the expense of the short range region. Specifically, the long range Rydberg approximation exhibits smaller curvature, and hence lower energy, near the minimum well-depth.

A cross-over occurs at the intermediate bond-length such that the areas between both curves for $R \leq r \leq \infty$ are equal before and after the cross-over point, i.e.

$$\int_R^C (U_{GM} - U_{Ryd}) dr = \int_C^\infty (U_{Ryd} - U_{GM}) dr \quad (19)$$

where C is the bond length denoting the cross-over point and U_{Ryd} refers to the long range Rydberg approximation. The cross-over point can be obtained by equating

$$(U_{GM})_{r=C} = (U_{Ryd})_{r=C}. \quad (20)$$

Solving numerically for the present example using the Biswas-Hamann parameters for the generalized Morse function and the Rydberg parameter using the long range case gives $(C/R) = 1.557346$.

4. Conclusions

The integral approach for obtaining relationships between the Rydberg and the generalized Morse parameters has been shown to be more reliable than the second derivative approach for large bond-stretching. The higher number of parameters for the generalized Morse function ($A_1, A_2, \lambda_1, \lambda_2$ or $D, R, \lambda_1, \lambda_2$) than those of the Rydberg function (D, R, a) implies a better long range bond-stretching data fitting for the former than the latter. This justifies the conversion of the generalized Morse parameters into Rydberg parameters for use as 2-body interaction energy description. Obviously, the choice of parameter conversion – whether Eq.(14) or Eq.(16) – depends on the extent of deformation.

From a practical viewpoint within the context of molecular mechanics, the parameter a obtained by second derivative is useful for bond compression and small bond stretching while the same parameter obtained by integration is more appropriate for large bond stretching. The switching of the numerical value of parameter a is analogous to the scaling factors 13.772 and 12 in the loose form of the Exponential-6 function for describing short and long range van der Waals energy in the DREIDING molecular mechanics software [27].

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