

# Application of extended-Rydberg parameters in general Morse potential functions

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**Abstract** The 3-parameter Rydberg and the 4-parameter general Morse functions have been adopted for describing bond-stretching in computation of molecular systems and many-body solid state systems. However the Extended-Rydberg function, such as the 5-parameter Murrell-Sorbie potential, has so far been confined to describing bond-stretching in very small molecules. Due to the superior functional flexibility of the Murrell-Sorbie potential, these parameters are converted into those of the general Morse potential due to the latter's application in computational chemistry. Imposition of (a) equal minimum well-depth curvature, and (b) equal equilibrium-to-dissociation energy integral on both functions enable the repulsive and the attractive indices of the general Morse potential to be extracted. Comparison of the Murrell-Sorbie energy of CO, FSi, MgS and CILi with the converted general Morse energy exhibits very good correlation.

**Keywords** Bond energy · Covalent bond · Potential function

## 1 Introduction

Arising from the Rydberg potential energy function [1,2], Murrell and Sorbie [3] proposed an extended Rydberg function of the form

$$U_{ER} = -D \left[ \sum_{i=0}^{\infty} a_i \rho^i \right] \exp(-a_1 \rho) \quad (1)$$

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where  $\rho = r - R$ ,  $a_0 = 1$  and  $a_i = 0$  ( $i \geq 4$ ). With  $D$  and  $R$  being the magnitude of the minimum well-depth and the equilibrium bond length respectively, the remaining three parameters  $a_i$  ( $i = 1, 2, 3$ ) control the shape of the potential energy curve. Although this potential function caters to a large degree of flexibility for curve-fitting, it is the original Rydberg function whereby  $a_i = 0$  ( $i \geq 2$ ) that is widely used in computation of many-body solid state system (e.g. [4–9]), presumably due to the original Rydberg function's simplicity with only one shape parameter,  $a_1$ . In this regard, the general Morse function

$$U_{GM} = D \left\{ \frac{\lambda_2}{\lambda_1 - \lambda_2} \exp \left[ \lambda_1 R \left( 1 - \frac{r}{R} \right) \right] - \frac{\lambda_1}{\lambda_1 - \lambda_2} \exp \left[ \lambda_2 R \left( 1 - \frac{r}{R} \right) \right] \right\} \quad (2)$$

with two shape parameters  $\lambda_i$  ( $i = 1, 2$ ) can be viewed as being more flexible or more accurate than the original Rydberg function, and more easily executable than the Murrell-Sorbie [3] function. Indeed, the general Morse function of the form

$$U_{GM} = A_1 \exp(-\lambda_1 R) + A_2 \exp(-\lambda_2 R) \quad (3)$$

has been used for quantifying the bond-stretching energy of solid state system [10]. The form expressed in Eq. (2) is obtained when the conditions  $(U_{GM})_{r=R} = -D$  and  $(\partial U_{GM}/\partial r)_{r=R} = 0$  are imposed on Eq. (3).

Since the number of parameters of the Murrell-Sorbie function is greater than that of the general Morse function, parameters of the former function can be converted into those of the latter function but not vice versa. Such conversion is justified considering the fact that the general Morse function is used for describing bond energy more widely than the Murrell-Sorbie function in solid state systems. The conversion of a more flexible function, such as the Murrell-Sorbie potential, into a less flexible one, such as the general Morse potential, enables parameters of the latter to be easily computed without experimentation. This saves time and effort. As such this paper describes a method by which parameters of the Murrell-Sorbie can be converted to those of the general Morse function.

## 2 Analysis

Recent years have seen the parameter conversion between different potential functions (e.g.  $U_1$  and  $U_2$ ) attained by imposing equal curvature and even higher order derivative at the minimum well-depth [11–14]

$$\left( \frac{\partial^n U_1}{\partial r^n} \right)_{r=R} = \left( \frac{\partial^n U_2}{\partial r^n} \right)_{r=R} ; \quad n \geq 2. \quad (4)$$

This approach gives valid parameter conversion for bond compression and small bond-stretching but not for large bond-stretching. The energy integral approach [15–18]

$$\int_R^\infty U_1 dr = \int_R^\infty U_2 dr, \quad (5)$$

on the other hand, was found to be valid for large bond-stretching but not for bond compression and small-bond stretching.

As such, the imposition of equal curvatures at the minimum well-depth for the general Morse and the extended Rydberg function gives

$$\prod_{i=1}^2 \lambda_i = a_1^2 - 2a_2 \quad (6)$$

while the imposition of equal energy integral from equilibrium to dissociation on both potential functions leads to

$$\frac{\sum_{i=1}^2 \lambda_i}{\prod_{i=1}^2 \lambda_i} = \sum_{i=0}^{\infty} \frac{i! a_i}{a_1^{i+1}}. \quad (7)$$

Reducing the extended Rydberg potential into the Murrell-Sorbie function, i.e.  $a_i = 0$  ( $i \geq 4$ ), the general Morse indices can be solved from Eqs. (6) and (7) as

$$\begin{Bmatrix} \lambda_1 \\ \lambda_2 \end{Bmatrix} = \frac{1}{2} \begin{bmatrix} +1 & +1 \\ +1 & -1 \end{bmatrix} \left\{ \frac{f_1 f_2}{\sqrt{(f_1 f_2)^2 - 4f_1}} \right\} \quad (8)$$

where

$$f_1 = a_1^2 - 2a_2 \quad (9)$$

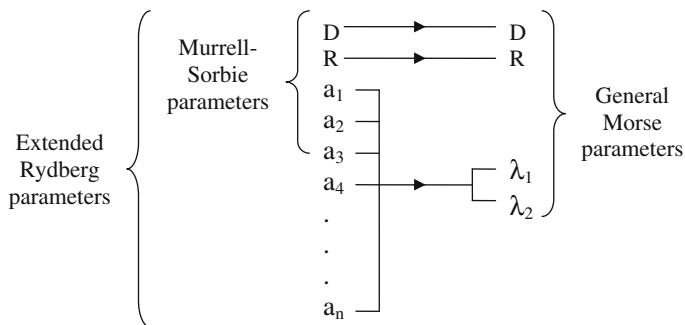
while

$$f_2 = \frac{2}{a_1} + \frac{2a_2}{a_1^3} + \frac{6a_3}{a_1^4} \quad (10a)$$

for Murrell-Sorbie parameters, or

$$f_2 = \frac{0! a_0}{a_1^1} + \frac{1! a_1}{a_1^2} + \frac{2! a_2}{a_1^3} + \frac{3! a_3}{a_1^4} + \dots \quad (10b)$$

for extended Rydberg parameters. A schematic diagram for the Extended-Rydberg to the general Morse parameter conversion is depicted in Fig. 1.



**Fig. 1** Schematic diagram for obtaining general Morse parameters from extended Rydberg or Murrell-Sorbie parameters

### 3 Results and discussion

Based on the Murrell-Sorbie parameters as reported by Huxley and Murrell [19], the corresponding general Morse parameters were calculated using Eqs. (8)–(10), and are listed in Table 1. The diatomic molecules CO, FSi, MgS, and CILi were selected due to their almost consistent interval in terms of their minimum well depth curvatures as well as their equilibrium-to-dissociation energy integral. Based on the parameters listed in Table 1, the non-dimensional Murrell-Sorbie and general Morse potential energy curves ( $U/D$ ) were plotted in terms of the change in bond length ( $\rho = r - R$ ) as

$$\frac{U_{MS}}{D} = - \left( 1 + a_1\rho + a_2\rho^2 + a_3\rho^3 \right) \exp(-a_1\rho) \quad (11)$$

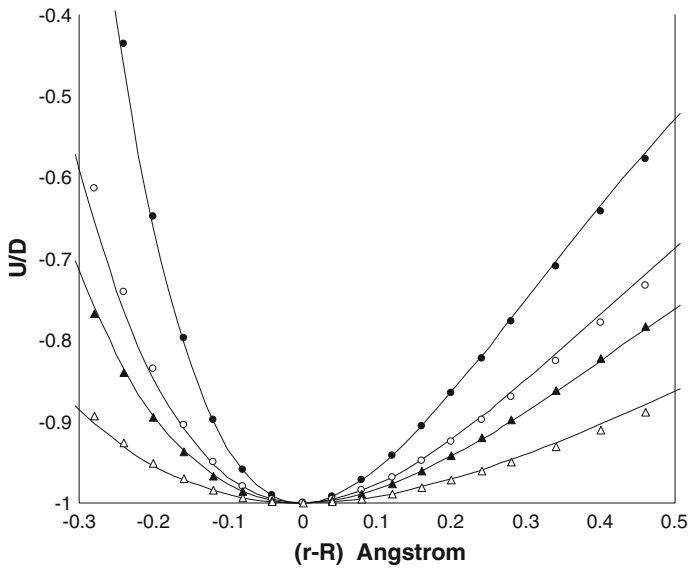
and

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

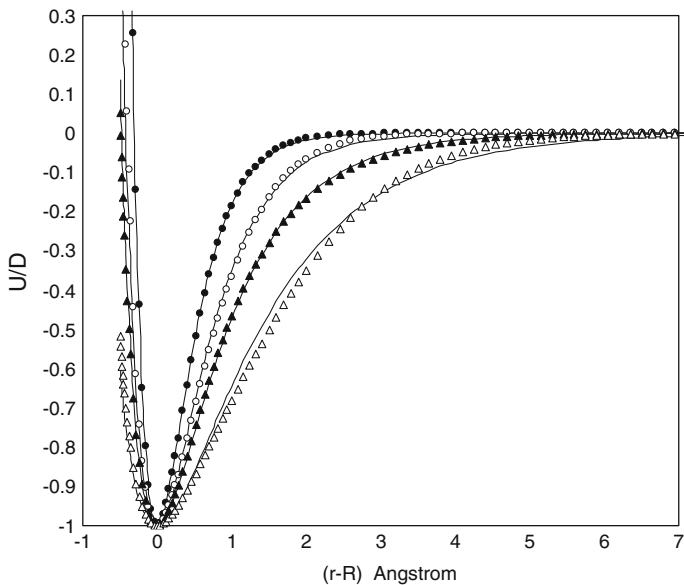
respectively. Figure 2 shows the Murrell-Sorbie energy and the corresponding general Morse energy near the minimum well depth, while Fig. 3 shows the potential energy curves over longer range. Very good agreement was found for the CO, FSi, and MgS diatomic molecules, while a fairly good approximation was observed for the

**Table 1** Murrell-Sorbie parameters from Huxley and Murrell [19] and the corresponding general Morse parameters

Diatoms	$D(eV)$	$R(\text{\AA})$	$a_1(\text{\AA}^{-1})$	$a_2(\text{\AA}^{-2})$	$a_3(\text{\AA}^{-3})$	$\lambda_1(\text{\AA}^{-1})$	$\lambda_2(\text{\AA}^{-1})$
CO	11.226	1.1283	3.897	2.305	1.898	4.333553	2.440632
FSi	5.623	1.6011	3.008	1.807	1.605	3.353374	1.620477
MgS	3.578	2.1425	1.78	-0.358	0.339	3.570455	1.087929
CILi	4.88	2.0207	1.7	0.533	0.496	2.445801	0.745768



**Fig. 2** Near equilibrium comparison between the general Morse potential energy (*smooth curves*) converted from the Murrell-Sorbie potential energy curves of CO (*black circles*), FSi (*white circles*), MgS (*black triangles*) and ClLi (*white triangles*)



**Fig. 3** Far range comparison between the general Morse potential energy (*smooth curves*) converted from the Murrell-Sorbie potential energy curves of CO (*black circles*), FSi (*white circles*), MgS (*black triangles*) and ClLi (*white triangles*)

CILi diatomic molecule. The slight discrepancy for the CILi molecule may well be attributed to the slow energy convergence as the bond separates, which leaves a large energy integral from equilibrium state to dissociation. A large area between the ( $r - R$ ) axis and the potential energy curve leaves room for discrepancy. Notwithstanding this slight discrepancy, the impositions of equal curvature at the minimum well-depth and equal energy integral for  $\rho \geq 0$  significantly limit the discrepancy. For cases where rapid convergence occurs (e.g. CO, FSi and MgS), the relatively small area of energy integral leaves little room for discrepancies. This results in almost perfect overlap between both sets of energy for these three diatomic molecules.

## 4 Conclusions

A method of using the Murrell-Sorbie parameters for general Morse potential function has been described herein due to the former's greater functional flexibility and the latter's comparative ease of execution. Unlike previous methods that either impose equal minimum well-depth curvature or impose equal energy integral, the present approach combines both approaches. As a result of the interlaced approach, the general Morse function obtained from the Murrell-Sorbie parameters demonstrate fairly accurate energy, especially for bonds that exhibit rapid rise in energy with bond stretching.

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