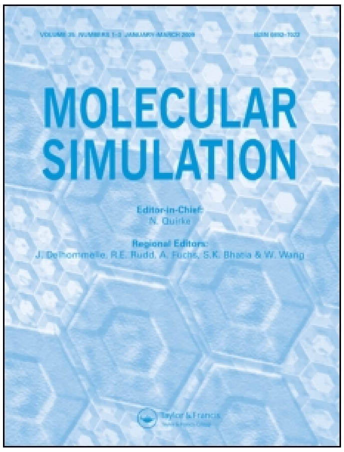

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# Alternative scaling factor between Lennard-Jones and Exponential-6 potential energy functions

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# Alternative scaling factor between Lennard-Jones and Exponential-6 potential energy functions

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In spite of the ease of computing the Lennard-Jones function for describing van der Waals energy of interaction, the Exponential-6 function is normally adopted due to its better description of short range interaction. Hence scaling factors of 13.772 and 12 have been used to give equal curvature at the minimum well-depth and equal long-range energy description, respectively, when compared to the Lennard-Jones (12-6) potential. This paper proposes an intermediate scaling factor of 12.6533 on the basis of zero integral error from the well-depth to infinite separation. It is herein shown that the use of this intermediate scaling factor divides the entire Exponential-6 computation into three stages instead of two, thereby smoothening the energy curve by reducing the computed energy drop at the scaling factor switching point. In cases where a single scaling factor is desired as a results highly complex dynamical molecular system, the proposed intermediate scaling factor gives significantly smaller overall error.

*Keywords*: Exponential-6; Lennard-Jones; Molecular interaction; Potential function; Scaling factor

## 1. Introduction

An important cornerstone of all molecular mechanics simulation is the van der Waals energy. Typical van der Waals potential energy functions are attributed to Lennard-Jones [1]:

$$U_{\mathrm{LJ}} = \frac{A_{\mathrm{LJ}}}{r^m} - \frac{B_{\mathrm{LJ}}}{r^n} = D\left[\frac{n}{m-n}\left(\frac{R}{r}\right)^m - \frac{m}{m-n}\left(\frac{R}{r}\right)^n\right] \quad (1)$$

and Buckingham [2]

$$U_B = A\mathrm{e}^{-Br} - \frac{C}{r^n} \quad (2)$$

where $r$ is the internuclear distance. In most practices, these potentials are utilized specifically as the LJ (12-6) function [3–6]

$$U_{12-6} = D\left[\left(\frac{R}{r}\right)^{12} - 2\left(\frac{R}{r}\right)^6\right] \quad (3)$$

and the Exponential-6 function [7,8]

$$U_{\mathrm{X6}} = A\mathrm{e}^{-Br} - \frac{C}{r^6}, \quad (4)$$

respectively. The choice of LJ (12-6) or Exponential-6 is normally dependent on the circumstances by which one of the functions is advantageous over the other. Mayo *et al.* [9] appreciated the fact that LJ (12-6) is simpler (two parameters instead of three) and, therefore, faster to compute. However, their experience is that the Exponential-6 form gives a better description of short range interactions. To enable conversion between these two potential functions, equation (4) can be written as [9,10]

$$U_{\mathrm{X6}} = D\left[\frac{6}{\xi-6}\mathrm{e}^{\xi\left(1-\frac{r}{R}\right)} - \frac{\xi}{\xi-6}\left(\frac{R}{r}\right)^6\right] \quad (5)$$

whereby the scaling factor $\xi = 12.0$ gives the same long-range attraction as the LJ (12-6) form, and $\xi = 13.772$ gives equal curvatures at the minimum well-depth ($r = R$). Obviously the scaling factor $\xi = 13.772$ sacrifices the accuracy beyond the minimum well-depth. This is unfortunate because for most instances the van der Waals interaction occurs well beyond the vicinity of the

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minimum well-depth. Although the scaling factor $\xi = 12.0$ gives credible accuracy as $r \rightarrow \infty$, most molecular mechanics softwares truncate the van der Waals energy beyond certain range [3–6]. This paper develops an alternative scaling factor to attain a good overall agreement between the two van der Waals potential energy functions.

## 2. Analysis

Previous techniques for relating interatomic potential functions have relied on the imposition of equal curvatures at the minimum well-depth [11–15], i.e. two potentials $U_1$ and $U_2$ are related as

$$\left(\frac{\partial^p U_1}{\partial r^p}\right)_{r=R} = \left(\frac{\partial^p U_2}{\partial r^p}\right)_{r=R}; \quad (p = 0, 1, \ldots, q) \tag{6}$$

where $q \geq 2$. In this paper, we relax the imposition of equation (6) for $q \geq 2$ so that only $p = 0$ and 1 apply. Since the Exponential-6 function consists of three parameters, an additional independent equation is required. Instead of increasing the order of derivative, we take anti-derivative of the two potential functions from the equilibrium point to infinite internuclear distance, i.e.

$$\int_R^\infty U_1 \mathrm{d}r = \int_R^\infty U_2 \mathrm{d}r. \tag{7}$$

Taking integral for the LJ (12-6) function, we have

$$\int_R^\infty U_{12-6} \mathrm{d}r = -\frac{17}{55} DR \tag{8}$$

The negative sign indicates that the area bounded by the LJ (12-6) and the horizontal axis for $R \leq r \leq \infty$ is below the horizontal axis. It is easily seen that

$$U_{12-6}|_{r=R} = -D \tag{9}$$

and

$$\left.\frac{\partial U_{12-6}}{\partial r}\right|_{r=R} = 0. \tag{10}$$

Performing similarly for the Exponential-6 function leads to

$$\int_R^\infty U_{\mathrm{X6}} \mathrm{d}r = \frac{A}{B} \mathrm{e}^{-BR} - \frac{C}{5R^5}, \tag{11}$$

$$U_{\mathrm{X6}}|_{r=R} = A\mathrm{e}^{-BR} - \frac{C}{R^6} \tag{12}$$

and

$$\left.\frac{\partial U_{\mathrm{X6}}}{\partial r}\right|_{r=R} = -AB\mathrm{e}^{-BR} - \frac{6C}{R^7}. \tag{13}$$

Let $\xi = BR$, then equating equations (10) and (13) gives the attractive coefficients in terms of the repulsive parameters of the Exponential-6 function as

$$\frac{C}{R^6} = \frac{\xi}{6} A\mathrm{e}^{-\xi} \tag{14}$$

while equating equations (9) and (12) expresses the repulsive parameters of the Exponential-6 function in terms of the dissociation energy $D$ as

$$A\mathrm{e}^{-\xi} = D\left(\frac{6}{\xi - 6}\right). \tag{15}$$

With the aid of equations (14) and (15), equating equations (8) and (11) allows the scaling factor to be solved as

$$\xi = \frac{17 \pm \sqrt{69}}{2}. \tag{16}$$

Since it is a requirement for $\xi > 6$ to give a physically admissible solution, the upper value of $\xi = 12.6533$ is selected over the lower value of 4.3467. Since equation (5) is recovered through substitution of equations (14) and (15) into equation (4), this new scaling factor can be compared to the previously known factors $\xi = 13.772$ and $\xi = 12.0$ on an equal basis.

## 3. Results and discussion

To examine the comparative advantage of the three scaling factors, we define the error between the Exponential-6 and the LJ (12-6) energy as

$$\text{error} = U_{\mathrm{X6}} - U_{12-6} \tag{17}$$

and plotted in non-dimensionalized plane, i.e. (error/$D$) versus ($r$/$R$), as shown in figure 1(a). It can be seen that when $\xi = 13.772$, the error has zero slope at $r = R$. It is obvious that this is due to the imposition of equal curvatures between the Exponential-6 and LJ (12-6) potential functions. Thereafter, this Exponential-6 curve overestimates the LJ (12-6) function for $r > R$. In contrast, the Exponential-6 with $\xi = 12.0$ gives zero error, but not zero slope, at $r = R$ and thereafter underestimates the LJ (12-6) function for $r > R$. The Exponential-6 function with $\xi = 12.6533$ gives a slight underestimation for $R \leq r < 1.36R$. It can be seen in Figure 1(b) that the Exponential-6 functions with $\xi = 13.772$ and $\xi = 12.0$ give error of magnitude exceeding 1% for the range $1.16R < r < 1.61R$ and $1.06R < r < 1.39R$, respectively, but the error corresponding to $\xi = 12.6533$ is less than 1% for the entire range of $r \geq R$. Table 1 shows the comparative advantages of the three scaling factors in terms of the interatomic distance.

Supposed a path of least error were to be followed on the Exponential-6 function with only $\xi = 13.772$ and 12.0, as in common molecular mechanics softwares, then the point at which the switch from the former to the latter takes place at $r = 1.285R$ with the change in error $\Delta$error $\approx 3.3D\%$. On the other hand, a path of least error

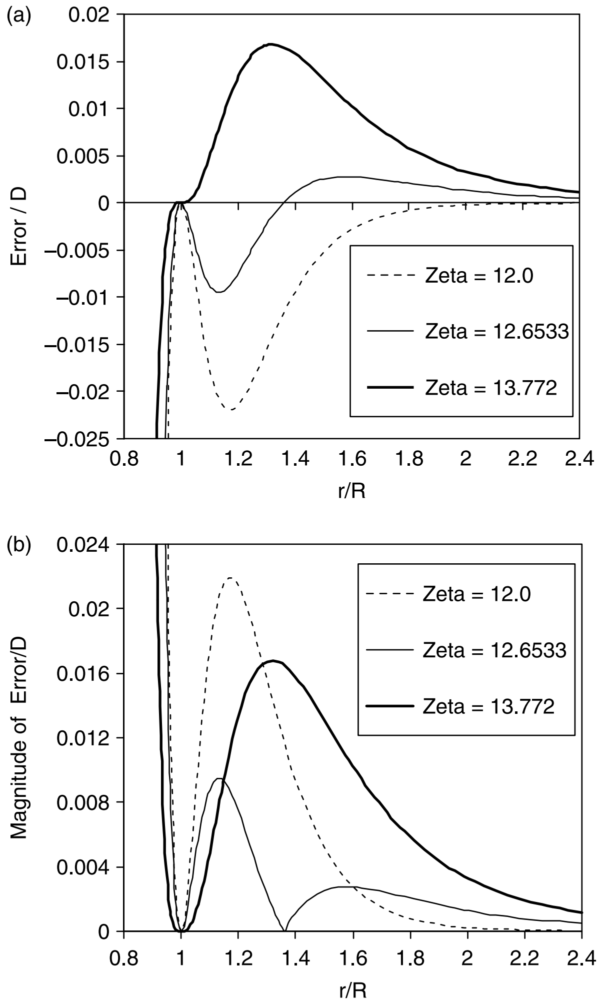

Figure 1. (a) Error distribution of Exponential-6 function for $\xi = 13.772$ (bold curve), $\xi = 12.6533$ (thin curve) and $\xi = 12.0$ (dash curve) with respect to LJ (12-6) potential energy, and (b) the error magnitude for computation.

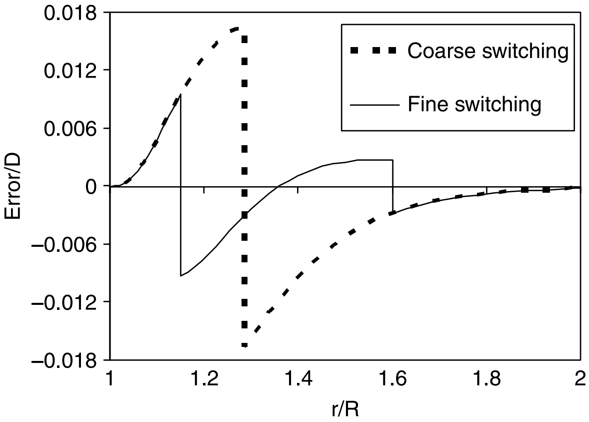

Figure 2. Error/D paths for single switching point using two scaling factors (dashed curve) and for double switching points using three scaling factors (continuous curve).

that incorporates $\xi = 12.6533$ separates the Exponential-6 energy into three regions as a result of two switching points. The first switching point occurs at $r = 1.15R$ as a result of switching from $\xi = 13.772$ to 12.6533 with $\Delta\text{error} \approx 1.9D\%$. The second switching point takes place at $r = 1.6R$ as a consequence of switching from $\xi = 12.6533$ to 12.0 with $\Delta\text{error} < 0.6D\%$.

The allowance of two switching points ensures smoother transition than the case of single switching point (figure 2). With increasing hardware performance, the adoption two switching points is fully justified.

For cases where the molecular simulation involves highly complex dynamical systems such that no switching of scaling factor is desired, then neither $\xi = 13.772$ nor $\xi = 12.0$ is advisable due to the comparative disadvantage for long range and short range applications, respectively. The choice of $\xi = 12.6533$ is suggested as this would give the least overall error.

Table 1. Comparative advantage of the three scaling factors of Exponential-6 in reference to LJ (12-6) functions.

| *Scaling factor* | *1 < (r/R) < 1.15* | *1.15 < (r/R) < 1.285* | *1.285 < (r/R) < 1.6* | *(r/R) > 1.6* |
|---|---|---|---|---|
| $\xi = 13.772$ | Best | Intermediate | Worst | Worst |
| $\xi = 12.6533$ | Intermediate | Best | Best | Intermediate |
| $\xi = 12.0$ | Worst | Worst | Intermediate | Best |

## 4. Conclusions

To date, the scaling factors $\xi = 13.772$ and 12.0 for the loose form of Exponential-6 potential function enables it to mimic the LJ (12-6) function for short range and long range, respectively. Although an intermediate scaling factor can be obtained as 12.886 and 12.8555 on the basis of arithmetic and geometric means, respectively, this paper adopts a physical basis to pinpoint the intermediate scaling factor as $\xi = 12.6533$. The use of integral approach enables the error to be minimized for the range from $r = R$ to $r \to \infty$. It has been shown that the use of $\xi = 12.6533$ significantly reduces the interatomic energy mismatch by splitting the van der Waals interaction energy into three regions instead of two. Furthermore, the use of the proposed scaling factor is beneficial in case switching of scaling factors is undesired due to the gross over- and under-estimation associated with $\xi = 13.772$ nor $\xi = 12.0$, respectively, for $r > R$.

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