

## Research Article

# Equivalent Potential-Energy Functions

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Many researchers have proposed their own potential-energy functions for the study of diatomic molecules, some of which have been proved to be equivalent. In this paper we suggest the application of a few simple rules to determine the equivalence between molecular potentials. The resulting systematic procedure is illustrated by means of several examples.

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## 1. Introduction

The starting point of most quantum-mechanical treatments of molecular systems is the Born-Oppenheimer approximation<sup>[1]</sup> that consists of two steps. One first solves the Schrödinger equation for the electrons with the nuclei clamped at a set of conveniently chosen configurations. This procedure yields the potential-energy surface. In the second step one solves the Schrödinger equation for the nuclei moving on the potential-energy surface obtained in the first step. In the case of diatomic molecules one obtains a potential-energy curve  $V(r)$ . For quite a long time, spectroscopists have made use of suitable analytical expressions for  $V(r)$ <sup>[2]</sup> and now and again scientists propose other such functions.

Some of those analytical expressions for  $V(r)$  have been proved to be identical or equivalent. For example, Jia et al.<sup>[3]</sup> proved the equivalence between the Sun and Tietz<sup>[4]</sup> potentials and Liang et al.<sup>[5]</sup> proved the equivalence between the Hua<sup>[6]</sup> and Tietz potentials. There are so many potentials that it is not unlikely that other such equivalences have passed unnoticed.

Sometimes it is not so easy to determine if two molecular potentials are equivalent. The purpose of this paper is to propose a simple procedure for comparing different potentials. The simplest way is to normalize them in the same way.

## 2. Normalization of molecular potentials

Suppose that  $V(r)$  is the analytical expression for a molecular potential that depends on some adjustable parameters. We propose to determine three of those parameters by means of the conditions

$$V(r_e) = 0, V'(r_e) = 0, \lim_{r \rightarrow \infty} V(r) = D_e. \quad (1)$$

Obviously, if  $V''(r_e) > 0$  then  $r_e > 0$  is the equilibrium bond length and  $D_e > 0$  is the dissociation energy. The resulting potential is positive definite:  $V(r) \geq 0$  for all  $0 < r < \infty$ .

We then write  $V(r)$  as

$$V(r) = D_e[1 - f(r)]^2, \quad (2)$$

from which we obtain two roots

$$f_{\pm}(r) = 1 \pm \sqrt{\frac{V(r)}{D_e}}. \quad (3)$$

Both yield the same potential but we choose  $f_-(r)$  that behaves asymptotically as  $f(r \rightarrow \infty) = 0$ .

Let us begin with two simple cases. If we insert

$$V(r) = a + \frac{b}{r} + \frac{c}{r^2}, \quad (4)$$

into equations (1) and solve for the adjustable parameters we obtain

$$a = D_e, b = -2D_e r_e, c = D_e r_e^2, \quad (5)$$

that lead to the well-known Kratzer-Fues potential<sup>[7], [8]</sup>

$$V_K(r) = D_e \left(1 - \frac{r_e}{r}\right)^2. \quad (6)$$

If we start with

$$V(r) = a + br^{-\alpha r} + ce^{-2\alpha r}, \alpha > 0, \quad (7)$$

we obtain

$$a = D_e, b = -2D_e e^{\alpha r_e}, c = D_e e^{2\alpha r_e}, \quad (8)$$

and the Morse potential<sup>[9]</sup>

$$V_M(r) = D_e \left[1 - e^{\alpha(r_e - r)}\right]^2. \quad (9)$$

In the next section we compare some analytical expressions for molecular potentials proposed by some researchers in order to determine possible equivalences.

### 3. Examples of equivalent potentials

Two potential-energy functions are said to be equivalent if there exists a bijective transformation of their parameters that maps one potential onto the other, yielding the same function  $V(r)$ . Equivalence is therefore a property of the function itself rather than of the particular parametrization used to represent it. The normalization procedure merely removes redundant parameters and recasts different potentials into a common form suitable for direct comparison.

One of the most relevant potentials for present analysis was proposed by Tietz<sup>[4]</sup> several years ago

$$V_T(r) = D_e + \frac{D_e [(a+b)e^{-2\beta r} - be^{-\beta r}]}{(1+ce^{-\beta r})^2}, \beta > 0, \quad (10)$$

where  $c \geq -1$  in order to avoid an unphysical singularity in  $0 < r < \infty$ . This potential satisfies one of the normalization conditions  $V(r \rightarrow \infty) = D_e$ ; from the remaining ones we obtain

$$a = e^{2\beta r_e} - 2e^{\beta r_e} - c(c+2), b = 2e^{\beta r_e} + 2c, \quad (11)$$

so that

$$V_T(r) = D_e \left( 1 - \frac{e^{\beta r_e} + c}{e^{\beta r} + c} \right)^2. \quad (12)$$

This expression is identical to the one derived by Jia et al.<sup>[3]</sup>

Hua<sup>[6]</sup> proposed the potential

$$U_H(r) = D_e \left[ \frac{1 - e^{-b(r-r_e)}}{1 - ce^{-b(r-r_e)}} \right]^2, b > 0 \quad (13)$$

where  $c \leq 1$ . This expression satisfies all the normalization conditions (1) so that it only remains to obtain the function  $f(r)$ :

$$f(r) = \frac{e^{br_e} (1-c)}{e^{br} - ce^{br_e}}. \quad (14)$$

If we define  $c' = -ce^{br_e}$ , we obtain

$$U_H(r) = D_e \left( 1 - \frac{e^{br_e} + c'}{e^{br} + c'} \right)^2, c' \geq -1, \quad (15)$$

that is equivalent to the Tietz potential. As stated in the introduction of present paper Jia et al.<sup>[3]</sup> already proved this equivalence.

Şimşek and Özçelik<sup>[10]</sup> proposed the four-parameter exponential type potential(FPEP)

$$V_{FPEP}(r) = \frac{Ae^{\lambda r}}{C + e^{\lambda r}} - \frac{Be^{\lambda r}}{(C + e^{\lambda r})^2}, A, B > 0. \quad (16)$$

In order to make this potential positive definite we add a constant  $V_0$  that does not change the physical features of the model and consider  $U_{FPEP}(r) = V_0 + V_{FPEP}(r)$ . It follows from the normalization conditions (1) that

$$V_0 = \frac{D_e e^{2\lambda r_e}}{C^2}, A = \frac{D_e (C^2 - e^{2\lambda r_e})}{C^2}, B = \frac{D_e (e^{\lambda r_e} + C)^2}{C}, \quad (17)$$

and

$$U_{FPEP}(r) = D_e \left( 1 - \frac{e^{\lambda r_e} + C}{e^{\lambda r} + C} \right)^2, \quad (18)$$

that is the Tietz potential.

Jia et al.<sup>[11]</sup> introduced a deformed five-parameter exponential-type potential (DFPEP)

$$V_{DFPEP}(r) = P_1 + \frac{P_2}{e^{2\alpha r} + q} + \frac{P_3}{(e^{2\alpha r} + q)^2}, \alpha > 0, \quad (19)$$

where  $q \geq -1$ . From the conditions (1) we obtain

$$P_1 = D_e, P_2 = -2D_e (e^{2\alpha r_e} + q), P_3 = D_e (e^{2\alpha r_e} + q)^2, \quad (20)$$

and

$$V_{DFPEP}(r) = D_e \left( 1 - \frac{e^{\beta r_e} + q}{e^{\beta r} + q} \right)^2, \beta = 2\alpha, \quad (21)$$

that is equivalent to the normalized Tietz potential (12).

Falaye et al.<sup>[12]</sup> proposed the shifted Tietz-Wei (sTW) oscillator

$$V_{sTW}(r) = V_e \frac{2(c_h - 1)e^{-b_h(r-r_e)} - (c_h^2 - 1)e^{-2b_h(r-r_e)}}{[1 - c_h e^{-b_h(r-r_e)}]^2}, b_h > 0. \quad (22)$$

This potential satisfies  $V(r_e) = -V_e$ ,  $V'(r_e) = 0$  and  $V(r \rightarrow \infty) = 0$ ; therefore  $U(r) = V(r) + V_e$  is positive definite. It follows from equation (3) that

$$f(r) = \frac{e^{b_h r_e} (1 - c_h)}{e^{b_h r} - c_h e^{b_h r_e}} = \frac{e^{b_h r_e} + c}{e^{b_h r} + c}, c = -c_h e^{b_h r_e}, \quad (23)$$

and

$$U_{sTW}(r) = D_e \left( 1 - \frac{e^{b_h r_e} + c}{e^{b_h r} + c} \right)^2, D_e = V_e. \quad (24)$$

Clearly, the sTW oscillator is equivalent to the Tietz potential.

Onate et al.<sup>[13]</sup> proposed the q-deformed six-parameter exponential-type potential model

$$V_{qDSPEP}(r) = Q_1 - \frac{Q_2}{1 - qe^{-2\alpha r}} + \frac{Q_3 e^{-2\alpha r}}{1 - qe^{-2\alpha r}} - \frac{Q_4 e^{-4\alpha r}}{(1 - qe^{-2\alpha r})^2}, \alpha > 0. \quad (25)$$

If we solve the normalization conditions (1) for  $Q_2$ ,  $Q_3$  and  $Q_4$  we obtain

$$Q_2 = Q_1 - D_e, Q_3 = q(Q_1 + D_e) - 2D_e e^{2\alpha r_e}, Q_4 = -D_e (e^{2\alpha r_e} - q)^2, \quad (26)$$

and

$$V_{qDSPEP}(r) = D_e \left( 1 - \frac{e^{\beta r_e} + c}{e^{\beta r} + c} \right)^2, \beta = 2\alpha, c = -q, \quad (27)$$

that is the Tietz potential.

Okorie et al.<sup>[14]</sup> proposed the deformed exponential-type potential (DEP)

$$U_{DEP}(r) = P_1 + \frac{P_2 e^{-2\alpha(r-r_0)}}{1 - qe^{-2\alpha(r-r_0)}} + \frac{P_3 e^{-4\alpha(r-r_0)}}{[1 - qe^{-2\alpha(r-r_0)}]^2}. \quad (28)$$

If we define  $P'_2 = P_2 e^{2\alpha r_0}$ ,  $P'_3 = P_3 e^{4\alpha r_0}$  and  $q' = qe^{2\alpha r_0}$  then we realize that this potential is equivalent to the DFPEP (19) and that  $r_0$  is an irrelevant parameter with no effect on the physics of the problem. In spite of this fact, Okorie et al. managed to obtain an expression for  $r_0$ . Although the normalization of the potential (28) follows directly from the results obtained previously for (19), it may be illustrative to carry out the normalization of the model (28). It follows from the conditions (1) that

$$P_1 = D_e, P_2 = 2D_e e^{-2\alpha r_0} (qe^{2\alpha r_0} - e^{2\alpha r_e}), P_3 = D_e e^{-4\alpha r_0} (qe^{2\alpha r_0} - e^{2\alpha r_e})^2, \quad (29)$$

and

$$U_{DEP}(r) = D_e \left( 1 - \frac{e^{\beta r_e} + c}{e^{\beta r} + c} \right)^2, c = -qe^{2\alpha r_0}, \beta = 2\alpha. \quad (30)$$

Clearly,  $U_{DEP}(r)$  is another potential that is equivalent to the Tietz one. Although Eyube et al.<sup>[15]</sup> corrected some flaws in the paper by Okorie et al.<sup>[14]</sup>, they still retained the utterly ineffective

parameter  $r_0$  in their equations.

## 4. Asymptotic behaviour

The function  $f(r)$  given in equation (2) should satisfy

$$V(r_e) = 0 \implies f(r_e) = 1, \quad (31a)$$

$$\lim_{r \rightarrow \infty} V(r) = D_e \implies \lim_{r \rightarrow \infty} f(r) = 0, \quad (31b)$$

$$V'(r_e) = 2D_e[f(r_e) - 1]f'(r_e) = 0, \quad (31c)$$

$$V''(r_e) = 2D_e f'(r_e)^2 = k > 0 \implies f'(r_e) \neq 0, \quad (31d)$$

$$V'''(r_e) = 6D_e f'(r_e) f''(r_e) = k_3. \quad (31e)$$

Since the force constant  $k$  and the anharmonicity coefficient  $k_3$  are given in terms of spectroscopic quantities<sup>[2]</sup> then we can use equations (31d) and (31e) in order to fix remaining model parameters like  $q$  and  $\alpha$ . For example, if we choose

$$f(r) = \frac{e^{\alpha r_e} + q}{e^{\alpha r} + q}, q \geq -1, \quad (32)$$

and solve equation (31d) for  $q$  we obtain

$$q = e^{\alpha r_e} \left( \sqrt{\frac{2D_e}{k} \alpha - 1} \right). \quad (33)$$

Upon substituting equation (33) into equation (31e) and solving for  $\alpha$  we have

$$\alpha = \sqrt{\frac{2k}{D_e}} + \frac{k_3}{3k}. \quad (34)$$

That is to say, if we know  $k$  and  $k_3$  we can obtain  $\alpha$  and  $q$ . But the main purpose of this section is the discussion of the asymptotic behaviour of the model potential  $V(r)$ .

It is well known that the molecular potential  $V(r)$  should tend to plus infinity at origin as  $r^{-1}$  because of the Coulomb repulsion of the nuclei<sup>[2]</sup>. On the other hand,  $D_e - V(r)$  should tend to zero as  $r^{-6}$ <sup>[2]</sup>. Although these exponential potentials are useful phenomenological models in the vicinity of the equilibrium distance, they do not reproduce the correct asymptotic behaviour at either short or long internuclear distances. It has been shown that a rational function is a straightforward way to obtain molecular potentials with suitable asymptotic behaviour<sup>[16][17][18]</sup>.

## 5. Conclusions

In this paper we have proposed a simple and systematic normalization procedure for the comparison of analytical potential-energy functions used in the study of diatomic molecules. The method consists of determining three adjustable parameters from the conditions (1), and then rewriting the resulting potential in the form (2). This representation greatly facilitates the direct comparison between different models.

The normalization procedure shows that several molecular potentials proposed in the literature are not genuinely different models but merely alternative parametrizations of the same function  $V(r)$ . In particular, the Hua, DFPEP, shifted Tietz-Wei, qDSPEP, and DEP potentials can all be transformed into the same normalized form of the Tietz potential by means of suitable bijective parameter transformations. This analysis also reveals the existence of redundant parameters, such as the parameter  $r_0$  appearing in the DEP model.

The examples discussed throughout the paper illustrate that potential equivalence is a property of the functional form of  $V(r)$  itself rather than of the particular parametrization chosen to represent it. In this context, normalization does not alter the physics of the problem but simply removes redundant degrees of freedom and recasts different models into a common representation. We have also shown that the normalized function  $f(r)$  provides a convenient framework for relating the parameters of the model potential to spectroscopic quantities such as the force constant and the anharmonicity coefficient. At the same time, the analysis of the asymptotic behaviour indicates that these exponential potentials do not reproduce the correct short- and long-range limits expected for realistic molecular interactions, although they may still provide useful phenomenological descriptions near the equilibrium internuclear distance.

The present approach may help identify unnoticed equivalences between apparently different molecular potentials, simplify their classification, and avoid the introduction of ostensibly new models that are functionally identical to previously known potentials.

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## Declarations

**Funding:** No specific funding was received for this work.

**Potential competing interests:** No potential competing interests to declare.