

# Equivalence of the deformed Rosen–Morse potential energy model and Tietz potential energy model

Chun-Sheng Jia · Tao Chen · Liang-Zhong Yi ·  
Shu-Rong Lin

Received: 21 October 2012 / Accepted: 3 June 2013 / Published online: 18 June 2013  
© Springer Science+Business Media New York 2013

**Abstract** By applying the dissociation energy and the equilibrium bond length for a diatomic molecule as explicit parameters, we generate an improved expression for the deformed Rosen–Morse potential energy model. It is found that the deformed Rosen–Morse potential model and the well-known Tietz potential model are the same empirical potential function for diatomic molecules. With the help of the energy spectrum expression of the deformed Rosen–Morse potential model, we obtain exact closed-form expressions of diatomic anharmonicity constants  $\omega_e x_e$  and  $\omega_e y_e$ .

**Keywords** Deformed Rosen–Morse potential model · Tietz potential model · Morse potential model

## 1 Introduction

Modeling the interaction potential of diatomic molecules has long been an active research field for both theoreticians and experimentalists [1–15]. The reason is that the potential energy function provides the most compact way to summarize what we know about a molecule. The first simple three-parameter empirical potential function proposed by Morse [1] has been widely used in investigating molecular spectroscopy

---

C.-S. Jia (✉)

State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation,  
Southwest Petroleum University, Chengdu 610500, People's Republic of China  
e-mail: chshjia@263.net

T. Chen · S.-R. Lin

Life and Physical Science College, Sichuan Agricultural University, Yaan 625014, Sichuan,  
People's Republic of China

L.-Z. Yi

Sichuan Police College, Luzhou 646000, Sichuan, People's Republic of China

[16–18], and in performing molecular dynamics simulations for predicting many issues such as lattice thermal conductivity [19], interfacial phonon transport [20], phase transition [21], thermal transport [22], formation mechanism and mechanics of dip-pen nanolithography [23], hydroxide anion interfacial activity [24], ligand vibrational relaxation [25], effects of the thermal annealing on the nanoimprinting process [26], etc.

Recently, equivalence of some empirical analytical potential functions has attracted attentions [27–29]. By using the dissociation energy and the equilibrium bond length for a diatomic molecule as explicit parameters, improved expressions of some empirical potential functions for diatomic molecules have been constructed. These empirical potential energy functions include the Rosen–Morse potential [2], Manning–Rosen potential [3], Frost–Musulin potential [4], Tietz potential [6], and Schiöberg potential [7]. With the comparison of improved expressions for several empirical potential functions, one has found that the Manning–Rosen potential, Schiöberg potential and Deng–Fan potential are the same empirical potential function for diatomic molecules [27]. Both versions of the Schiöberg potential function are the Rosen–Morse potential function and Manning–Rosen potential functions [28], respectively. The Wei potential and the well-known Tietz potential function are also the same solvable empirical potential function [29]. The Tietz potential is remarkably good agreement with the experimental RKR (Rydberg–Klein–Rees) data points and *ab initio* calculations [16,30].

By using the deformed hyperbolic functions introduced for the first time by Arai [31], Eğriş et al. [32] constructed the deformed Rosen–Morse potential as a diatomic potential model. The deformed hyperbolic functions have been widely used in many issues [32–35]. By applying the supersymmetric Wentzel–Kramers–Brillouin (SWKB) method, Yılmaz et al. [36] obtained the bound state energy eigenvalues of the deformed Rosen–Morse potential. In Ref. [37], the authors investigated the *s*-wave bound state solutions of the Klein–Gordon equation with the deformed Rosen–Morse potential. Motivated by the recent works about the equivalence of some empirical potential energy functions, we attempt to study the equivalence between the deformed Rosen–Morse potential function [32] and the Tietz potential function [6] for diatomic molecules. In the present work, we also derive analytical expressions of diatomic anharmonicity constants for the deformed Rosen–Morse potential model.

## 2 Equivalence of the deformed Rosen–Morse potential and the Tietz potential

An empirical potential energy function  $U(r)$  for diatomic molecules should satisfy the following conditions:

$$\left. \frac{dU(r)}{dr} \right|_{r=r_e} = 0, \quad (1)$$

$$U(\infty) - U(r_e) = D_e, \quad (2)$$

$$\left. \frac{d^2U(r)}{dr^2} \right|_{r=r_e} = k_e = \mu\omega_e^2, \quad (3)$$

where  $D_e$  is the dissociation energy,  $r_e$  is the equilibrium bond length,  $\mu$  is the reduced mass of a diatomic molecule, and  $\omega_e$  is the equilibrium harmonic vibrational frequency.

The deformed Rosen–Morse potential function proposed by Eđrifes et al. [32] is defined as

$$U_{\text{DRM}}(r) = B_0 \tanh_q \alpha r - \frac{U_0}{\cosh_q^2 \alpha r}, \tag{4}$$

where  $B_0, U_0, \alpha$ , and  $q$  are four potential parameters. Eđrifes et al. [32] applied the deformed hyperbolic functions, which are defined as [31]

$$\begin{aligned} \sinh_q x &= \frac{e^x - qe^{-x}}{2}, & \cosh_q x &= \frac{e^x + qe^{-x}}{2}, \\ \tanh_q x &= \frac{\sinh_q x}{\cosh_q x}, & \operatorname{sech}_q x &= \frac{1}{\cosh_q x}, \end{aligned} \tag{5}$$

where  $q > 0$  is a real parameter. The deformed parameter  $q$  has been extended to the cases of  $q < 0$  and complex domain [33,34]. The bound state energy spectra for the deformed Rosen–Morse potential are given by [36]

$$\begin{aligned} E_{vJ} = -\frac{2\hbar^2\alpha^2}{\mu} & \left[ \frac{1}{16} \left( -(2v+1) + \sqrt{1 + \frac{8\mu U_0}{\hbar^2\alpha^2 q}} \right)^2 \right. \\ & \left. + \frac{\frac{\mu^2 B_0^2}{\hbar^4 \alpha^4}}{\left( -(2v+1) + \sqrt{1 + \frac{8\mu U_0}{\hbar^2\alpha^2 q}} \right)^2} \right], \end{aligned} \tag{6}$$

where  $\hbar = \frac{h}{2\pi}$ ,  $h$  is the Planck constant, and  $v$  denotes the vibrational quantum number.

Substituting expression (4) into condition (1) yields

$$r_e = \frac{1}{2\alpha} \ln \left( \frac{q(2U_0 - qB_0)}{2U_0 + qB_0} \right). \tag{7}$$

In terms of condition (2) and expression (7), we obtain the relation

$$B_0 - \left[ -\frac{1}{4} \frac{q^2 B_0^2 + 4U_0^2}{qU_0} \right] = D_e. \tag{8}$$

Solving Eqs. (7) and (8) for  $U_1$  and  $U_2$  leads us to obtain

$$B_0 = \frac{D_e (q^2 - e^{4\alpha r_e})}{2q^2}, \tag{9}$$

$$U_0 = \frac{D_e (q + e^{2\alpha r_e})^2}{4q}. \tag{10}$$

On the right hand of expression (4), we add one term  $\frac{1}{4} \frac{q^2 B_0^2 + 4U_0^2}{qU_0} = \frac{1}{2} \frac{D_e(q^2 + e^{4\alpha r_e})}{q^2}$ , this only produce an energy of zero at the potential minimum, i.e.  $U_{\text{DRM}}(r_e) = 0$ , and does not affect the physical properties of the original deformed Rosen–Morse potential function. Substituting expressions (9) and (10) into expression (4) and making some algebraic simplifications, we can write the deformed Rosen–Morse potential as

$$U_{\text{DRM}}(r) = D_e \left( 1 - \frac{e^{2\alpha r_e} + q}{e^{2\alpha r} + q} \right)^2. \quad (11)$$

The well-known Tietz potential energy function for diatomic molecules reads [6]

$$U_{\text{T}}(r) = D_e + D_e \frac{(a+b)e^{-2\alpha r} - be^{-\alpha r}}{(1+he^{-\alpha r})^2}. \quad (12)$$

This is conventionally defined in terms of five parameters, but only four parameters are independent. The Tietz potential function has been rewritten in an improved expression [29]

$$U_{\text{T}}(r) = D_e \left( 1 - \frac{e^{\alpha r_e} + h}{e^{\alpha r} + h} \right)^2. \quad (13)$$

If we replace  $2\alpha$  by  $\alpha$ , and  $q$  by  $h$ , expression (11) turns into expression (13). This tells us that the deformed Rosen–Morse potential and the Tietz potential are the same empirical potential function for diatomic molecules.

Substituting expressions (9) and (10) into (6), we obtain the energy spectra for deformed Rosen–Morse potential (11) with zero orbital angular momentum,

$$E_{vJ} = \frac{1}{2} \frac{D_e (q^2 + e^{4\alpha r_e})}{q^2} - \frac{2\hbar^2 \alpha^2}{\mu} \left[ \frac{1}{16} \left( -(2v+1) + \sqrt{1 + \frac{2\mu D_e (q + e^{2\alpha r_e})^2}{\hbar^2 \alpha^2 q^2}} \right)^2 + \frac{\left( \frac{\mu D_e (q^2 - e^{4\alpha r_e})}{2\hbar^2 \alpha^2 q^2} \right)^2}{\left( -(2v+1) + \sqrt{1 + \frac{2\mu D_e (q + e^{2\alpha r_e})^2}{\hbar^2 \alpha^2 q^2}} \right)^2} \right], \quad (14)$$

The four-parameter potential function for diatomic molecules proposed by Wei [8] can be expressed as [29]

$$U_{\text{W}}(r) = D_e \left( 1 - \frac{e^{br_e} - he^{br_e}}{e^{br} - he^{br_e}} \right)^2, \quad (15)$$

which is also the same with the well-known Tietz potential energy function [29]. Replacing  $b$  by  $2\alpha$ , and  $-he^{br_e}$  by  $q$ , we can make expression (15) turn into expression (11).

Morse potential energy function reads [1]

$$U_M(r) = D_e \left(1 - e^{-\alpha(r-r_e)}\right)^2. \tag{16}$$

The energy spectra for the Morse potential with zero orbital angular momentum are given by [1]

$$E_{vJ} = \frac{\hbar^2\alpha^2}{2\mu} \left[ \frac{\sqrt{2\mu D_e}}{\hbar\alpha} - \left(v + \frac{1}{2}\right) \right]^2. \tag{17}$$

**3 Evaluation of anharmonicity constants  $\omega_e x_e$  and  $\omega_e y_e$**

Dunham [38] expressed the rovibrational energy spectra for diatomic molecules in a double series,

$$E_{vJ} = \sum_{i,j} Y_{i,j} \left(v + \frac{1}{2}\right)^i (J(J+1))^j, \tag{18}$$

where the coefficients  $Y_{i,j}$  are related to spectroscopic constants. The rovibrational energy levels  $E_{vJ}$  are also written in the following form

$$\frac{E_{vJ}}{hc} = G_v + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + \dots, \tag{19}$$

where the pure vibrational energy levels are expressed as

$$G_v = T_e + \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \omega_e y_e \left(v + \frac{1}{2}\right)^3 + \dots. \tag{20}$$

In expression (22),  $\omega_e$  is the equilibrium harmonic vibrational frequency,  $\omega_e x_e$  and  $\omega_e y_e$  are anharmonicity constants.

By using the energy spectrum expressions (14) and (17), we can derive analytical expressions of anharmonicity constants  $\omega_e x_e$  and  $\omega_e y_e$  for the Morse potential and deformed Rosen–Morse potential, respectively,

$$\omega_e x_e(M) = \frac{\hbar^2\alpha^2}{2\mu hc}, \tag{21}$$

$$\omega_e y_e(M) = 0, \tag{22}$$

$$\begin{aligned} \omega_e x_e(DRM) = & \frac{\hbar^2\alpha^2}{2\mu hc} \left( q^4 \hbar^4 \alpha^4 + 4\mu D_e q^4 \hbar^2 \alpha^2 + 4\mu D_e e^{4\alpha r_e} q^2 \hbar^2 \alpha^2 \right. \\ & \left. + 8\mu D_e e^{2\alpha r_e} q^3 \hbar^2 \alpha^2 + 16\mu^2 D_e^2 e^{2\alpha r_e} q^3 + 16\mu^2 D_e^2 q^4 \right) \end{aligned}$$

$$+16\mu^2 D_e^2 e^{6\alpha r_e} q + 16\mu^2 D_e^2 e^{8\alpha r_e}) / (q^2 \hbar^2 \alpha^2 + 2\mu D_e e^{4\alpha r_e} + 4\mu D_e e^{2\alpha r_e} q + 2\mu D_e q^2)^2, \quad (23)$$

$$\omega_e y_e (\text{DRM}) = - \frac{16\hbar^3 \alpha^3 q \mu D_e^2 (e^{4\alpha r_e} - q^2)^2}{hc (q^2 \hbar^2 \alpha^2 + 2\mu D_e e^{4\alpha r_e} + 4\mu D_e e^{2\alpha r_e} q + 2\mu D_e q^2)^{5/2}}. \quad (24)$$

By using condition (3), we derive the following expressions satisfied by the potential parameter  $\alpha$  in the Morse potential function (16) and the deformed Rosen–Morse potential function (11), respectively,

$$\alpha_M = \sqrt{\frac{k_e}{2D_e}}, \quad (25)$$

$$\alpha_{\text{DRM}} = \frac{1}{2} \sqrt{\frac{k_e}{2D_e}} + \frac{1}{2r_e} W \left( r_e q \sqrt{\frac{k_e}{2D_e}} e^{-\frac{r_e}{2} \sqrt{\frac{k_e}{2D_e}}} \right), \quad (26)$$

where subscripts M and DRM denote the Morse potential and deformed Rosen–Morse potential, respectively. In expression (26),  $W$  denotes the Lambert  $W$  function, which satisfies  $z = W(z)e^{W(z)}$ .

**Table 1** Spectroscopic constants and the parameter  $q$  used in the present work

Molecule state	$D_e$ (cm <sup>-1</sup> )	$r_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$q$	Ref.
Na <sub>2</sub> : X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	6022.6	3.07908	159.177	4.77172	[8]
Cl <sub>2</sub> : X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	20,276	1.987	559.7	7.73121	[16]
N <sub>2</sub> : X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	79,885	1.097	2358.6	0.68671	[16]
O <sub>2</sub> <sup>+</sup> : X <sup>2</sup> I <sub>g</sub>	54,688	1.116	1904.8	0.47836	[16]
N <sub>2</sub> <sup>+</sup> : X <sup>2</sup> Σ <sub>g</sub> <sup>+</sup>	71,365	1.116	2207.0	0.28175	[16]
NO <sup>+</sup> : X <sup>1</sup> Σ <sup>+</sup>	88,694	1.063	2376.4	0.53878	[16]

**Table 2** Comparison of experimental values of  $\omega_e x_e$  and  $\omega_e y_e$  with calculated values obtained by using the Morse potential and deformed Rosen–Morse potential

Molecular state	$\omega_e x_e$ (obs)	$\omega_e x_e$ (M)	$\omega_e x_e$ (DRM)	$\omega_e y_e$ (obs)	$\omega_e y_e$ (M)	$\omega_e y_e$ (DRM)
Na <sub>2</sub> : X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	0.70866	1.05176	0.87990	-0.004632	0	-0.0018038
Cl <sub>2</sub> : X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	2.69427	3.86249	3.52417	-0.003325	0	-0.0042166
N <sub>2</sub> : X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	14.324	17.40938	16.86483	-0.00226	0	-0.0077790
O <sub>2</sub> <sup>+</sup> : X <sup>2</sup> I <sub>g</sub>	16.489	16.58619	16.26977	0.02057	0	-0.00540337
N <sub>2</sub> <sup>+</sup> : X <sup>2</sup> Σ <sub>g</sub> <sup>+</sup>	16.0616	17.06316	16.83234	-0.04289	0	-0.00352018
NO <sup>+</sup> : X <sup>1</sup> Σ <sup>+</sup>	16.255	15.91787	15.46209	-0.01562	0	-0.00592573

All quantities are in cm<sup>-1</sup>

The experimental data of three spectroscopic constants and the parameter  $q$  for six diatomic molecule states are taken from the literatures [8] and [16]. In Table 1, we list the values of spectroscopic constants and the parameter  $q$  used in the present work. Taking the experimental values of  $D_e$ ,  $r_e$  and  $\omega_e$  as inputs, we calculate the potential parameters  $\alpha$  by using expressions (25) and (26). By using expressions (21)–(24), we calculate the values of anharmonicity constants  $\omega_e x_e$  and  $\omega_e y_e$  for six diatomic molecule states. In Table 2, we give the corresponding calculated values and experimental data for  $\omega_e x_e$  and  $\omega_e y_e$ . The experimental data of  $\omega_e x_e$  and  $\omega_e y_e$  for the six diatomic molecule states are taken from the literature [39]. Table 2 shows that the calculated values of the anharmonicity constant  $\omega_e x_e$  by employing the deformed Rosen–Morse potential are closer to the observed values than those calculated by using the Morse potential. The Morse potential always gives zero value for the anharmonicity constant  $\omega_e y_e$ . However, the values obtained by the deformed Rosen–Morse potential are nonzero. The values of the anharmonicity constant  $\omega_e y_e$  for actual molecules are nonzero.

## 4 Conclusions

By using the dissociation energy and the equilibrium bond length for a diatomic molecule as explicit parameters, we generate improved expression for the deformed Rosen–Morse potential energy function. It is found that the deformed Rosen–Morse potential model and the well-known Tietz potential model are the same empirical potential function for diatomic molecules. In terms of the exact energy spectrum expression for the deformed Rosen–Morse potential, we obtain the exact expressions for anharmonicity constants  $\omega_e x_e$  and  $\omega_e y_e$  for diatomic molecules. The values of anharmonicity constants  $\omega_e x_e$  and  $\omega_e y_e$  determined by using the deformed Rosen–Morse potential are closer to the experimental values than those determined by applying the Morse potential.

**Acknowledgments** This work was supported by the National Natural Science Foundation of China under Grant No. 10675097, the Natural Science Foundation of the Sichuan Education Bureau of China under Grant No. 11ZA021, and the Science Foundation of State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation of China under Grant No. PLN-ZL001.

## References

1. P.M. Morse, Phys. Rev. **34**, 57 (1929)
2. N. Rosen, P.M. Morse, Phys. Rev. **42**, 210 (1932)
3. M.F. Manning, N. Rosen, Phys. Rev. **44**, 953 (1933)
4. A.A. Frost, B. Musulin, J. Chem. Phys. **22**, 1017 (1954)
5. Z.H. Deng, Y.P. Fan, Shandong Univ. J. **7**, 162 (1957)
6. T. Tietz, J. Chem. Phys. **38**, 3036 (1963)
7. D. Schiöberg, Mol. Phys. **59**, 1123 (1986)
8. H. Wei, Phys. Rev. A **42**, 2524 (1990)
9. A.A. Zavitsas, J. Am. Chem. Soc. **113**, 4755 (1991)
10. P.G. Hajigeorgiou, R.J. Le Roy, J. Chem. Phys. **112**, 3949 (2000)
11. R.H. Xie, J. Gong, Phys. Rev. Lett. **95**, 263202 (2005)
12. P.G. Hajigeorgiou, J. Mol. Spectrosc. **263**, 101 (2010)

13. J.A. Coxon, P.G. Hajigeorgiou, *J. Mol. Spectrosc.* **150**, 1 (1991)
14. R.J. Le Roy, Y. Huang, C. Jary, *J. Chem. Phys.* **125**, 164310 (2006)
15. A. Shayesteh, R.D.E. Henderson, R.J. Le Roy, P.F. Bernath, *J. Phys. Chem. A* **111**, 12495 (2007)
16. J.A. Kunc, F.J. Gordillo-Vzquez, *J. Phys. Chem. A* **101**, 1595 (1997)
17. F.J. Gordillo-Vzquez, J.A. Kunc, *J. Thermophys. Heat Transfer* **12**, 52 (1998)
18. Z. Rong, H.G. Kjaergaard, M.L. Sage, *Mol. Phys.* **101**, 2285 (2003)
19. B. Qiu, X.L. Ruan, *Phys. Rev. B* **80**, 165203 (2009)
20. S. Shin, M. Kaviany, T. Desai, R. Bonner, *Phys. Rev. B* **82**, 081302 (2010)
21. E. Demiralp, T. Çağın, W.A. Goddard III, *Phys. Rev. Lett.* **82**, 1708 (1999)
22. T. Luo, J.R. Lloyd, *J. Appl. Phys.* **109**, 034301 (2011)
23. C.D. Wu, T.H. Fang, J.F. Lin, *Langmuir* **26**, 3237 (2010)
24. C.D. Wick, L.X. Dang, *J. Phys. Chem. A* **113**, 6356 (2009)
25. M. Devereux, M. Meuwly, *J. Phys. Chem. B* **113**, 13061 (2009)
26. T.H. Fang, C.D. Wu, W.J. Chang, S.S. Chi, *Appl. Surf. Sci.* **255**, 6043 (2009)
27. P.Q. Wang, L.H. Zhang, C.S. Jia, J.Y. Liu, *J. Mol. Spectrosc.* **274**, 5 (2012)
28. P.Q. Wang, J.Y. Liu, L.H. Zhang, S.Y. Cao, C.S. Jia, *J. Mol. Spectrosc.* **278**, 23 (2012)
29. C.S. Jia, Y.F. Diao, X.J. Liu, P.Q. Wang, J.Y. Liu, G.D. Zhang, *J. Chem. Phys.* **137**, 014101 (2012)
30. A.T. Royappa, V. Suri, J.R. McDonough, *J. Mol. Struct.* **787**, 209 (2006)
31. A. Arai, *J. Math. Anal. Appl.* **158**, 63 (1991)
32. H. Eğriş, D. Demirhan, F. Büyükkılıç, *Phys. Scr.* **60**, 195 (1999)
33. C.S. Jia, S.C. Li, Y. Li, L.T. Sun, *Phys. Lett. A* **300**, 115 (2002)
34. C.S. Jia, Y. Li, Y. Sun, J.Y. Liu, L.T. Sun, *Phys. Lett. A* **311**, 115 (2003)
35. M. Eshghi, H. Mehraban, *Few-Body Syst.* **52**, 41 (2012)
36. H. Yılmaz, D. Demirhan, F. Büyükkılıç, *J. Math. Chem.* **47**, 539 (2010)
37. L.Z. Yi, Y.F. Diao, J.Y. Liu, C.S. Jia, *Phys. Lett. A* **333**, 212 (2004)
38. J.L. Dunham, *Phys. Rev.* **41**, 721 (1932)
39. K.K. Irikura, *J. Phys. Chem. Ref. Data* **36**, 389 (2007)