

Modification of Morse potential in conventional force fields for applying FPDP parameters

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Abstract Although the Morse potential function is widely used in molecular modeling software, newer potential functions that possess more parameters provide greater accuracy. Against this backdrop, the Four-Parameter-Diatomic-Potential (FPDP) was selected for converting its parameter into those of the Morse potential due to the former's resemblance to the latter. A pair of modified Morse indices was extracted by imposing equal force constant for infinitesimal bond stretching and equal energy integral for complete interatomic separation. Results reveal very good agreement for both bond compression and bond stretching. The developed parameter conversion would enable all FPDP parameters to be converted into the modified Morse parameters. Only minor algorithm alterations are required for incorporating the modified Morse function into molecular modeling packages that adopt the conventional Morse potential for describing 2-body bonded interaction.

Keywords Morse · Morse-like · Potential functions · Parameter conversions

1 Introduction

Conventional molecular force fields in computational chemistry packages normally adopt potential energy functions to describe the bond-stretching (2-body), bond-bending (3-body), bond-twisting (4-body), van der Waals and electrostatic energy, i.e.

$$U_{\text{Total}} = U_{2b} + U_{3b} + U_{4b} + U_{vdW} + U_{el}. \quad (1)$$

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For bond stretching energy, a number of molecular force fields (e.g. [1–4]) adopt the Morse potential function [5]

$$U_{\text{Morse}} = D \left[e^{-\alpha(r-R)} - 1 \right]^2 \quad (2)$$

or

$$U_M = U_{\text{Morse}} - D = D \left[e^{-2\alpha(r-R)} - 2e^{-\alpha(r-R)} \right], \quad (3)$$

where D is the dissociation energy, r is the interatomic bond length, and R is the equilibrium bond length. The parameter α controls the shape of the potential energy curve. Later, a Four-Parameter Diatomic Potential (FPDP)

$$\frac{U_{\text{FPDP}}}{D} = \left(\frac{e^a - \lambda}{e^{a\frac{r}{R}} - \lambda} \right)^2 - 2 \left(\frac{e^a - \lambda}{e^{a\frac{r}{R}} - \lambda} \right) \quad (4)$$

was proposed by Sun [6] and was used by Gang [7] for solving the Dirac equation. It is readily seen that when $\lambda = 0$, the FPDP function reduces to the Morse potential described in Eq. (3). With two shape parameters (a, λ) instead of one, the FPDP function allows greater flexibility for curve fitting with spectroscopic data and ab initio data. The other two of the FPDP parameters (D, R) are identical to those of the Morse potential. Although the FPDP function can be implemented in new molecular force fields for new computational chemistry packages, the availability of numerous existing softwares would not make it economically viable. Alternatively, modification of existing computational chemistry packages to include the FPDP function would require extensive hard-coding to existing algorithm. The third, and most viable approach in both technical and economic sense, would be to do minimal hard-coding on the computational chemistry packages that adopt the Morse potential. This approach was proposed recently [8] whereby the Morse function was split into 3 parts—near, mid and far ranges. A drawback of this approach is the inherent functional discontinuity that takes place when the shape parameter α switches from near to mid range, and also from mid to far range. In this paper, it is shown that the Morse potential can be modified in such a way that no switching of parameter value is required regardless of the interatomic distance, thereby ensuring a seamless energy curve.

2 Analysis

Recall that the general form of the Morse potential

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

was used by Biswas and Hamann [9]. On the basis of

$$\left(\frac{\partial U_{\text{GM}}}{\partial r} \right)_{r=R} = 0 \quad (6)$$

and

$$(U_{GM})_{r=R} = -D, \quad (7)$$

this expression can be recasted as

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

The parameters D and R are common for both potentials, with only the need to relate the FPDP shape parameters (a, λ) with those of the general Morse (λ_1, λ_2) . Imposing equal force constant

$$\left(\frac{\partial^2 U_{GM}}{\partial r^2}\right)_{r=R} = \left(\frac{\partial^2 U_{FPDP}}{\partial r^2}\right)_{r=R}, \quad (9)$$

we have

$$\lambda_1 \lambda_2 = 2 \left(\frac{a}{R}\right)^2 \left(\frac{e^a}{e^a - \lambda}\right)^2. \quad (10)$$

Imposing equal bond stretching energy integral from equilibrium to dissociation

$$\int_R^\infty U_{GM} dr = \int_R^\infty U_{FPDP} dr, \quad (11)$$

we obtain

$$\begin{aligned} -D \left(\frac{\lambda_1 + \lambda_2}{\lambda_1 \lambda_2}\right) &= \frac{(e^a - \lambda)^2 DR}{a} \int_{\exp(a)}^\infty \frac{dx}{x(x - \lambda)^2} \\ &\quad - \frac{2(e^a - \lambda)DR}{a} \int_{\exp(a)}^\infty \frac{dx}{x(x - \lambda)}. \end{aligned} \quad (12)$$

The integrals can be evaluated as

$$\int_{\exp(a)}^\infty \frac{dx}{x(x - \lambda)} = \left[\frac{1}{-\lambda} \ln \left| \frac{x}{x - \lambda} \right| \right]_{\exp(a)}^\infty \quad (13)$$

and

$$\int_{\exp(a)}^\infty \frac{dx}{x(x - \lambda)^2} = \left[\frac{1}{\lambda(\lambda - x)} + \frac{1}{\lambda^2} \ln \left| \frac{x}{x - \lambda} \right| \right]_{\exp(a)}^\infty \quad (14)$$

to give

$$\frac{\lambda_1 + \lambda_2}{\lambda_1 \lambda_2} = (e^a - \lambda) \left(\frac{R}{a} \right) \left\{ \frac{e^a + \lambda}{\lambda^2} [a - \ln(e^a - \lambda)] - \frac{1}{\lambda} \right\}. \quad (15)$$

As such, the general Morse shape parameters can be calculated from

$$\begin{Bmatrix} \lambda_1 \\ \lambda_2 \end{Bmatrix} = \frac{1}{2} \begin{bmatrix} +1 & +1 \\ +1 & -1 \end{bmatrix} \begin{Bmatrix} -CI \\ \sqrt{(CI)^2 - 4C} \end{Bmatrix} \quad (16)$$

where

$$C = 2 \left[\frac{e^a}{e^a - \lambda} \left(\frac{a}{R} \right) \right]^2 \quad (17)$$

and

$$I = (e^a - \lambda) \left(\frac{R}{a} \right) \left\{ \frac{1}{\lambda} - \frac{e^a + \lambda}{\lambda^2} [a - \ln(e^a - \lambda)] \right\}. \quad (18)$$

3 Results and discussion

The validity of the modified Morse parameters described in Eqs. (16)–(18) can be assessed through comparison amongst the FPDP, original Morse and modified Morse energy curves. The HH and HF diatomic molecules were selected due to their parameter availability. The FPDP parameters (α, λ) were obtained from Sun [6] while the equilibrium bond length were obtained from Huxley and Murrell [10]. The expansion for C, I, λ_1 and λ_2 were calculated from Eqs. (16)–(18) and listed in Table 1. The non-dimensional energy (U/D) versus non-dimensional bond length (r/R) for HH and HF diatomic molecules were plotted in Figs. 1 and 2, respectively based on the parameters furnished in Table 1, with the original Morse shape parameter as $\alpha = a/R$. It can be seen from both figures that the simple conversion from FPDP to the original Morse potential by imposing $\lambda = 0$ does not give good agreement. For both illustrations, the original Morse energy by the simple conversion underestimates the FPDP energy. The error is reversed, i.e. the original Morse energy overestimates the FPDP energy, when $\lambda < 0$. In any case, the discrepancies are more significant for λ of greater magnitudes. The good agreement between the FPDP and the modified

Table 1 Parameters of HH and HF potential according to the FPDP function and the modified Morse function

Diatoms	R (Å)	a	λ	C	I	λ_1	λ_2
HH	0.7414	1.1967	0.56278	7.564996	-0.85413	4.925644	1.535839
HF	0.9168	1.7734	0.75271	9.836448	-0.72916	5.325117	1.84718

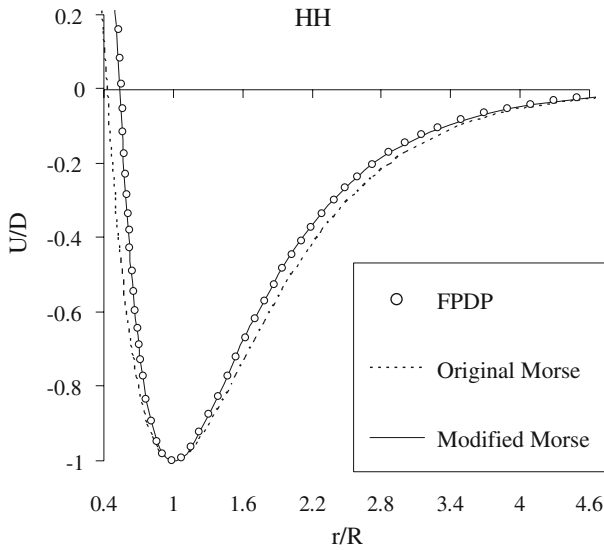


Fig. 1 Potential energy curve for HH diatomic molecule according to the FPDP (*circles*), the original Morse (*dashed curve*) and the modified Morse (*continuous curve*)

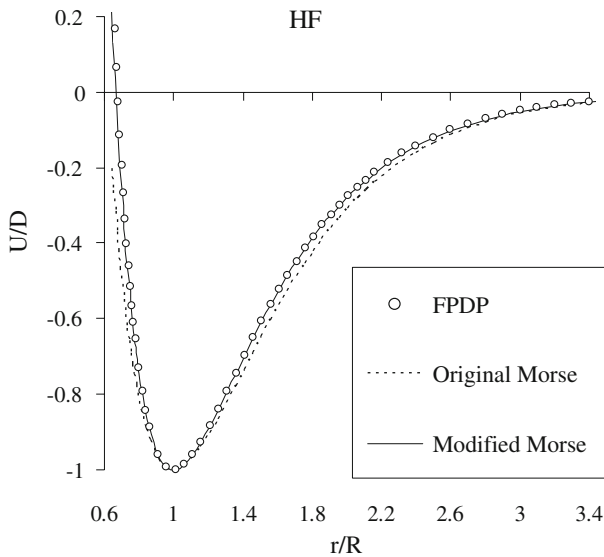


Fig. 2 Potential energy curve for HF diatomic molecule according to the FPDP (*circles*), the original Morse (*dashed curve*) and the modified Morse (*continuous curve*)

Morse potential energy may well be elucidated from past experience. The sole imposition of equal force constant enables good agreement for bond compression and very small bond stretching [11, 12] but significant discrepancies for large bond stretching (e.g. [13]). On the other hand, the sole imposition of equal bond stretching energy integral from equilibrium to dissociation gives very good agreement for large bond

stretching [14, 15] with minor compromise near the minimum well-depth and large discrepancies for bond compression. With these past results in mind, the present approach combines the impositions of equal force constant and equal equilibrium-to-dissociation energy integral to enable good agreement at all range. Unlike the recent approaches [8, 16, 17] that separates the Morse function into three parts, which leads to discontinuities, the present approach retains the Morse function with the same parameter value across various bond lengths, thereby eliminating discontinuities while achieving accurate description of bond compression and stretching.

4 Conclusions

A set of parameter conversion for applying the FPDP parameters in a modified Morse potential has been developed by imposing equal curvature at the well-depth minimum and equal energy integral from the minimum point to infinite separation. The adoption of these simultaneous impositions ensures for all range of bond length. The modified Morse parameters obtain from the FPDP function allows parameters of the latter to be used in molecular force fields that adopt the Morse potential with minor adjustment to computational code.

References

1. S. Lifson, A.T. Hagler, P. Dauber, *J. Am. Chem. Soc.* **101**, 5111 (1979)
2. S.L. Mayo, B.D. Olafson, W.A. Goddard III, *J. Phys. Chem.* **94**, 8897 (1990)
3. A.K. Rappe, C.J. Casewit, K.S. Colwell, W.A. Goddard III, W.M. Skiff, *J. Am. Chem. Soc.* **114**, 10024 (1992)
4. S. Barlow, A.A. Rohl, S. Shi, C.M. Freeman, D. O'Hare, *J. Am. Chem. Soc.* **118**, 7578 (1996)
5. P.M. Morse, *Phys. Rev.* **34**, 57 (1929)
6. J.X. Sun, *Acta Phys. Sinica* **48**, 1992 (1999)
7. C. Gang, *Phys. Lett. A* **328**, 116 (2004)
8. T.C. Lim, *Internet Electron. J. Mol. Des* **7**, 77 (2008)
9. R. Biswas, D.R. Hamann, *Phys. Rev. Lett.* **55**, 2001 (1985)
10. P. Huxley, J.N. Murrell, *J. Chem. Soc. Faraday Trans. II* **79**, 323 (1983)
11. T.C. Lim, *Chem. Phys.* **320**, 54 (2005)
12. T.C. Lim, *Chem. Phys.* **331**, 270 (2007)
13. T.C. Lim, *Phys. Scripta* **70**, 347 (2004)
14. T.C. Lim, *Mol. Phys.* **105**, 1013 (2007)
15. T.C. Lim, *Mol. Phys.* **106**, 753 (2008)
16. T.C. Lim, *Mol. Simul.* **33**, 1029 (2007)
17. T.C. Lim, *J. Mol. Model.* **14**, 103 (2008)