

Exploring the Morse Potential

by

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Introduction

In many texts the Morse potential for a bond or a diatomic molecule is not shown with units and we often wonder how the author generated the plot from the equations given in the text. Here we will explore the creation of a Morse potential function for HCl and include all of the units used in each step. Later we can change the various parameters in the Morse potential and see the effect of each parameter on the shape of the potential curve. Last we can relate these parameters to molecular properties.

Goal

To provide practice with the Morse potential function for diatomic molecules and the unit conversions used in preparing plots of the Morse potential as a function of internuclear distance.

Prerequisites

1. Moderate skill with Mathcad in performing simple calculations and preparing plots.
2. Familiarity with the Morse potential function.
3. The concept of the bond length as being that interatomic distance found at the bottom of a potential well.

Performance Objectives

At the end of this exercise you will be able to:

1. plot the Morse potential for any bond given the bond energy, equilibrium bond length, and vibrational constant for the bond;
2. explain the significance of each component of the Morse potential;
3. discuss the effect of force constant, equilibrium bond length, and dissociation energy on the shape of the Morse potential curve.
4. Explain the limits of the Morse potential as a model for a diatomic bond.

Warm-up Exercises

1. Read the sections in your text that discuss the Morse potential and its properties. Find one other source of information on this function. How do the descriptions in the two sources compare? Summarize your observations in your notebook.
2. Write the Morse potential function in your notebook. Identify the fundamental mathematical form of this function. Recall that covalent bonds are due to orbital overlap. How do the hydrogenic functions used to describe covalent bonding compare to the Morse potential energy function? Explain the significance of your observations about the functions.
3. The bottom of a potential well identifies the equilibrium bond length for a bond represented by any potential. Use the calculus to find the equilibrium bond length of a Morse potential.
4. The curvature at the bottom of a potential well is determined by the force constant of a bond. Use calculus to determine the force constant of a bond represented by a Morse potential.

Setting up the calculation

First enter the essential HCl parameters into the Mathcad work sheet. Obtain these parameters either from experiment, a text, or from the primary literature. The values used in this document were taken from Physical Chemistry 3rd edition by J. Noggle, p 768. Hints for the calculation were found in example 12.10 of the book "Physical Chemistry Using Mathcad" by Noggle.

$$\omega_e := 2.899 \cdot 10^3 \cdot \text{cm}^{-1} \quad \text{The vibrational constant}$$

$$\omega_e x_e := 52.05 \cdot \text{cm}^{-1} \quad \text{Anharmonicity constant}$$

$$c := 2.99792 \cdot 10^8 \cdot \frac{\text{m}}{\text{sec}} \quad \text{Speed of light}$$

$$h := 6.62608 \cdot 10^{-34} \cdot \text{joule} \cdot \text{sec} \quad \text{Planck's constant}$$

$$R_e := 1.275 \cdot 10^{-8} \cdot \text{cm} \quad \text{Equilibrium bond length for HCl}$$

$$L := 6.0221 \cdot 10^{23} \quad \text{Avogadro's number}$$

$$eV := 1.602 \cdot 10^{-19} \cdot \text{joule} \quad \text{Define the conversion between eV and joules. This is a per molecule number of joules.}$$

$$D_0 := 4.436 \cdot \text{eV}$$

$$D_0 = 7.10647 \cdot 10^{-19} \cdot \text{kg} \cdot \text{m}^2 \cdot \text{sec}^{-2}$$

Here Mathcad converted eV to fundamental SI units.

Remember always to check the units on D_0 . We might have been reminded of it when we use reduced mass for the diatomic molecule below. Forgetting to convert to single molecule values is a common mistake when doing molecular calculations.

$$E_{\text{vib}}(n) := h \cdot c \cdot \left[(n + .5) \cdot \omega_e - (n + 0.5)^2 \cdot \omega_e x_e \right]$$

This is the energy obtained by solving the vibrational eigenvalue problem with a Morse potential. Here we see, in the second term, the anharmonic correction to the harmonic oscillator energy.

$$E_{\text{vib}}(0) = 2.8535 \cdot 10^{-20} \cdot \text{kg} \cdot \text{m}^2 \cdot \text{sec}^{-2}$$

$$D_e := D_0 + E_{\text{vib}}(0)$$

D_e is equal to D_0 + the zero point vibration correction.

$$D_e = 7.39182 \cdot 10^{-19} \cdot \text{kg} \cdot \text{m}^2 \cdot \text{sec}^{-2}$$

This produces a small correction

$$m_{\text{H}} := 1.00794 \cdot \frac{\text{gm}}{\text{L}} \quad m_{\text{Cl}} := 35.453 \cdot \frac{\text{gm}}{\text{L}}$$

$$\mu := \frac{m_{\text{H}} \cdot m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}}$$

Compute the reduced mass

$$\mu = 1.62747 \cdot 10^{-27} \cdot \text{kg}$$

$$R_e := 1.275 \cdot 10^{-8} \cdot \text{cm}$$

R_e here is in cm but the software changes it to m. You can check this by typing $R_e =$.

$$\beta := 2 \cdot \pi \cdot c \cdot \omega_e \cdot \sqrt{\frac{\mu}{2 \cdot D_e}}$$

β is a parameter in the Morse potential

$$\beta = 1.81181 \cdot 10^{10} \cdot \text{m}^{-1}$$

Notice that β has the correct units.

Exercise: Calculate B_e , the rotational constant, for HCl. Compare your calculated value to that found in the literature.

Computing the Morse potential energy as a function of the internuclear distance

$$r := 0.08 \cdot 10^{-9} \cdot \text{m}, .085 \cdot 10^{-9} \cdot \text{m} .. .4 \cdot 10^{-9} \cdot \text{m}$$

Setting the range of distances for the plot.

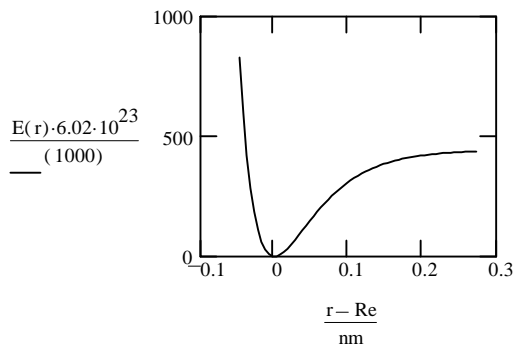
$$E(r) := D \cdot e \cdot (1 - \exp(-\beta \cdot (r - R_e)))^2$$

Calculating the energy as a function of interatomic distance.

What is the unit associated with $E(r)$?

Plotting the Morse potential

$$\text{nm} := 10^{-9} \cdot \text{m} \quad \text{a conversion factor}$$



$E(R)$ comes out to be a bunch of small numbers and this is not convenient to plot. So here we converted joules per molecule to kilo joules per mole. The conversion is seen in the graph. The net result is that we obtain graphs that look like the ones in the books and we have a clearer idea of the units.

Exercises. Exploration of the properties Morse potential function:

1. Create your own Morse potential function plot for a diatomic molecule. Choose an appropriate set of parameters for the potential and vary β systematically. What is the effect of β on the shape of the curve?
2. Use your Morse potential and vary the equilibrium bond length systematically. How does this affect the shape of the Morse potential?
3. In a separate experiment vary the D_e value systematically. How does this affect the shape of the Morse potential curve?
4. Another form of the Morse potential is $E(T, \beta, R_e, D_e, r) := T + D_e \cdot (1 - \exp(-\beta \cdot (r - R_e)))^2$. What is the significance of T in this expression?
5. How would the Morse potential for an electronically excited state bond vibration differ from the Morse potential for the electronic ground state of the same bond? Use graphs to explain your reasoning.
6. Redraw the graph above but this time plot $E(r)$ vs. r . What are the advantages of each type of plot? Explain.
7. Replot the data using eV units for energy.

Reflections:

It would be comforting to think that the Morse potential is the final word on the shape of a potential function. If this were so we could close the book on the subject after memorizing the function, no need to think about it further. However, the Morse potential is not the last word on the subject of the shape of the potential function that describes the variation of energy with respect to internuclear distance.

The Morse potential is a model just as the harmonic oscillator is a model for a chemical bond. The Morse potential, because of its exponential component follows the shape of experimentally determined potential functions over a wider range of internuclear distances than does the harmonic oscillator. The Morse potential also accounts for the fact that the energy levels get closer together as the potential energy increases for a quantum mechanical oscillator.

Because the Morse potential is a model it has a range of applicability for real systems. In the case of diatomic molecules the Morse potential starts to fail when the bond length is stretched beyond 0.5 to 1.0 Angstrom. For iodine this corresponds to about a 20% increase in bond length. An excellent figure showing the experimental and Morse potential for iodine can be found in the paper by Verma (1960). In this paper the author demonstrates that between $r = 4.6$ and 6.4 Å the potential function for iodine obeys the van der Waals $\frac{c}{r^6}$ law with $c = 3.7 \times 10^6$ (Verma, pages 777 and 778). It is left to the student to write a concluding analysis and discussion of the role of models and data analysis used for describing molecular structure.

Mastery Level Exercise:

Use the data in the paper by Verma to determine the relative statistical goodness of fit of the Morse potential and the van der Waals sixth power function. Determine the standard deviation in the fitting parameters for both function. Present your work in tabular form. Using statistical arguments, choose the function you would use for the potential in this region of internuclear distances. What is the consequence of the failure of the Morse potential for the design of molecular modeling software? How might software developers solve the problem of the failure of the Morse potential at longer bond lengths?

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