

Wavefunctions of the Morse Potential

The Schrödinger equation for the Morse potential can be solved analytically. The derivation below is adapted from the original work of Philip Morse (*Physical Review*, **34**, 57, 1929).

$$V(r) = D_e \cdot \left[1 - e^{-\beta \cdot (r-r_e)} \right]^2 \quad \text{Morse Potential}$$

$V(r)$ qualitatively reproduces the potential energy surface (PES) for diatomics: minima at r_e , strong internuclear repulsion at $r < r_e$, and dissociation at energy D_e with increasing r . The parameter β determines the anharmonicity of the PES. Solution of the Schrödinger equation leads to an expression for the radial wavefunction, Ψ , (angular momentum not considered)

$$\Psi(\beta, k, v, x) := \left(\frac{k \cdot \beta}{N(v)} \right)^{\frac{1}{2}} \cdot e^{\frac{-k}{2} \cdot e^{-\beta \cdot x}} \cdot (k \cdot e^{-\beta \cdot x})^{\frac{k-2v-1}{2}} \cdot L(v, k-2 \cdot v-1, k \cdot e^{-\beta \cdot x})$$

and vibrational energy levels

$$E_v = \omega_e \cdot \left(v + \frac{1}{2} \right) - \omega_e x_e \cdot \left(v + \frac{1}{2} \right)^2$$

ω_e is the harmonic constant, $\omega_e x_e$ ($\omega_e x_e$) is the anharmonic constant, v is the vibrational quantum number, and x is the displacement from equilibrium ($x = r - r_e$). The Morse potential is unique in that there exists a finite number of vibrational levels. The parameter k is twice $v_{\max} \cdot D_e$ and β can be rewritten in terms of ω_e and $\omega_e x_e$. μ is the reduced mass.

$$D_e = \frac{\omega_e^2}{4 \cdot \omega_e x_e} \quad \beta = \sqrt{\frac{8 \cdot \pi^2 \cdot c \cdot \mu \cdot \omega_e x_e}{h}} \quad v_{\max} = \frac{\omega_e}{2 \cdot \omega_e x_e}$$

N_v is a normalization constant (which doesn't work right now...)

$$N(v) = \Gamma(k-v)^2 \cdot \sum_{s=0}^v \frac{\Gamma(k-2 \cdot v+s-1)}{\Gamma(s+1)} \quad N(v) \equiv 1$$

$L(n, \alpha, x)$ is the general Laguerre function, calculated via its recurrence relation, (Handbook of Mathematical Functions).

$$L(n, \alpha, x) \equiv \begin{cases} \text{Laguerre}_0 \leftarrow 1 \\ \text{Laguerre}_1 \leftarrow 1 + \alpha - x \\ m \leftarrow 1 \\ \text{while } m < n \\ \quad \left| \text{Laguerre}_{m+1} \leftarrow \frac{(2 \cdot m + \alpha + 1 - x) \cdot \text{Laguerre}_m - (m + \alpha) \cdot \text{Laguerre}_{m-1}}{m + 1} \right. \\ \quad \left. m \leftarrow m + 1 \right. \\ \text{Laguerre}_n \end{cases}$$

Molecular and Spectroscopic Parameters

$$\text{mass}_1 := 4 \cdot \frac{\text{gm}}{\text{mol}}$$

$$\text{mass}_2 := 4 \cdot \frac{\text{gm}}{\text{mol}}$$

weights of the atoms or *effective* masses in DIM approximation

$$\mu := \frac{\text{mass}_1 \cdot \text{mass}_2}{\text{mass}_1 + \text{mass}_2}$$

$$\mu = 2.000 \frac{\text{gm}}{\text{mol}}$$

reduced mass

Lower State

Upper State

$$r_{e.GS} := 1.041 \cdot \text{\AA}$$

$$r_{e.XS} := 1.067 \cdot \text{\AA}$$

equilibrium bond length

$$\omega_{e.GS} := 1861.3 \cdot \text{cm}^{-1}$$

$$\omega_{e.XS} := 1765.8 \cdot \text{cm}^{-1}$$

harmonic constant

$$\omega_{x_e.GS} := 35.3 \cdot \text{cm}^{-1}$$

$$\omega_{x_e.XS} := 34.4 \cdot \text{cm}^{-1}$$

anharmonic constant

$$\text{vib}_{\text{max.GS}} := \frac{\omega_{e.GS}}{2 \cdot \omega_{x_e.GS}}$$

$$\text{vib}_{\text{max.XS}} := \frac{\omega_{e.XS}}{2 \cdot \omega_{x_e.XS}}$$

maximum vibrational quanta in PES

$$\text{vib}_{\text{max.GS}} = 26$$

$$\text{vib}_{\text{max.XS}} = 26$$

$$\text{vib}_{\text{max.GS}} := 4$$

$$\text{vib}_{\text{max.XS}} := 4$$

maximum vibrational quanta to consider

Range & Graphing Parameters

$$\frac{\omega_{e.GS}^2}{4 \cdot \omega_{x_e.GS}} = 24535.678 \text{ cm}^{-1}$$

$$r_{\text{min}} := 0.6 \cdot \text{\AA}$$

$$r_{\text{max}} := 2.0 \cdot \text{\AA}$$

$$\text{points} := 500$$

$$\text{chart}_{\text{max}} := \begin{cases} a_0 \leftarrow \frac{1.4}{\text{cm}^{-1}} \cdot \left[\omega_{e.GS} \cdot (\text{vib}_{\text{max.GS}} + 0.5) - \omega_{x_e.GS} \cdot (\text{vib}_{\text{max.GS}} + 0.5)^2 \right] \\ a_1 \leftarrow \frac{1.4}{\text{cm}^{-1}} \cdot \left[\omega_{e.XS} \cdot (\text{vib}_{\text{max.XS}} + 0.5) - \omega_{x_e.XS} \cdot (\text{vib}_{\text{max.XS}} + 0.5)^2 \right] \\ \max(a) \end{cases}$$

$$t := 0 \dots \text{chart}_{\text{max}}$$

$$\text{factor} := 300$$

expansion factor to display the wavefunction

Electronic Potential, Wavefunctions, and Energies

Ψ has the following column structure:

x axis | **electronic PES** | **v=0 wavefunction** | **v=1** | **v=2** ...
 /Å /cm⁻¹ /Å^{0.5}

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Ψ_gen(ω_e, ω_x_e, r_e, vibs) :=
  β ← √(8 · π² · c · μ · ω_x_e / h)           constants
  k ← floor(ω_e / ω_x_e)
  D_e ← ω_e² / (4 · ω_x_e)
  for i ∈ 0 .. points - 1
    r_i ← r_min + ((r_max - r_min) / (points - 1)) · i   generates the x-range at regular intervals
    V_i ← D_e · [1 - e-β · (r_i - r_e)]²                generates the PES
  temp ← r / Å
  temp ← augment(temp, V / cm-1)
  for i ∈ 0 .. vibs                                     generates the vibrational wavefunctions for
    for j ∈ 0 .. points - 1                             each vibrational level
      Ψ_temp_j ← Ψ(β, k, i, r_j - r_e) · √A
    temp ← augment(temp, Ψ_temp)
  Δx ← temp1,0 - temp0,0
  for i ∈ 0 .. vibs                                     normalizes the wavefunction
    Norm ← Δx · ∑ (temp<i+2>)²
    temp<i+2> ← temp<i+2> / √Norm
  temp
  
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$\Psi_{GS} := \Psi_{gen}(\omega_{e.GS}, \omega_{x_e.GS}, r_{e.GS}, vibs_{max.GS})$ generates the PESs for the lower and upper states

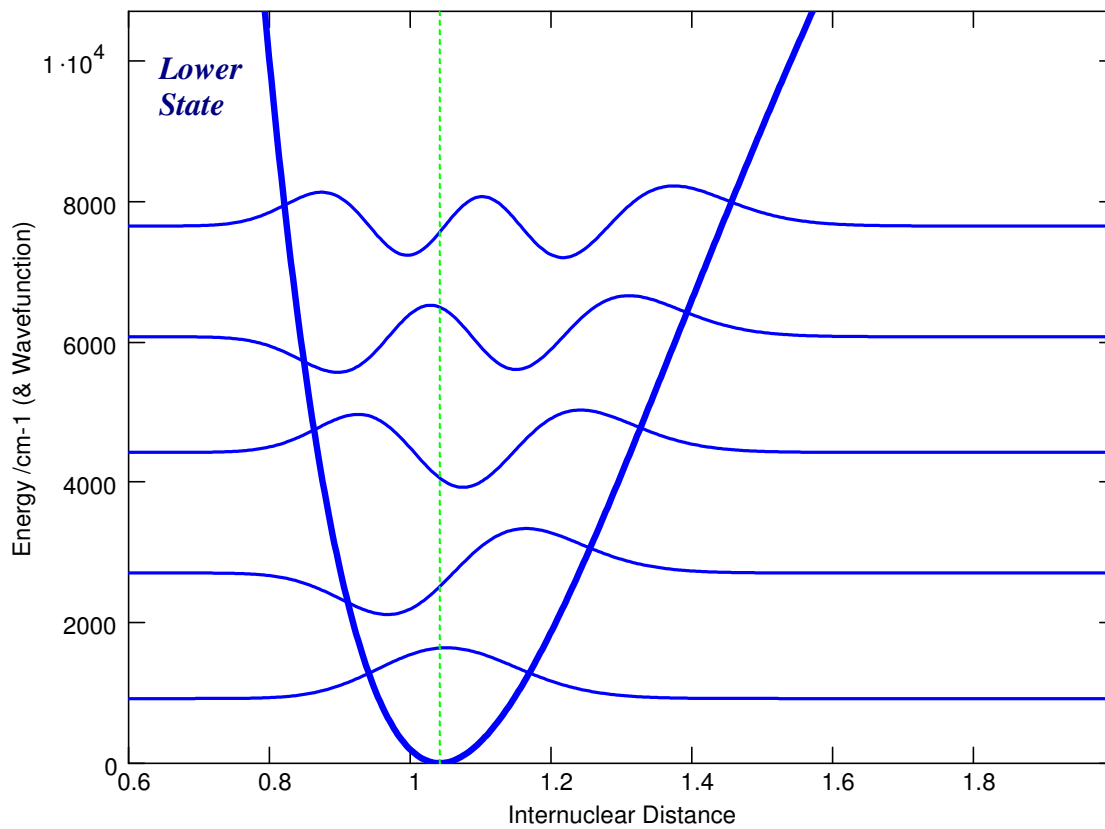
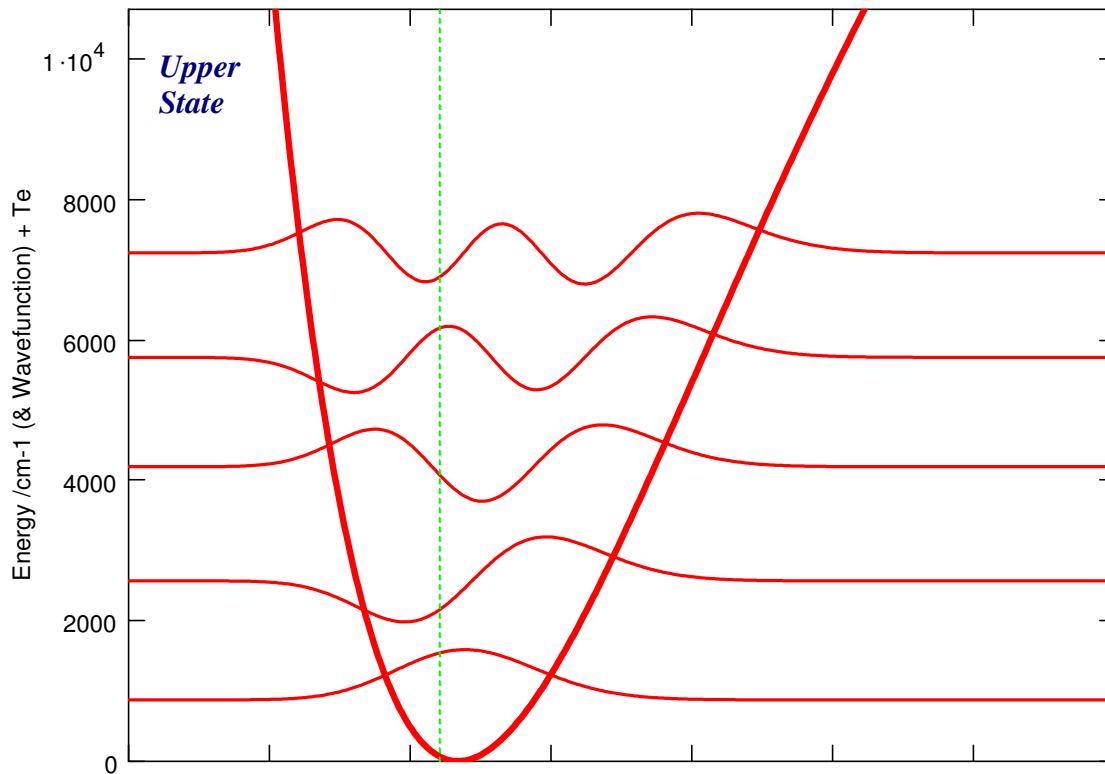
$\Psi_{XS} := \Psi_{gen}(\omega_{e.XS}, \omega_{x_e.XS}, r_{e.XS}, vibs_{max.XS})$

$$E_{\text{gen}}(\omega_e, \omega_x e, \Psi, \text{vibs}) := \left| \begin{array}{l} \text{temp} \leftarrow \text{submatrix}(\Psi, 0, \text{points} - 1, 2, \text{vibs} + 2) \cdot \text{factor} \\ \text{for } i \in 0 \dots \text{vibs} \\ \quad \left| \begin{array}{l} E_i \leftarrow \omega_e \cdot (i + 0.5) - \omega_x e \cdot (i + 0.5)^2 \\ \text{temp}^{(i)} \leftarrow \text{temp}^{(i)} + \frac{E_i}{\text{cm}^{-1}} \end{array} \right. \\ \text{temp} \end{array} \right. \quad \begin{array}{l} \text{adds energy to the vibrational} \\ \text{wavefunctions to separate when} \\ \text{displaying} \end{array}$$

$$E_{\text{GS}} := E_{\text{gen}}(\omega_{e.\text{GS}}, \omega_{x e.\text{GS}}, \Psi_{\text{GS}}, \text{vibs}_{\text{max.GS}})$$

$$E_{\text{XS}} := E_{\text{gen}}(\omega_{e.\text{XS}}, \omega_{x e.\text{XS}}, \Psi_{\text{XS}}, \text{vibs}_{\text{max.XS}})$$

Morse Potential Wavefunctions



Franck-Condon Factor (overlap of wavefunctions)

$$\Delta x := \Psi_{GS_1,0} - \Psi_{GS_0,0}$$

$$S := \begin{matrix} \text{for } i \in 0 \dots \text{vibsmax.GS} \\ \text{for } j \in 0 \dots \text{vibsmax.XS} \\ S_{i,j} \leftarrow \left| \sum_{k=0}^{\text{points}-1} \Psi_{GS_{k,i+2}} \cdot \Psi_{XS_{k,j+2}} \cdot \Delta x \right| \\ S \end{matrix}$$

$$S = \begin{pmatrix} 0.982 & 0.183 & 0.045 & 0.013 & 0.004 \\ 0.189 & 0.947 & 0.249 & 0.075 & 0.025 \\ 0.004 & 0.265 & 0.912 & 0.293 & 0.102 \\ 0.001 & 0.005 & 0.323 & 0.878 & 0.324 \\ 0.000 & 0.001 & 0.007 & 0.371 & 0.845 \end{pmatrix}$$