

Visualizing the Formally Forbidden Overtone Vibrational Transitions in HCl

Using the harmonic oscillator model, the selection rule for molecular vibrations is $\Delta v = +/- 1$. However, overtone transitions ($\Delta v = 2, 3, \dots$) are observed experimentally. In what follows it will be shown that under the Morse oscillator (anharmonic) model, overtone vibrational transitions are weakly allowed.

Schrodinger's equation for the Morse oscillator model for HCl is integrated numerically for the first five energy states. (Integration algorithm taken from J. C. Hansen, *J. Chem. Educ. Software*, **8C2**, 1996.)

Set integration parameters (in atomic units):

$$n := 150 \quad x_{\min} := 1.4 \quad x_{\max} := 8 \quad \Delta := \frac{x_{\max} - x_{\min}}{n - 1}$$

Enter the Morse parameters for HCl (in atomic units):

$$\mu := 1785.64 \quad D := .1655 \quad \beta := 1.0051 \quad x_e := 2.4086$$

Calculate position vector, the potential energy matrix, and the kinetic energy matrix. Then combine them into a total energy matrix.

$$i := 1..n \quad j := 1..n \quad x_i := x_{\min} + (i - 1) \cdot \Delta$$

$$V_{i,j} := \text{if} \left[i = j, D \cdot \left[1 - \exp \left[-\beta \cdot (x_i - x_e) \right] \right]^2, 0 \right] \quad T_{i,j} := \text{if} \left[i = j, \frac{\pi^2}{6 \cdot \mu \cdot \Delta^2}, \frac{(-1)^{i-j}}{(i-j)^2 \cdot \mu \cdot \Delta^2} \right]$$

Hamiltonian energy matrix: $H := T + V$

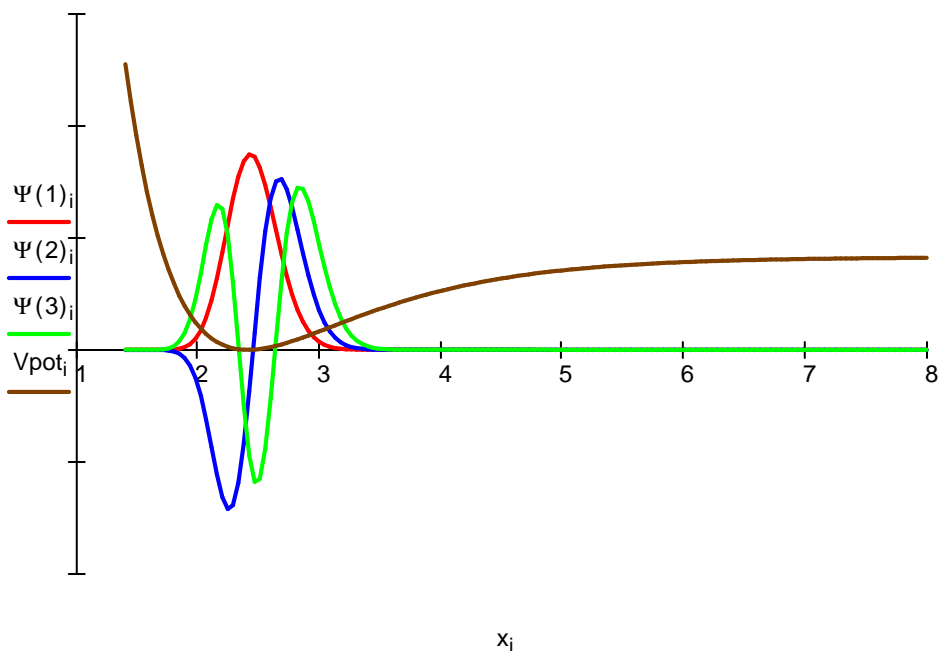
Find eigenvalues: $E := \text{sort}(\text{eigenvals}(H))$ Selected eigenvalues: $m := 1..5$ $E_m =$

Calculate eigenvectors: $\Psi(k) := \text{eigenvec}(H, E_k)$

Plot diagonal elements of potential energy matrix and selected eigenfunctions:

$$V_{\text{pot}_i} := V_{i,i}$$

| | |
|-------|------------|
| E_1 | 0.00677149 |
| E_2 | 0.01989016 |
| E_3 | 0.03244307 |
| E_4 | 0.04443024 |
| E_5 | 0.05585166 |



Because of the way the integration algorithm is implemented the initial index is $m = 1$. This corresponds to the $v = 0$ vibrational ground state. In other words, subtract 1 from the m index to get the v quantum number.*

Demonstrate numerically that the solutions form an orthonormal set:

$$\begin{aligned} \sum_i (\Psi(1)_i)^2 &= 1.00 & \sum_i (\Psi(2)_i)^2 &= 1.00 & \sum_i (\Psi(3)_i)^2 &= 1.00 \\ \sum_i (\Psi(1)_i \cdot \Psi(2)_i) &= 0.00 & \sum_i (\Psi(1)_i \cdot \Psi(3)_i) &= 0.00 & \sum_i (\Psi(2)_i \cdot \Psi(3)_i) &= 0.00 \end{aligned}$$

Calculate the transition dipole moment to demonstrate that the $v = 0$ to $v = 2$ transition, which is forbidden for the harmonic oscillator, is (slightly) allowed. Compare this result to $v = 0$ to $v = 1$, $v = 1$ to $v = 2$ transitions which are allowed. (See * above.)

$$\sum_i (\Psi(1)_i \cdot x_i \cdot \Psi(3)_i) = -0.01 \quad \sum_i (\Psi(1)_i \cdot x_i \cdot \Psi(2)_i) = 0.14 \quad \sum_i (\Psi(2)_i \cdot x_i \cdot \Psi(3)_i) = 0.21$$

Animate these transitions to confirm that they lead to oscillating dipole character.

Select quantum numbers of initial and final states: $v_i := 1$ $v_f := 3$

Energy of transition: $\Delta E := E_{v_f} - E_{v_i}$ $\Delta E = 0.02567158$ Define animation parameter: $t := \frac{\text{FRAME}}{10^{-8}}$

Time-dependent superposition of initial and final states:

$$\Phi_i := \frac{\Psi(v_i)_i \cdot \exp(-i \cdot E_{v_i} \cdot t) + \Psi(v_f)_i \cdot \exp(-i \cdot E_{v_f} \cdot t)}{\sqrt{2}}$$

To animate click on **Tools**, **Animation**, **Record** and follow the instructions in the dialog box.

Recommended setting: From 0 To 40 in 5 Frames/Sec.

