

**Harmonic Oscillator**

1. For a classical harmonic oscillator, the particle cannot go beyond the points where the total energy equals the potential energy. Identify these points for a quantum-mechanical harmonic oscillator in its ground state. Write an integral giving the probability that the particle will go beyond these classically-allowed points. (You don't need to evaluate the integral.)

*Useful:*

$$\psi_n = N_n H_n \left( \alpha^{\frac{1}{2}} x \right) e^{-\frac{1}{2} \alpha x^2}; n = 0, 1, 2, 3, \dots \alpha = \frac{\sqrt{mk}}{\hbar}$$

$$\text{where } N_n \text{ is the normalization constant, } N_n = \left( \frac{\alpha}{\pi} \right)^{\frac{1}{4}} \left( \frac{1}{n! 2^n} \right)^{\frac{1}{2}}$$

The parameters  $H_n$  are a special set of polynomials as the **Hermite Polynomials**, let  $y = \alpha^{\frac{1}{2}} x$ ,  
The Hermite polynomials are:

$$H_0(y) = 1$$

$$H_1(y) = 2y$$

$$H_2(y) = 4y^2 - 2$$

...

Consider the relation between the total energy and the potential energy.

The turning points for quantum number occur where the kinetic energy equals 0, so that the potential energy equals the total energy. For quantum number  $n$ , this is determined by

$$\frac{1}{2} k x_{\max}^2 = \left( n + \frac{1}{2} \right) \hbar \omega$$

where,  $\omega = \sqrt{\frac{k}{m}}$ , we have,

$$x_{\max}^2 = (2n + 1) \frac{\hbar}{\sqrt{km}}$$

$$P(x_{\max} \leq x \leq \infty) = P(-\infty \leq x \leq -x_{\max}) = \int_{x_{\max}}^{\infty} |\psi_n(x)|^2 dx$$

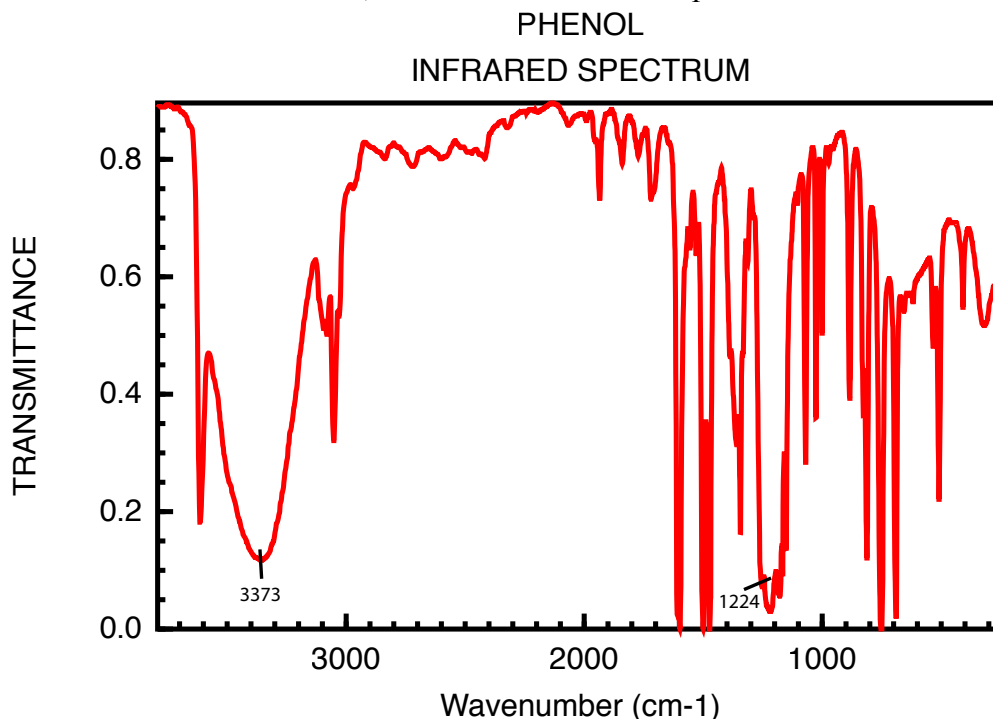
\*Optional:

For  $n = 0$ , let  $\alpha = \frac{\sqrt{mk}}{\hbar}$

$$P_{\text{outside}} = 2 \int_{1/\sqrt{\alpha}}^{\infty} \left( \frac{\alpha}{\pi} \right)^{1/2} e^{-\alpha x^2} dx = \frac{2}{\sqrt{\pi}} \int_1^{\infty} e^{-\xi^2} d\xi = \text{erfc}(1) \approx 0.158$$

where erfc is the complementary error function. This result means that in the ground state, there is a ~16% chance that the oscillator will “tunnel” outside its classical allowed region.

2. Under the assumption of molecular vibration as that of a harmonic oscillator. There are two strong infrared bands of phenol ( $C_6H_6O$ ) that correspond to the C-O and O-H stretching. The wavenumbers are given on the IR spectrum, at  $3373\text{ cm}^{-1}$  and  $1224\text{ cm}^{-1}$ . In general, the force constant,  $k$ , depends on the bond strength. In general, it values around  $500\text{ N} \cdot \text{m}^{-1}$  for single bond,  $1000\text{ N} \cdot \text{m}^{-1}$  for double bond, and  $2000\text{ N} \cdot \text{m}^{-1}$  for triple bond.



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Hint: Each stretching behaves like diatomic molecule within polyatomic molecule, if the associated stretching frequency is different from other vibrational frequencies within the molecule.

- Find the reduced mass for each stretching.
- Can you assign the bands based on your current chemistry knowledge and lab experience? YES! Assign them.
- Justify your assignment by finding the force constant for each stretching. Briefly explain the assignment and comment on the bond strength.

Based on the current knowledge,  $\tilde{\nu}(C - O) = 1224\text{ cm}^{-1}$ ;  $\tilde{\nu}(O - H) = 3373\text{ cm}^{-1}$

$$\therefore \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\therefore k = \mu \cdot (2\pi c \tilde{\nu})^2$$

For C-O stretching:

$$\mu_{C-O} = \frac{m_{C_6H_5} \cdot m_{OH}}{m_{C_6H_5} + m_{OH}} \cdot \frac{1}{N_A} = \frac{77 \times 17}{94 N_A} = \frac{13.926}{N_A} (\text{gram}) = \frac{13.926}{1000 N_A} (\text{kg})$$

$$k_{C-O} = \frac{13.926}{1000N_A} \times (2\pi \times 3 \times 10^8 \times 122400)^2 = 1231 \text{ N/m}$$

- If we use  $3373 \text{ cm}^{-1}$  to calculate the force constant, the value will be 9348 N/m.

For O-H stretching:

$$\mu_{O-H} = \frac{m_{C_6H_5O} \cdot m_H}{m_{C_6H_5O} + m_H} \cdot \frac{1}{N_A} = \frac{93 \times 1}{94N_A} = \frac{0.989}{N_A} (\text{gram}) = \frac{0.989}{1000N_A} (\text{kg})$$

$$k_{O-H} = \frac{0.989}{1000N_A} \times (2\pi \times 3 \times 10^8 \times 337300)^2 = 664 \text{ N/m}$$

- If we use  $1224 \text{ cm}^{-1}$  to calculate the force constant, the value will be 87.4 N/m.

Comment: the C-O bond is stronger than the O-H bond, based on the force constants.