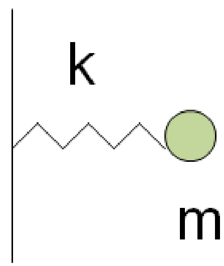
Classical harmonic oscillator

A

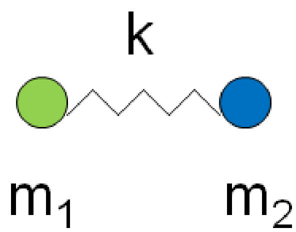
Mass on a spring



Force constant k

B

Diatomic

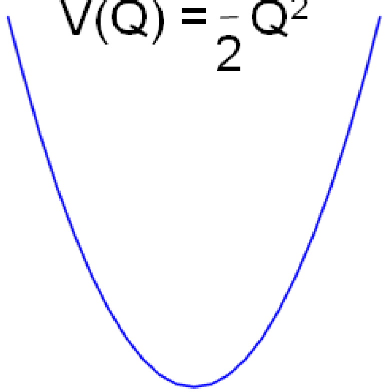


Reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

C

$$V(Q) = \frac{k}{2} Q^2$$



D

$$\frac{\mu}{2}\left(\frac{\partial Q}{\partial t}\right)^2 + \frac{k}{2} Q^2 = 0$$

The classical harmonic oscillator obeys a Hooke's law equation:

$$F = -kQ$$

where k is a restoring force. A trial solution is:

$$Q(t) = Q_0 cos(\omega t)$$

When substituted into the Hooke's law equation:

$$-\mu\omega^2 Q_0 cos(\omega t) = -kQ_0 cos(\omega t)$$

We can solve for the natural frequency of the spring
And we can also express that in cm^{-1}.

$$\omega = \sqrt{\frac{k}{\mu}} \qquad \tilde{\nu}(cm^{-1}) = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

Harmonic approximation

$$V(Q) = V(Q_0) + \left(\frac{\partial V}{\partial Q}\right)(Q - Q_0) + \frac{1}{2}\left(\frac{\partial^2 V}{\partial Q^2}\right)(Q - Q_0)^2 + \cdots$$

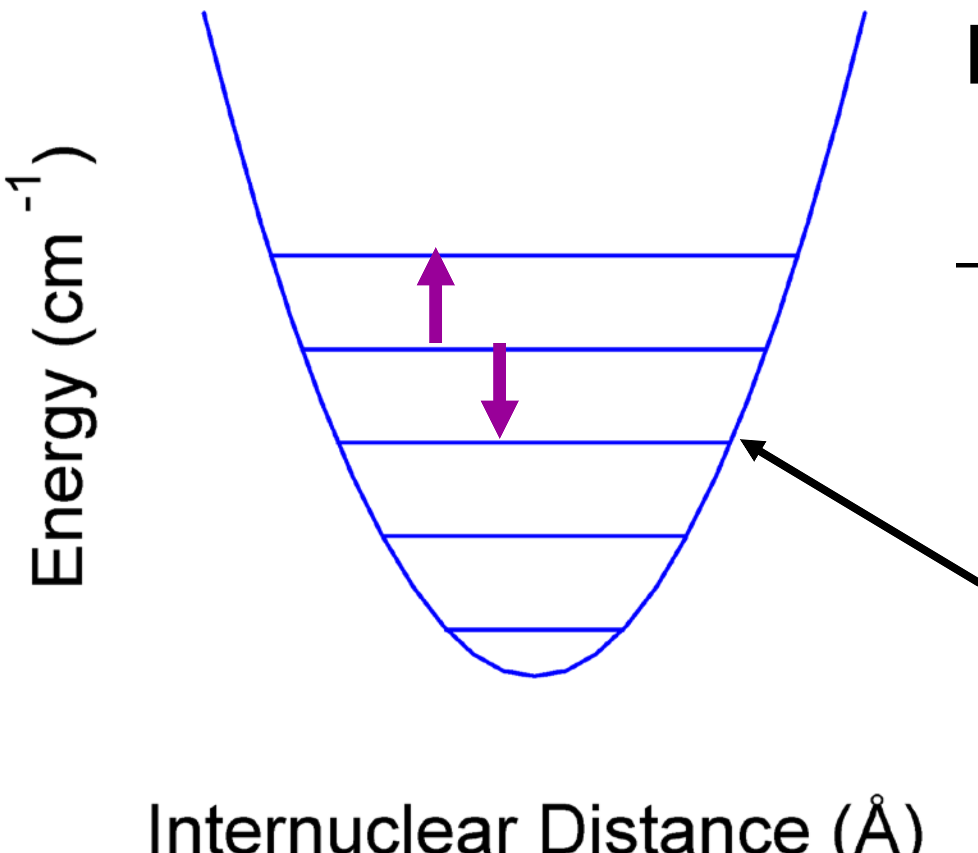
At equilibrium

$$\left(\frac{\partial V}{\partial Q}\right) = 0$$

Assume terms higher than quadratic are zero.
By definition

$$k = \left(\frac{\partial^2 V}{\partial Q^2}\right)$$

Quantum approach to the vibrational harmonic oscillator



Q

Solution is Gaussian

Energy is quantized

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial Q^2}\chi + \frac{k}{2}Q^2\chi = E\chi$$

$$E = \left(\mathrm{v} + \frac{1}{2}\right)h\nu$$

v is the quantum number

Allowed transitions

v’ → v + 1, v’ → v - 1

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$$y = \sqrt{\alpha}Q \quad \text{where}\ \alpha = \frac{\mu\omega}{\hbar}\ \text{and}\ \epsilon = \frac{2E}{\hbar\omega}$$

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$$\mathrm{y} = \sqrt{\alpha}\mathrm{Q} \quad \text{where } \alpha = \frac{\mu\omega}{\hbar} \text{ and } \epsilon = \frac{2\mathrm{E}}{\hbar\omega}$$

Noting that

$$\frac{\partial^2}{\partial Q^2} = \frac{\mu\omega}{\hbar}\frac{\partial^2}{\partial y^2}$$

we can write the equation as

$$-\frac{\partial^2}{\partial y^2}\chi + y^2\chi = \epsilon\chi$$

One approach to solving such an equation is to find an asymptotic solution g(y) assuming that $\varepsilon \sim 0$. Then, we can assume that the true solution is the product of g(y) and a function f(y). The asymptotic solution is:

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f(y) can be a series expansion that will give different solutions for various values of ε. A Gaussian function is an appropriate trial solution for the this equation,

$$\chi_{trial} = e^{-y^2/2} \qquad \frac{\partial^2}{\partial y^2}\chi_{trial} = (y^2 - 1)e^{-y^2/2}$$

For large values of y we have

$$\frac{\partial^2}{\partial y^2}\chi_{trial} \approx y^2 e^{-y^2/2}$$

Thus, our trial solution for the general equation is

$$\chi_{trial} = f(y)e^{-y^2/2}$$

Substitution of the trial solution

In order to substitute this equation we need the derivatives.
We have

$$\frac{\partial \chi_{trial}}{\partial y} = \left(\frac{\partial f}{\partial y} - fy\right) e^{-y^2/2}$$

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Substituting this into the above equation gives us

$$\frac{\partial^2 f}{\partial y^2} - 2y\frac{\partial f}{\partial y} + (\epsilon - 1)f = 0$$

Frobenius series

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$$\frac{\partial^2 f}{\partial y^2} = \sum_{n=0}^{\infty} n(n-1) a_n y^{n-2} = \sum_{n=0}^{\infty} (n+1)(n+2) a_{n+2} y^n$$

Series solution of the equation

$$\sum_{n=0}^{\infty}(n+1)(n+2)a_{n+2}y^n - 2y\sum_{n=0}^{\infty}na_ny^{n-1} + (\epsilon-1)\sum_{n=0}^{\infty}a_ny^n = 0$$

$$\sum_{n=0}^{\infty}\big((n+1)(n+2)a_{n+2} + (\epsilon-1-2n)a_n\big)y^n = 0$$

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Once we choose a value for ε there is one and only one sequence of coefficients, a_n that defines the function f(y). Therefore, the sum can be zero for all values of y if and only if the coefficient of each power of

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$$(n+1)(n+2)a_{n+2} + (\epsilon-1-2n)a_n = 0$$

And y vanishes separately. Thus,

$$a_{n+2} = \frac{1+2n-\epsilon}{(n+1)(n+2)}a_n$$

Energies of the quantum oscillator

Rather than finding an infinite series (which would actually be divergent in this case!) we will assume that the solution is a polynomial that terminates after a finite number of terms, n. The condition for the series to terminate is

$$a_{n+2} = 0$$

or

$$1 + 2n - \epsilon = 0$$

which implies

$$\epsilon = 2\mathrm{n} + 1$$

Therefore, from the above we have

$$\mathrm{E} = \frac{1}{2}(2\mathrm{n} + 1)\hbar\omega = \left(\mathrm{n} + \frac{1}{2}\right)\hbar\omega$$

Wave functions of the quantum harmonic oscillator

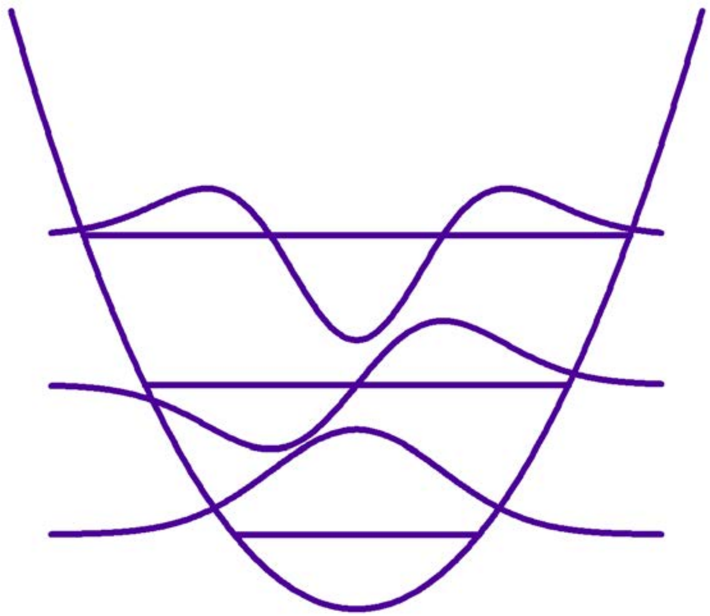
Using the definition of α, the solutions have the form:

$$\chi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha Q^2/2}$$

$$\chi_1 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \sqrt{2\alpha} Q e^{-\frac{\alpha Q^2}{2}}$$

$$\chi_2 = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{(4\alpha Q^2 - 2)}{2\sqrt{2}} e^{-\alpha Q^2/2}$$

Vibrational wavefunctions and energies



- Energy levels are given by

$$E_v = (v + 1/2)\hbar\omega$$

- Typical energies are of the order of 0 - 3200 cm^{-1}
- Wavefunctions are

$$\Psi_v = N_v H_v e^{-y^2/2}$$

where H_v is the Hermite polynomial

Solutions to harmonic oscillator

The Hermite polynomials are derivatives of a Gaussian

$$y = \sqrt{\alpha} Q \quad \text{where } \alpha = \frac{\mu\omega}{\hbar}$$

The Hermite generating function is

$$H_v(y) = (-1)^v e^{y^2/2} \frac{d^v}{dy^v} e^{-y^2/2}$$

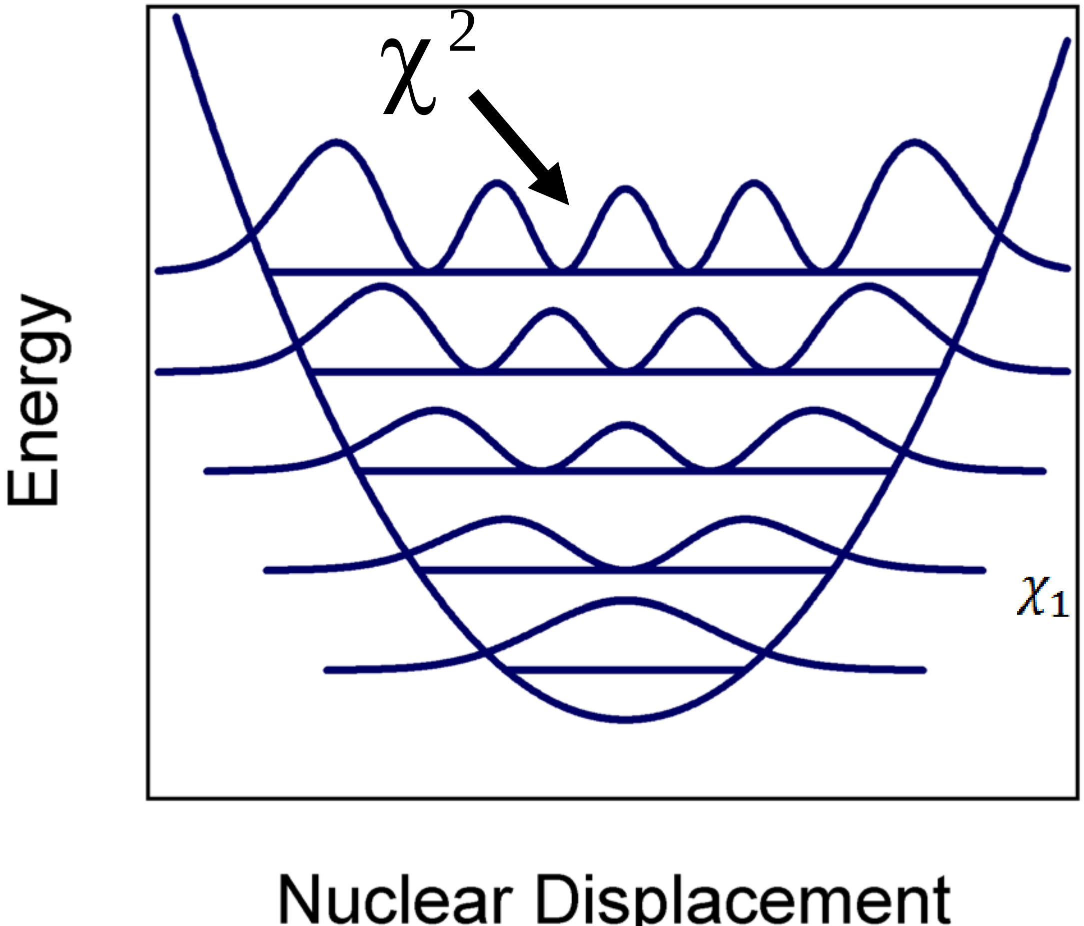
The normalization constant is

$$N_v = \frac{1}{\sqrt{\alpha \pi^{1/2} 2^v v!}}$$

Hermite polynomials

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$

The square of the wave function gives rise to the probability distribution



The probability is shown in the figure.

Solutions are Gaussians multiplied by polynomial functions.

$$\chi_1 = \left(\frac{\alpha}{\pi}\right)^{1/2} \sqrt{2\alpha} Q exp\{-\alpha Q^2/2\}$$

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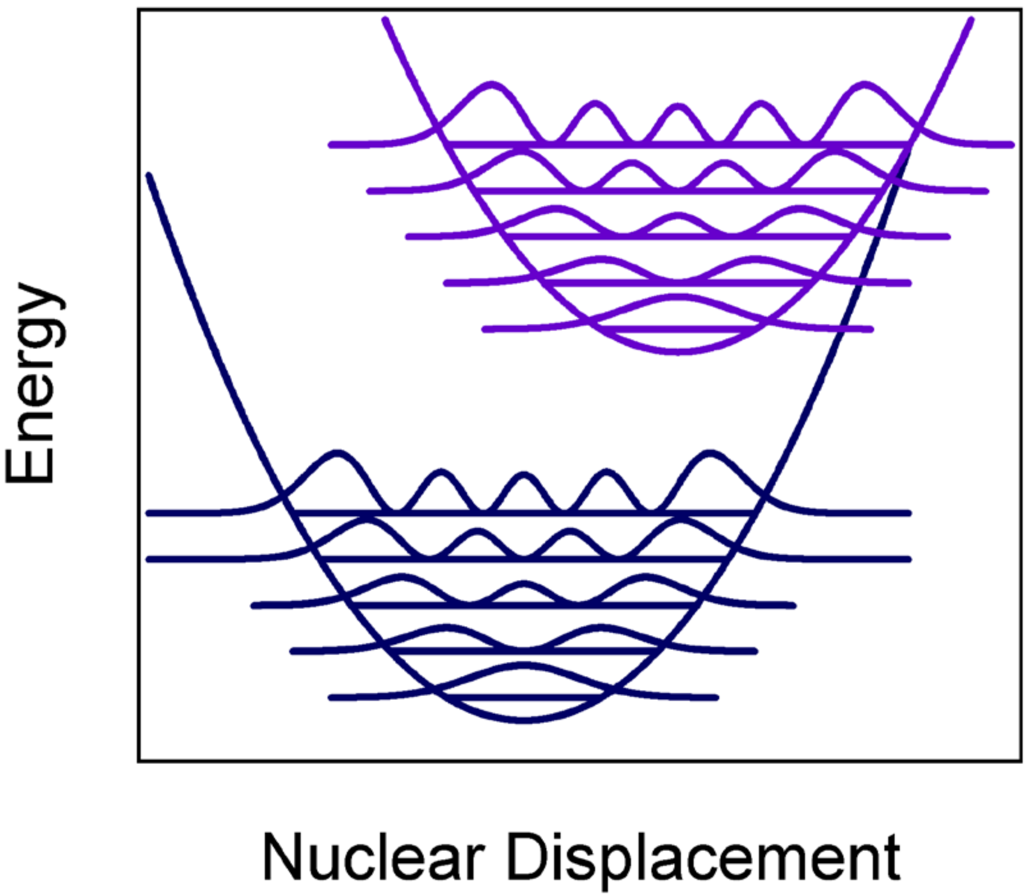
There is a potential energy surface that corresponds to each electronic state of the molecule



The shift in the nuclear displacement arises from the fact that the bond length increases in the σ^* state compared to the σ state. We will show that the overlap of the vibra- -tional wave functions is key to understanding the shape of absorption bands.