

Quantum Chemistry

Lecture 10

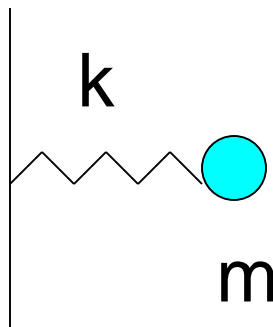
Harmonic Oscillator

NC State University

Classical Vibration of a Diatomic

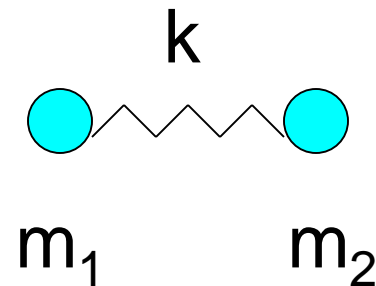
As was the case for rotation, we can consider a simple model of a mass on a spring attached to a wall of infinite mass and a diatomic molecule as two simple examples.

Mass on a spring



k is the force constant

Diatomic



Reduced mass

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

Harmonic approximation

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

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

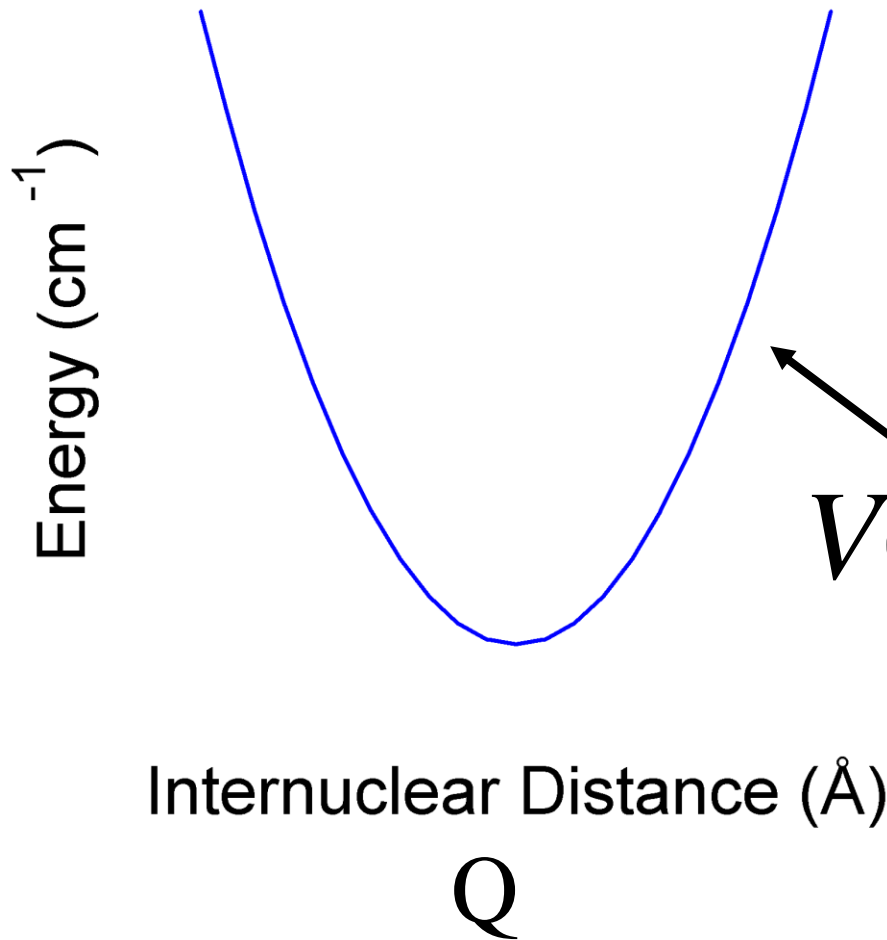
Assume terms higher than quadratic are zero

By definition

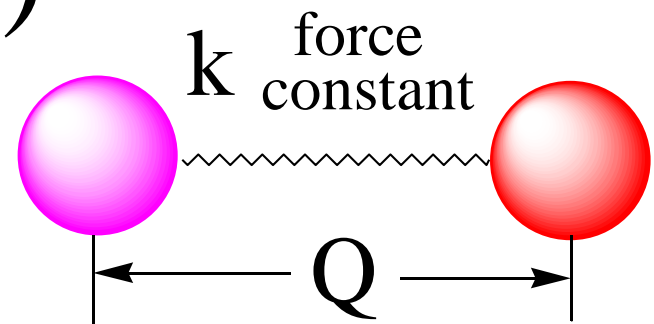
$$\left(\frac{\partial^2 V}{\partial Q^2}\right) = k, \text{ the force constant}$$

Classical approach to vibration

Solution is oscillatory
Any energy is possible



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



Classical vibrational motion

- A particle undergoes harmonic motion if it experiences a restoring force that is proportional to its displacement, x .
- $F = -kQ$ (k is a force constant)
- $F = -dV/dQ$ and $V = 1/2kQ^2$.
- The classical harmonic oscillator can also be written as:

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

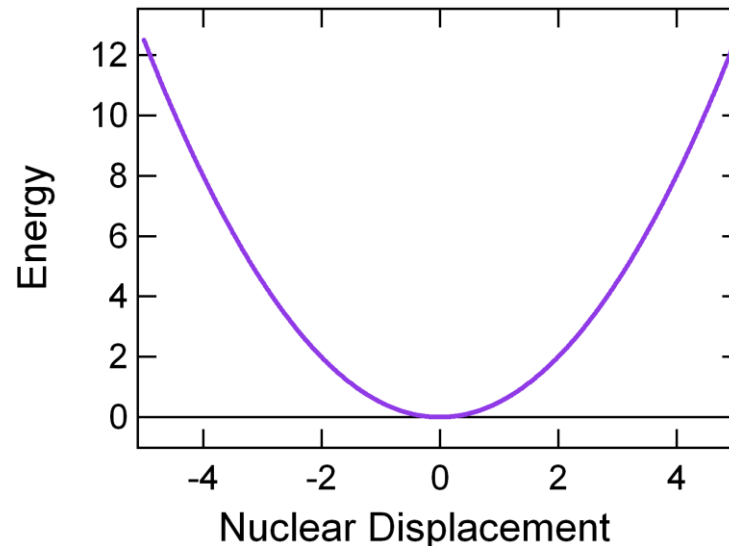
- Solutions have the form of $Q(t) = \cos(\omega t)$.
- These solutions imply that

$$\omega = \sqrt{\frac{k}{\mu}}$$

- Reduced mass is
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Classical potential function

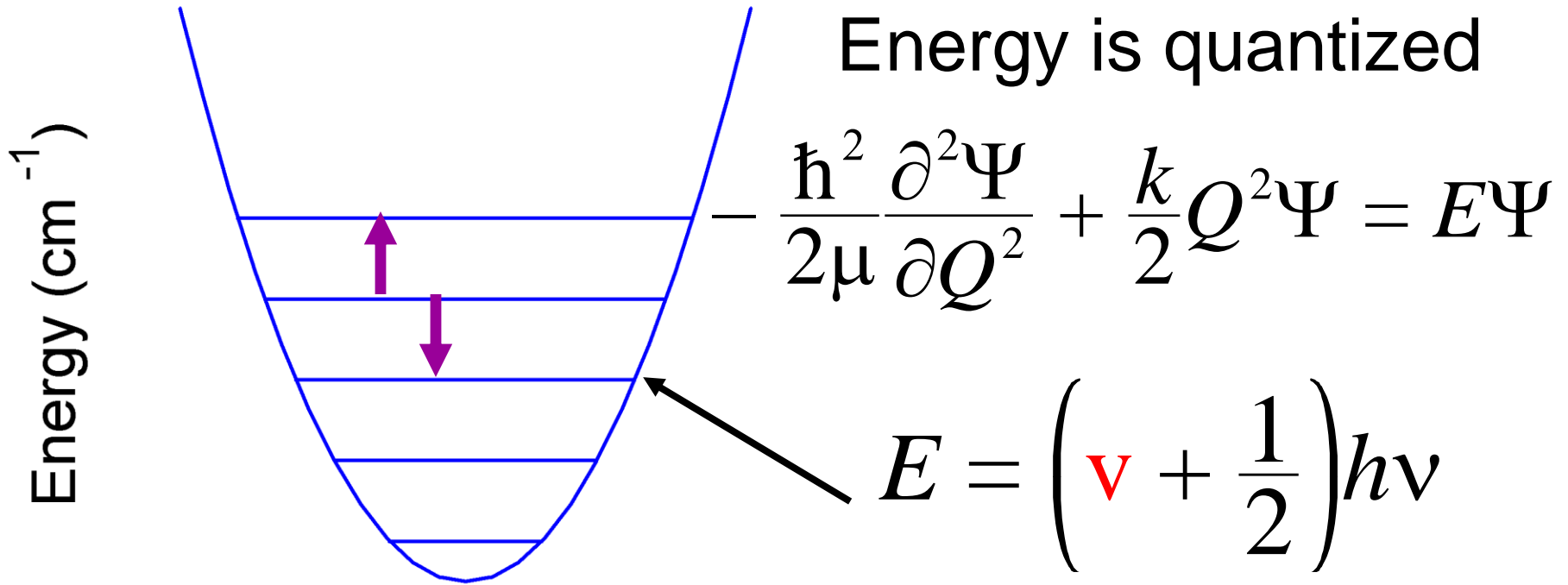
- The potential is $V = 1/2kQ^2$, which is a parabolic function.
- This potential is called a harmonic potential.



- The force constant k has units of Newtons/meter (N/m) or Joules/meter² (J/m²).
- The angular frequency $\omega = 2\pi\nu$, ν is the frequency in Hz.

Quantum approach to the vibrational harmonic oscillator

Solution is Gaussian
Energy is quantized



Energy (cm^{-1})

Internuclear Distance (\AA)

Q

ν is the quantum number

Allowed transitions

$\nu' \rightarrow \nu + 1, \nu' \rightarrow \nu - 1$

We can use a harmonic potential in the Schrödinger equation to calculate the wave functions and energies of the vibrations of molecules.

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

Making the definitions,

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

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:

$$\frac{\partial^2}{\partial y^2} \chi \approx y^2 \chi$$

$f(y)$ 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,

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

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

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

and

$$\frac{\partial^2 \chi_{trial}}{\partial y^2} = \left(\frac{\partial^2 f}{\partial y^2} - 2y \frac{\partial f}{\partial y} + (y^2 - 1)f \right) e^{-y^2/2}$$

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

If we assume that $f(y)$ has the form of a series

$$f(y) = \sum_{n=0}^{\infty} a_n y^n$$

Then the derivatives are

$$\frac{\partial f}{\partial y} = \sum_{n=0}^{\infty} n a_n y^{n-1}$$

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

Series solution of the equation

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

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

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

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

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

$$\epsilon = 2n + 1$$

Therefore, from the above we have

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

Wave functions of the quantum harmonic oscillator

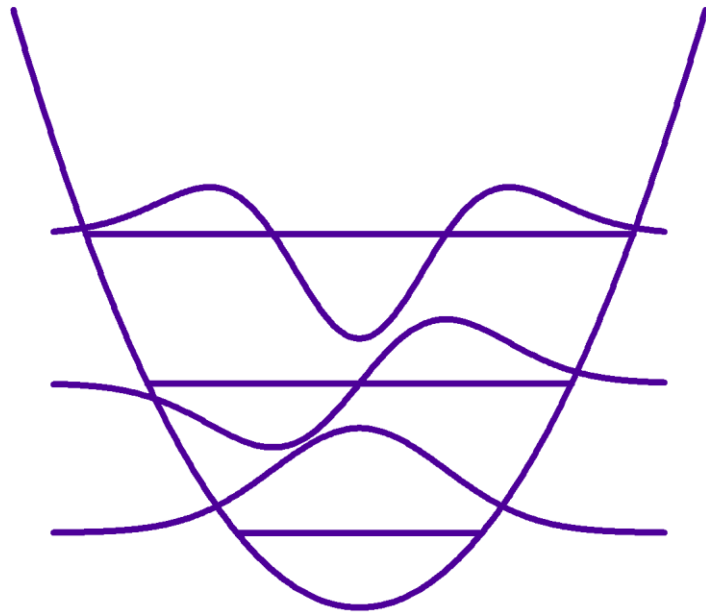
Using the definition of α , the solutions have the form:

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

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

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

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

You should know the energy level formula and be able to sketch the wave functions on the potential surface.

Solutions to harmonic oscillator

The Hermite polynomials are derivatives of a Gaussian, $y = \alpha^{1/2}Q$

$$\alpha = \frac{\sqrt{\mu k}}{\hbar}$$

$$v \quad H_v(y)$$

$$0 \quad 1$$

$$1 \quad 2y$$

$$2 \quad 4y^2 - 2$$

$$3 \quad 8y^3 - 12y$$

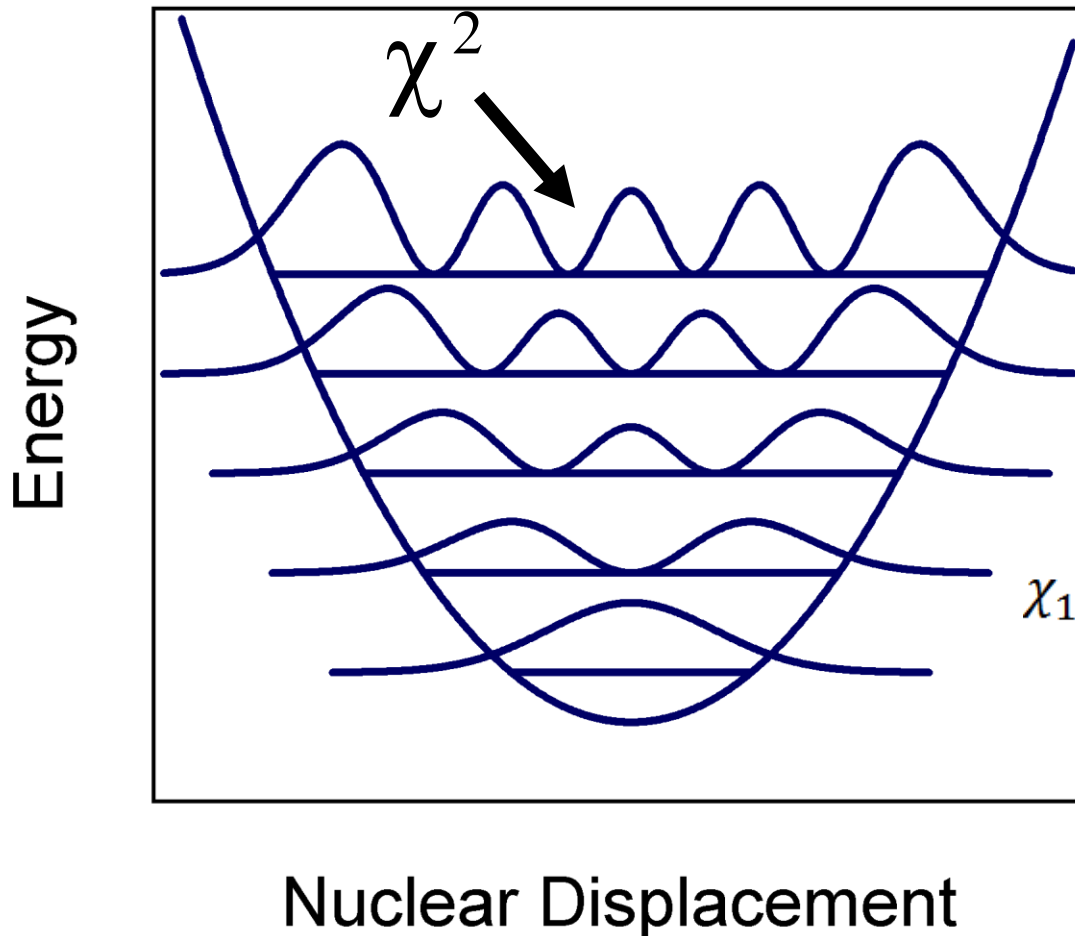
$$H_v(y) = (-1)^v e^{y^2} \left(\frac{d}{dy} \right)^v e^{-y^2}$$

The normalization constant is

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

This information is provided for completeness.
It is not an exam topic.

The bonding electronic state gives rise to a potential energy surface for the nuclear motion



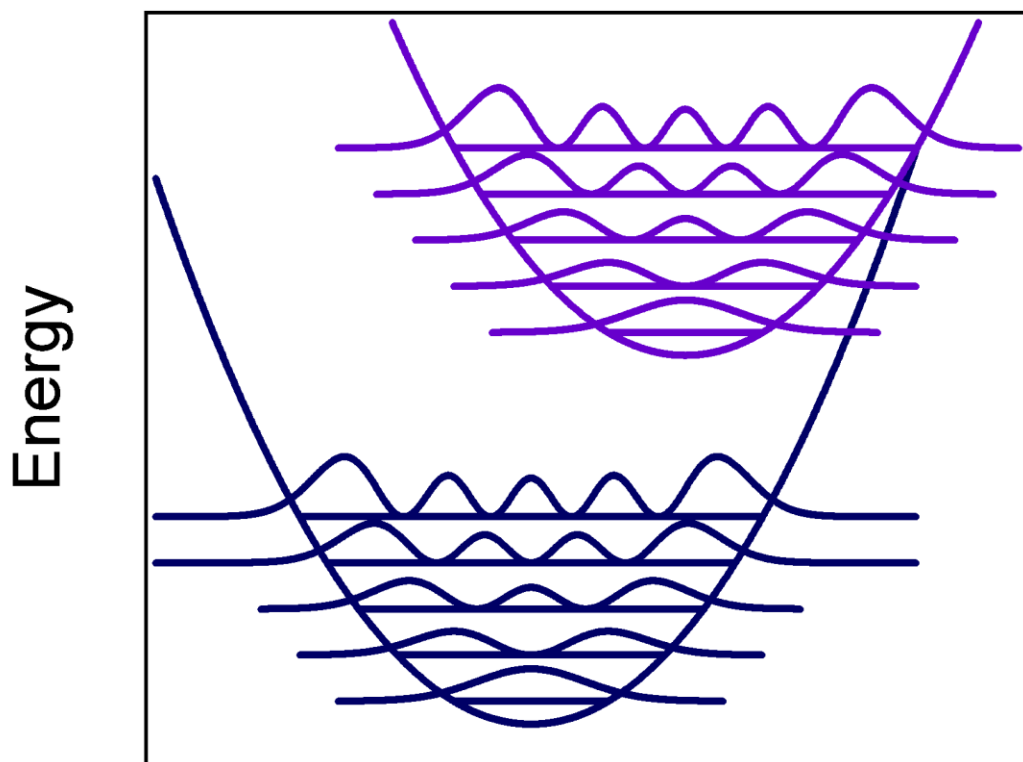
The probability is shown in the figure.

Solutions are Gaussians multiplied by polynomial functions.

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

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

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



Nuclear Displacement

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 vibrational wave functions is key to understanding the shape of absorption bands.

The zero point energy

- The lowest level is $E_0 = 1/2\hbar\omega$
- The lowest vibrational level is not zero in energy.
- This is consistent with the uncertainty principle. If atoms were completely still at absolute zero then we would know both their position and moment to arbitrary accuracy.
- The width of the wavefunction is related to positional uncertainty of an atom.
- We call E_0 the zero point energy.

Polyatomic Molecules

- There are $3N$ total degrees of freedom in a molecule that contains N atoms.
- There are three translational degrees of freedom. These correspond to motion of the center of mass of the molecule.
- In a linear molecule there are two rotational degrees of freedom. In a non-linear molecule there are 3 rotational degrees of freedom.
- The remaining degrees of freedom are vibrational.

There are $3N-6$ vibrational degrees of freedom in a molecule with N atoms

Three degrees of freedom are required for translation.

Three degrees of freedom are required for rotation.

For example, in H_2O there are 9 total degrees of freedom and 3 vibrational degrees of freedom.

In C_6H_6 there are 36 degrees of freedom and 30 vibrational degrees of freedom.

Exception: In linear molecules there are only 2 rotational degrees of freedom and therefore the number of vibrations is $3N - 5$.

The vibrational degrees of freedom can be expressed as normal modes.

All normal modes have the same form for the harmonic oscillator wavefunction and differ only in the force constant k and mass m .

The total wavefunction is a product of normal modes.

The total nuclear wavefunction for water is $\chi_1\chi_2\chi_3$.

The normal mode wavefunctions of water correspond to the symmetric stretch, bend, and asymmetric stretch.

These are linear combinations of the stretching and bending internal coordinates of H_2O .

Normal Modes of Vibration

Polyatomic molecules can be considered as a set of coupled harmonic oscillators. Although this is a classical model we shall see that it can be used to interpret spectra using the quantum-mechanical harmonic oscillator wave functions. The collective motions of the atoms in a molecule are decomposed into normal modes of vibration within the harmonic approximation. The normal modes are mutually orthogonal. That is they represent linearly independent motions of the nuclei about the center-of-mass of the molecule.

Cartesian equations of motion

$$T = \frac{1}{2} \sum_{i=1}^N m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2)$$

$$V = V_0 + \sum_{i=1}^N \left(\left(\frac{\partial V}{\partial x_i} \right) x_i + \left(\frac{\partial V}{\partial y_i} \right) y_i + \left(\frac{\partial V}{\partial z_i} \right) z_i \right) \\ + \sum_{i=1}^N \left(\left(\frac{\partial^2 V}{\partial x_i^2} \right) x_i^2 + \left(\frac{\partial^2 V}{\partial y_i^2} \right) y_i^2 + \left(\frac{\partial^2 V}{\partial z_i^2} \right) z_i^2 \right) \\ + \sum_{i,j=1}^N \left(\left(\frac{\partial V}{\partial x_i \partial y_j} \right) x_i y_j + \left(\frac{\partial V}{\partial y_i \partial z_j} \right) y_i z_j + \left(\frac{\partial V}{\partial z_i \partial x_j} \right) z_i x_j \right)$$

T is the kinetic energy and V is the potential energy expressed as a Taylor's series in x, y and z.

Mass-weighted coordinates

$$T = \frac{1}{2} \sum_{i=1}^{3N} \dot{\eta}_i^2$$

$$V = \frac{1}{2} \sum_{i,j=1}^{3N} a_{ij} \eta_i \eta_j$$

$$\eta_1 = \sqrt{m_1} x_1, \eta_2 = \sqrt{m_1} y_1, \eta_3 = \sqrt{m_1} z_1, \dots, \eta_{3N} = \sqrt{m_N} z_N$$

$$a_{ij} = \left(\frac{\partial V}{\partial \eta_i \partial \eta_j} \right)$$

The equations of motion are:

$$\ddot{\eta}_i + \sum_{j=1}^{3N} a_{ij} \eta_j = 0$$

Solutions

Trial solutions have the form:

$$\eta_i = \eta_i^0 \sin(\sqrt{\lambda} t + \delta)$$

$$\dot{\eta}_i = \sqrt{\lambda} \eta_i^0 \cos(\sqrt{\lambda} t + \delta)$$

$$\ddot{\eta}_i = -\lambda \eta_i^0 \sin(\sqrt{\lambda} t + \delta)$$

These give a linear system of coupled equations:

$$-\lambda \eta_i^0 + \sum_{j=1}^{3N} a_{ij} \eta_j^0 = 0$$

Which is equivalent to the matrix equation:

$$(\mathbf{A} - \lambda \mathbf{I}) \boldsymbol{\eta}^0 = 0$$

\mathbf{A} is the matrix of coefficients. \mathbf{I} is the identity matrix.
 λ are the eigenvalues.

Diagonalization of the matrix

The general form of the matrix equations is

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \dots & \lambda_1 & 0 & 0 \dots \\ a_{21} & a_{22} & a_{23} \dots & 0 & \lambda_2 & 0 \dots \\ a_{31} & a_{32} & a_{33} \dots & 0 & 0 & \lambda_3 \dots \\ \dots & & & \dots & & \dots \end{pmatrix} \begin{pmatrix} \eta_1^0 \\ \eta_2^0 \\ \eta_3^0 \\ \dots \end{pmatrix} = 0$$

There is a trivial solution in which all of the terms in the η^0 column vector are zero. The interesting solution, however, is the solution for which the determinant of the matrix $|A - \lambda I|$ is equal to zero.

$$V = \frac{1}{2} \eta^T \mathbf{A} \eta \qquad V = \frac{1}{2} (\eta_1 \ \eta_2 \ \eta_3 \ \dots) \begin{pmatrix} a_{11} & a_{12} & a_{13} \dots \\ a_{21} & a_{22} & a_{23} \dots \\ a_{31} & a_{32} & a_{33} \dots \\ \dots & & \dots \end{pmatrix} \begin{pmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \\ \dots \end{pmatrix}$$

Definition of normal coordinates

In fact, the procedure of finding $\det |A - \lambda I|$ is a matrix diagonalization of A . To perform this diagonalization we transform to normal coordinates Q_i where:

$$Q_j = \sum_{k=1}^{3N} l_{ki} \eta_k$$

In matrix form $Q = L^T \eta$, which can also be written:

$$\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \\ \vdots \end{pmatrix} = \begin{pmatrix} l_{11} & l_{21} & l_{31} & \dots \\ l_{12} & l_{22} & l_{32} & \dots \\ l_{13} & l_{23} & l_{33} & \dots \\ \dots & & & \dots \end{pmatrix} \begin{pmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \\ \dots \end{pmatrix}$$

The Q are normal coordinates

L is a unitary matrix; its inverse is equal to its transpose $L^{-1} = L^T$. The matrix L will diagonalize A .

$$L^T A L = \Lambda = \begin{pmatrix} \lambda_1 & 0 & 0 & \dots \\ 0 & \lambda_2 & 0 & \dots \\ 0 & 0 & \lambda_3 & \dots \\ \dots & & & \dots \end{pmatrix}$$

Diagonalization of the matrix

The eigenvalues are

$$\sqrt{\lambda_i} = \omega_i = 2\pi\nu_i$$

The kinetic energy is:

$$T = \frac{1}{2} \dot{\mathbf{Q}}^T \mathbf{L}^T \mathbf{L} \dot{\mathbf{Q}} = \frac{1}{2} \dot{\mathbf{Q}}^T \dot{\mathbf{Q}} = \frac{1}{2} \sum_{i=1}^{3N} \dot{Q}_i^2$$

$$V = \frac{1}{2} \mathbf{Q}^T \mathbf{L}^T \mathbf{A} \mathbf{L} \mathbf{Q} = \frac{1}{2} \mathbf{Q}^T \mathbf{\Lambda} \mathbf{Q} = \frac{1}{2} \sum_{i=1}^{3N} \lambda_i Q_i^2$$

The uncoupled equations of motion are now represented by

$$Q_i = Q_i^0 \sin(\sqrt{\lambda_i} t + \delta)$$

These solutions represent collective motions of the nuclei.

Each Q contains simultaneous displacements of many nuclei.

Internal Coordinates

Cartesian coordinates are less convenient than a coordinate system defined in terms of the bonds, angles, etc. of the molecule. Such a coordinate system is called an internal coordinate system. Only motions relative to the center-of-mass are included and thus there are $3N - 6$ internal coordinates for a non-linear polyatomic with N atoms. For linear polyatomic molecules there are $3N - 5$ internal coordinates. The internal coordinates are

Stretch Δr

Bend $\Delta\theta$

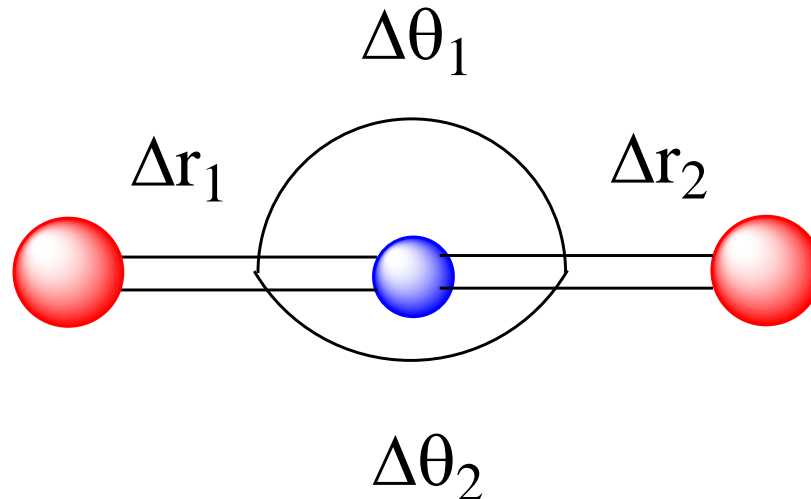
Torsion $\Delta\tau$

Wag $\Delta\omega$

Example: CO₂

For example, for CO₂ we have the following internal coordinates.

$$R = \begin{pmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta \theta_1 \\ \Delta \theta_2 \end{pmatrix}$$



Example: CO₂

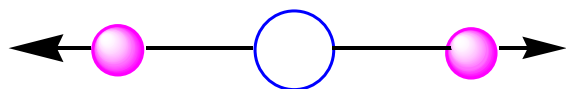
For example, for CO₂ we have the following internal coordinates.

$$V = \frac{1}{2} \left(k_r \Delta r_1^2 + k_r \Delta r_2^2 + k_\theta \Delta \theta_1^2 + k_\theta \Delta \theta_2^2 + k_{r\theta} \Delta r_1 \Delta \theta_1 \right) + \frac{1}{2} \left(k_{r\theta} \Delta r_2 \Delta \theta_1 + k_{r\theta} \Delta r_2 \Delta \theta_2 + k_{r\theta} \Delta r_1 \Delta \theta_2 + k_{rr} \Delta r_1 \Delta r_2 + \dots \right)$$

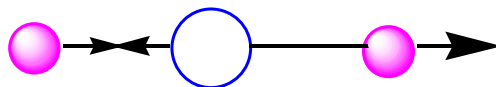
$$2T = \dot{\eta}^T \dot{\eta} = \dot{R}^T (\mathbf{B}\mathbf{B}^T)^{-1} \dot{R} = \dot{R}^T \mathbf{G}^{-1} \dot{R}$$

$$\det(\mathbf{F}\mathbf{G} - \lambda \mathbf{I}) = 0$$

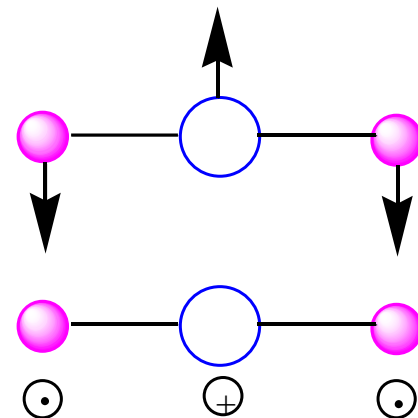
Normal modes - CO₂



Symmetric stretch
 ν_1 2289 cm⁻¹
(Raman active)



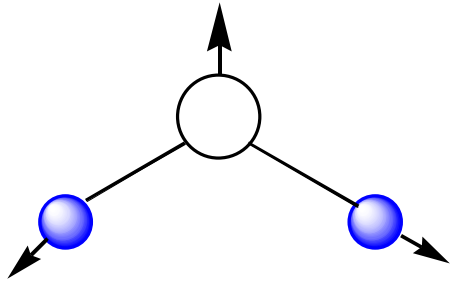
Asymmetric stretch
 ν_3 2349 cm⁻¹
(IR active)



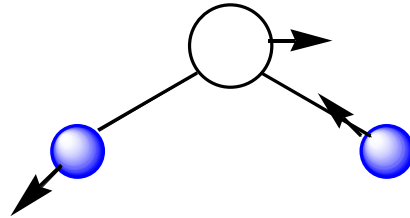
Bends
 ν_2 667 cm⁻¹
(IR active)

There are 4 normal modes ($3N - 5$). Three of them are infrared active since they show a dipole moment change in their motion.

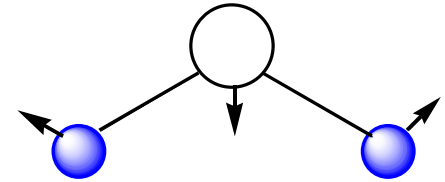
Normal modes - water



Symmetric Stretch
 ν_1 3825 cm^{-1}



Asymmetric Stretch
 ν_3 3935 cm^{-1}



Bend
 ν_2 1654 cm^{-1}

There are 3 normal modes ($3N - 6$). All of them are infrared active since all show a dipole moment change in their motion. The harmonic approximation can be applied to each normal mode.

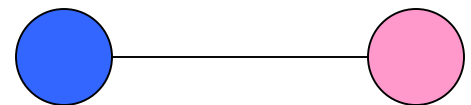
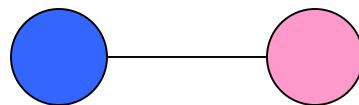
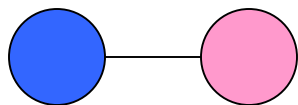
Vibrational Transitions

The Dipole Moment Expansion

The permanent dipole moment of a molecule oscillates about an equilibrium value as the molecule vibrates. Thus, the dipole moment depends on the nuclear coordinate Q .

$$\mu(Q) = \mu_0 + \left(\frac{\partial \mu}{\partial Q} \right) Q + \dots$$

where μ is the dipole operator.

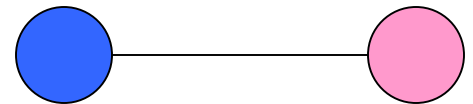
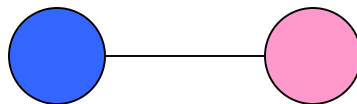
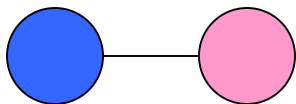


The Dipole Moment Expansion

The permanent dipole moment of a molecule oscillates about an equilibrium value as the molecule vibrates. Thus, the dipole moment depends on the nuclear coordinate Q .

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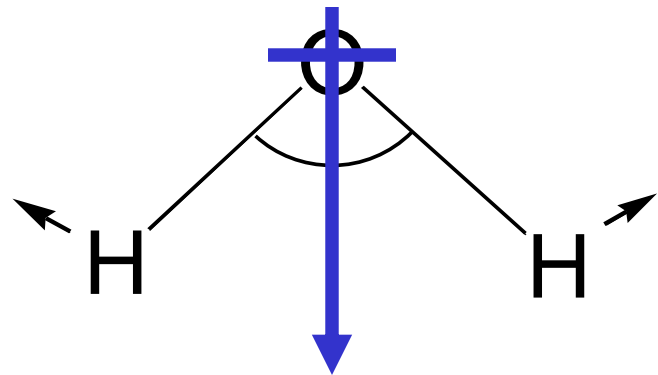
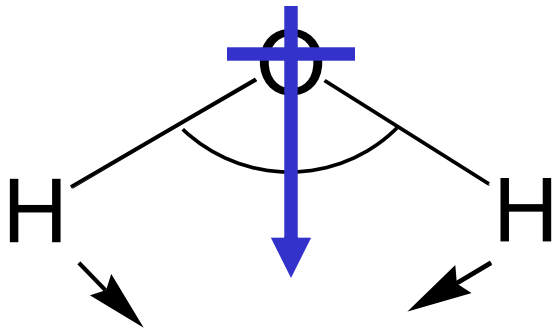
Vibrational transitions

Note that this result is a statement of the vibrational selection rule. Within the harmonic approximation transitions can only occur between states separated by one quantum number ($\Delta v = 1$ or $\Delta v = -1$).

This general rule can be seen by considering integrals of the type shown in the previous slide.

Transition dipoles

In order for infrared light to be absorbed the polarization must be aligned with the direction of the transition moment. For a vibrational mode this is determined by the directional change in the dipole moment. This is shown below for the bending mode of H_2O .



Transition dipoles

The change in ground state dipole moment during vibration interacts with light.

$$\mu = \mu_g + \left(\frac{\partial \mu_g}{\partial Q} \right) Q +$$

The first term is static and does not contribute to the transition. Calling the vibrational wavefunctions χ_i the transition moment is:

$$\mu_{10} = \left(\frac{\partial \mu_g}{\partial Q} \right) \int \chi_1 Q \chi_0 dQ,$$

Dipole derivatives

The vibrational wavefunctions χ_i are Gaussians, thus the transition moment for transition from vibrational state 0 to vibrational state 1 is calculated on the next slide.

The transition dipole moment is proportional to the dipole derivative. This is true for any normal mode of vibration (i.e. harmonic).

Vibrational transitions

Vibrational transitions arise because of the oscillation of the molecule about its equilibrium bond configuration. As the molecule oscillates infrared radiation can interact to alter the quantum state.

$$\mu(Q) = \mu_0 + \left(\frac{\partial \mu}{\partial Q} \right) Q + \dots$$

$$M_{vib} = \left(\frac{\partial \mu}{\partial Q} \right) \int_{-\infty}^{\infty} \chi_{v+1}^* Q \chi_v dQ$$

Mathematical note

Gaussian integrals have the solutions:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

A Gaussian times an odd polynomial has a value of zero over the even limits of $-\infty$ to ∞ .

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} x dx = 0$$

The even polynomials time Gaussians are not zero.

Mathematical note

For example,

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} x^2 dx = \frac{1}{2\alpha} \sqrt{\frac{\pi}{\alpha}}$$

If we multiply any two adjacent vibrational wave functions we obtain an odd function. Therefore, the integral of this product is zero. We call this property orthogonality and we say that the wave functions are orthogonal.

Mathematical note

For example,

$$\int_{-\infty}^{\infty} \chi_0 \chi_1 dQ = 0$$

We can see this by plugging in the wave functions.

$$\left(\frac{\alpha}{\pi}\right)^{1/2} \sqrt{2\alpha} \int_{-\infty}^{\infty} Q \exp\{-\alpha Q^2\} dQ = 0$$

However, if radiation can couple into the Vibrations by the term

$$\left(\frac{\partial \mu}{\partial Q}\right) Q$$

Mathematical note

We have instead that

$$\left(\frac{\partial \mu}{\partial Q}\right) \int_{-\infty}^{\infty} \chi_0 Q \chi_1 dQ = 0 ?$$

We can see this by plugging in the wave functions that

$$\left(\frac{\partial \mu}{\partial Q}\right) \left(\frac{\alpha}{\pi}\right)^{1/2} \sqrt{2\alpha} \int_{-\infty}^{\infty} Q^2 \exp\{-\alpha Q^2\} dQ \neq 0$$

The result is an even function times a Gaussian, which is not zero. Let's investigate.

Vibrational transitions

As an example we can calculate the transition moment between the state $v = 0$ and $v = 1$.

$$\chi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha Q^2/2}, \quad \chi_1 = \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{2\alpha} Q e^{-\alpha Q^2/2}$$

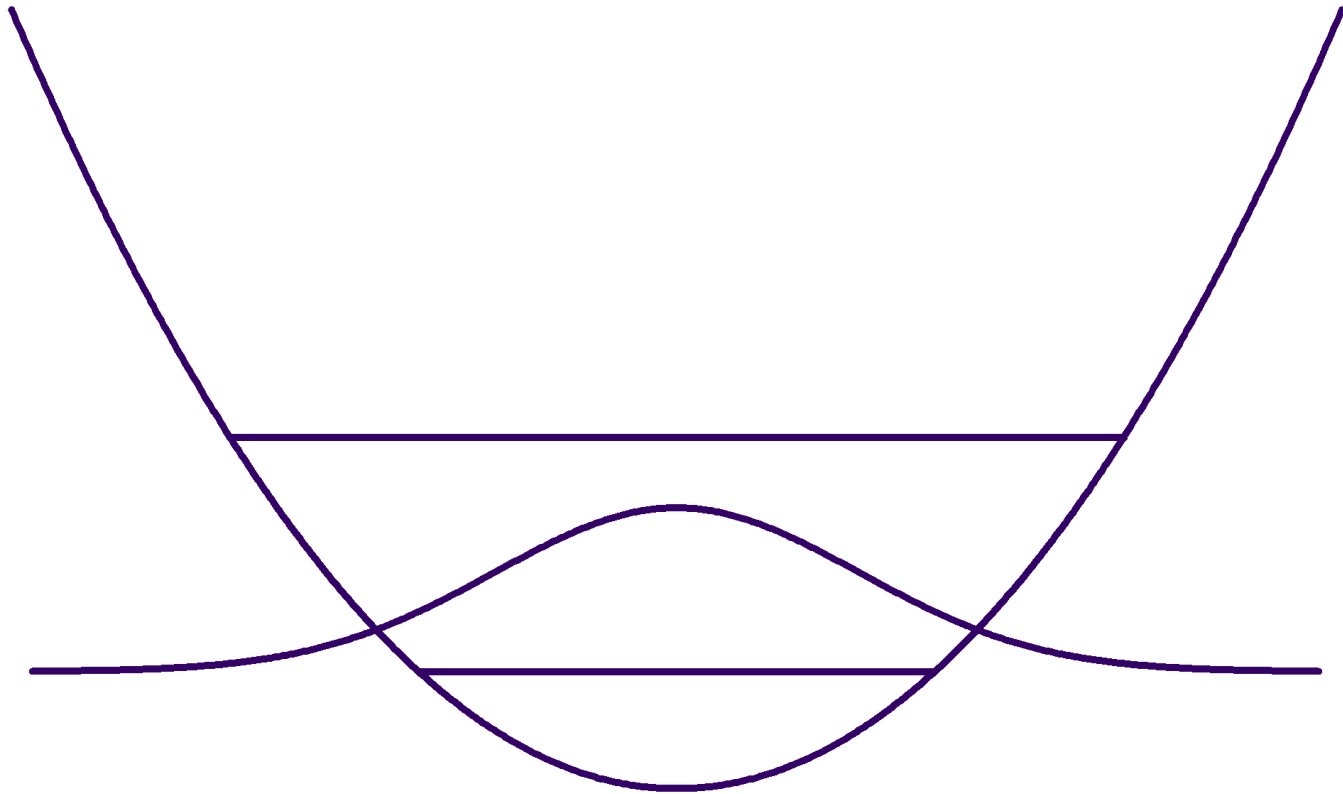
$$\begin{aligned} M_{vib} &= \left(\frac{\partial \mu}{\partial Q}\right) \left(\frac{\alpha}{\pi}\right)^{1/2} \sqrt{2\alpha} \int_{-\infty}^{\infty} e^{-\alpha Q^2/2} Q^2 e^{-\alpha Q^2/2} dQ \\ &= \left(\frac{\partial \mu}{\partial Q}\right) \left(\frac{\alpha}{\pi}\right)^{1/2} \sqrt{2\alpha} \frac{\sqrt{\pi}}{2\alpha^{3/2}} = \left(\frac{\partial \mu}{\partial Q}\right) \frac{1}{\sqrt{2\alpha}} \end{aligned}$$

Vibrational transitions

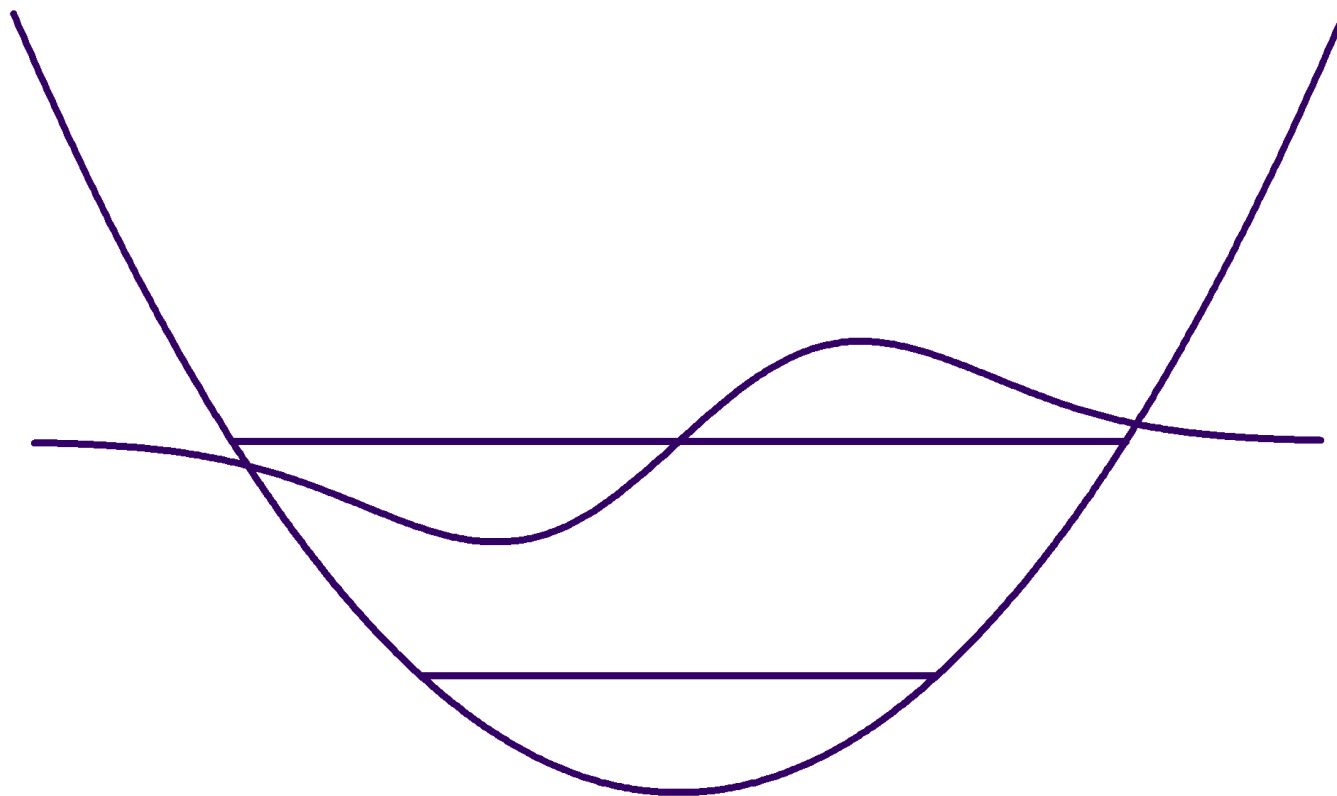
Note that this result is a statement of the vibrational selection rule. Within the harmonic approximation transitions can only occur between states separated by one quantum number ($\Delta v = 1$ or $\Delta v = -1$).

This general rule can be seen by considering integrals of the type shown in the previous slide.

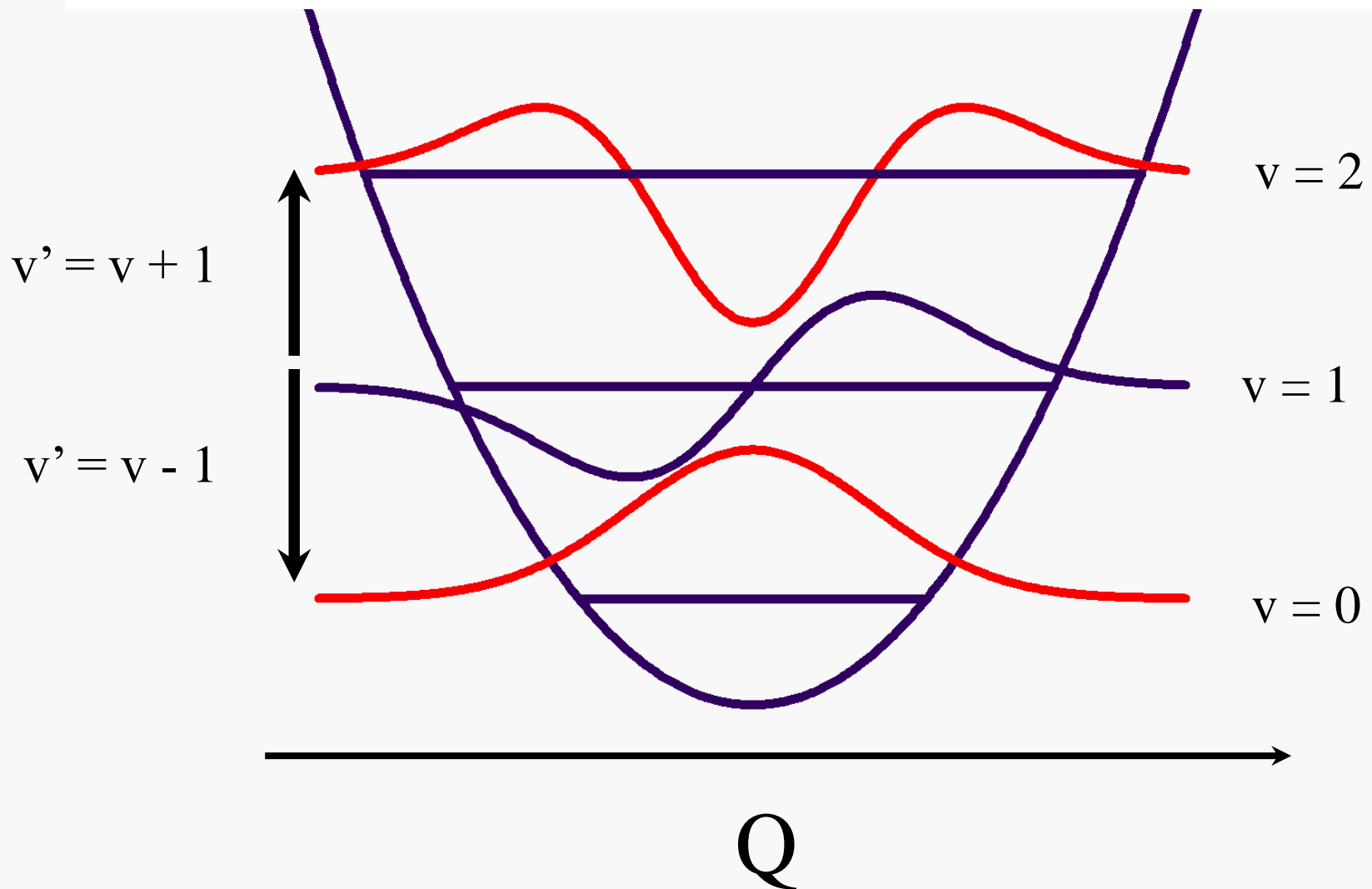
Vibrational Transition



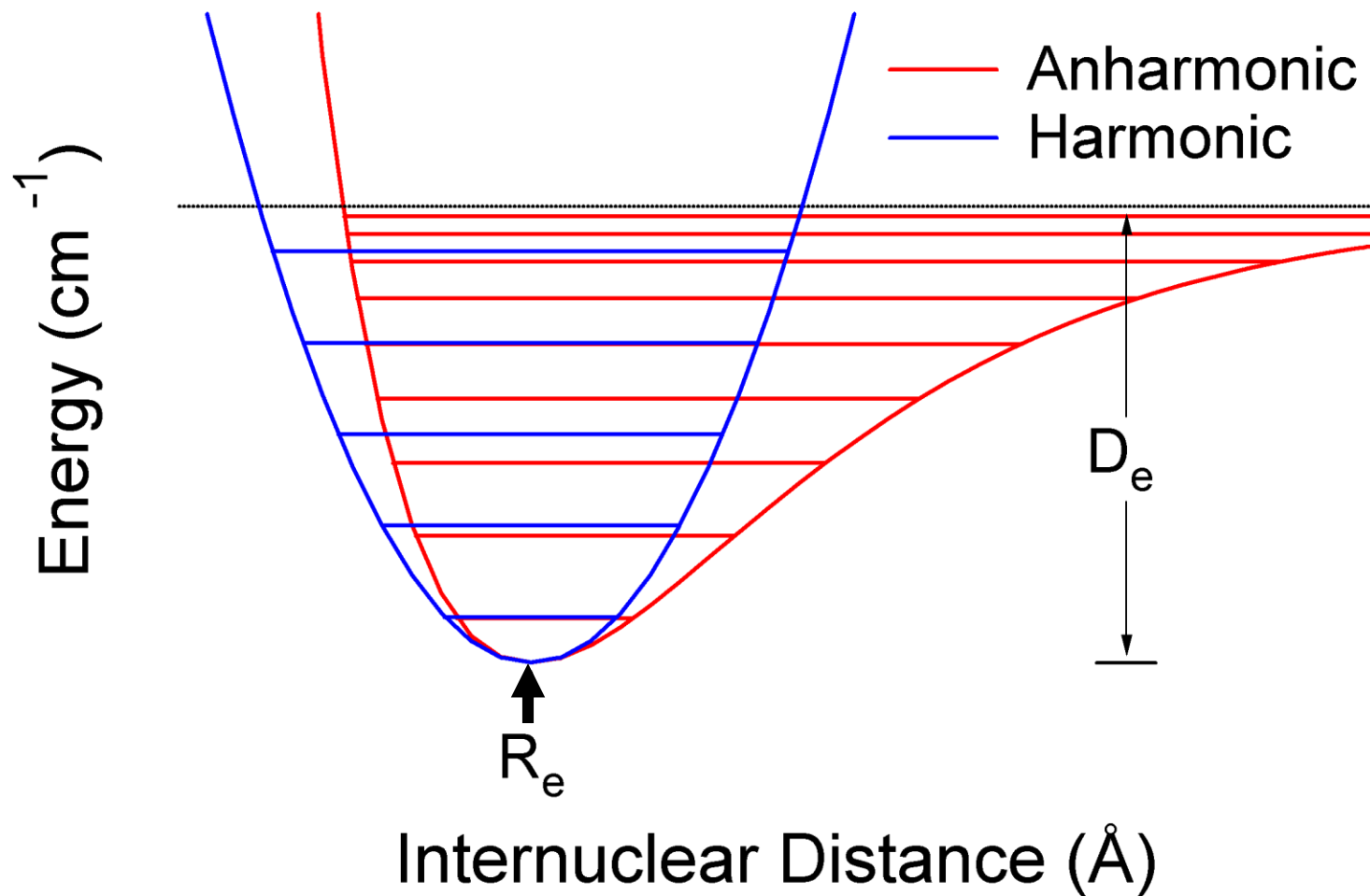
Vibrational Transition



Vibrational Selection Rule



Comparison of harmonic and anharmonic potentials



Overtone of water

Even in water vapor

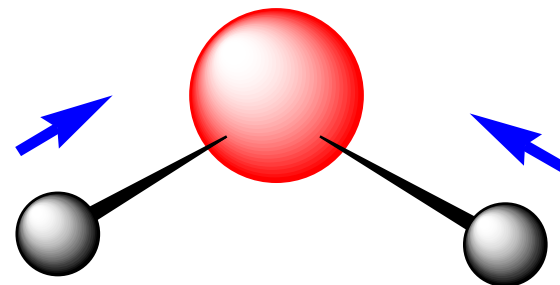
$\nu_1 \approx \nu_3$, but symmetries are different, $\Gamma_1 \neq \Gamma_3$.

However, the third overtone of mode 1 has the same symmetry as the combination band

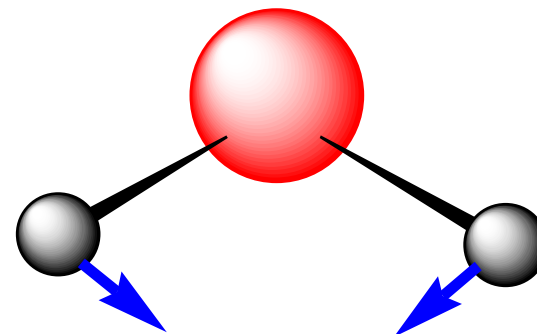
$$\Gamma_1 \Gamma_1 \Gamma_1 = \Gamma_1 \Gamma_3 \Gamma_3.$$

Strong anharmonic coupling leads to strong overtones at 11,032 and 10,613 cm^{-1} .

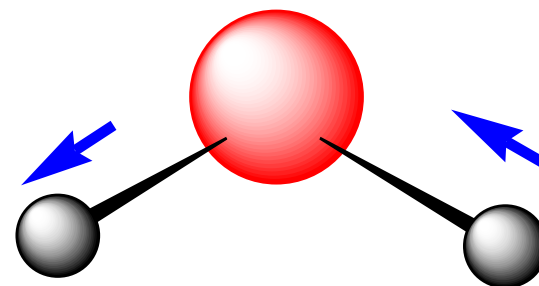
These intense bands give water and ice their blue color.



ν_1 symmetric stretch 3825 cm^{-1}



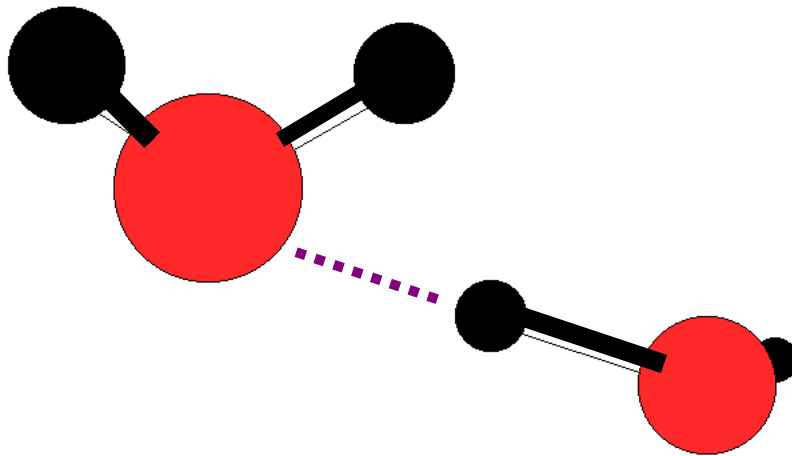
ν_2 bend 1654 cm^{-1}



ν_3 asymmetric stretch 3935 cm^{-1}

Frequency shift due to molecular interactions

Hydrogen bonding lowers O-H force constant and H-O-H bending force constant.



| | vapor | → | liquid |
|---------|-------|---|--------|
| ν_1 | 3825 | → | 3657 |
| ν_2 | 1654 | → | 1595 |
| ν_3 | 3935 | → | 3756 |