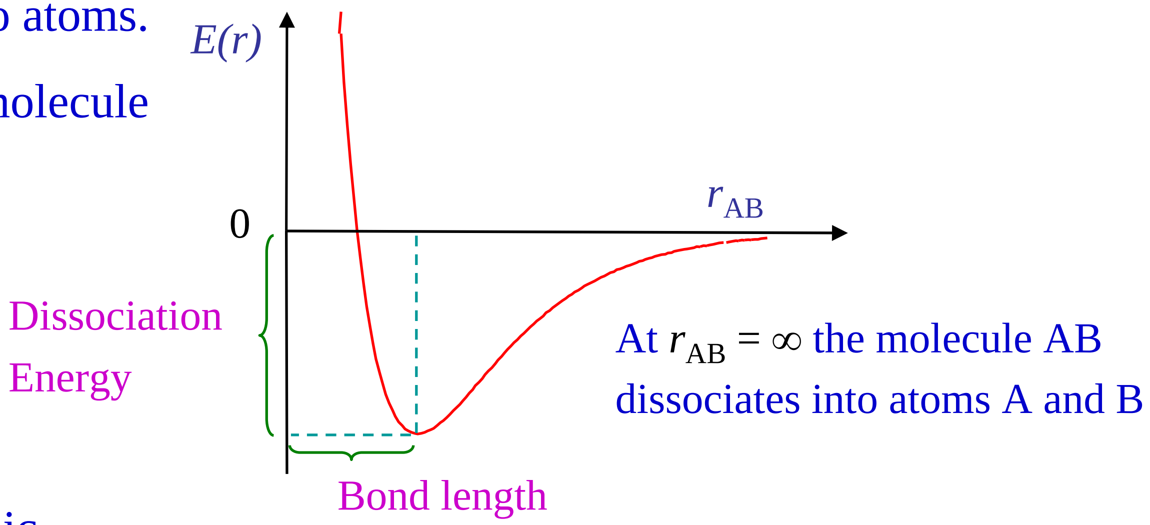
Molecular Vibrations

In general, the vibrations of a polyatomic molecule involve motion of *all* nuclei about the molecule’s centre of mass.

In some cases the normal modes of vibration can be approximated by motion of individual pairs of nuclei, which can be treated as if they are diatomic molecules.

To solve the Schrödinger Equation we need to know the potential energy for the interaction between the two atoms.

The energy of a diatomic molecule varies with bond length:



At $r_{AB} = \infty$ the molecule AB dissociates into atoms A and B

Near the minimum
the curve is roughly parabolic,
so bond vibrations are often treated as if harmonic.

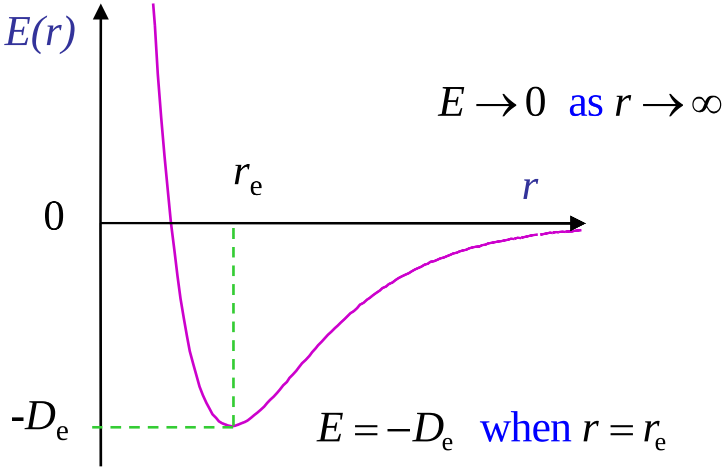
The asymmetric distortion from the parabola is called anharmonicity.

The Morse Potential

$$E = D_e\left[1-e^{-a(r-r_e)}\right]^2 - D_e$$

$$= D_e\left[1-2e^{-a(r-r_e)}+e^{-2a(r-r_e)}\right]-D_e$$

$$= D_e\left[e^{-2a(r-r_e)}-2e^{-a(r-r_e)}\right]$$



$E \to 0$ as $r \to \infty$

$E = -D_e$ when $r = r_e$

Note that for small extensions $(r - r_e)$

$$\left[1-e^{-a(r-r_e)}\right]^2 = \left[1-1+a(r-r_e)\right]^2 = a^2(r-r_e)^2$$

Compare this with the potential energy of a Simple Harmonic Oscillator $V(x) = \tfrac{1}{2}kx^2$

whose force constant $k = \left[\dfrac{d^2V}{dx^2}\right]_{x=0} \equiv \left[\dfrac{d^2E}{dr^2}\right]_{r=r_e} = 2a^2D_e$

The Morse potential is empirical. It has the correct properties to *model* vibrational potential. It does not represent any theory.

The Simple Harmonic Oscillator

A harmonic oscillator has a restoring force proportional to the deviation from equilibrium: $F = k\,x$ k is the force constant

Examples: simple pendulum, vibrating spring, bond vibration.

$$\hat{\mathrm{H}} = -\frac{\hbar^2}{2\mu}\nabla^2 + V = -\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \tfrac{1}{2}k\,x^2 \qquad \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{2\mu}{\hbar^2}\left[E - \tfrac{1}{2}k\,x^2\right]\psi = 0 \qquad \mu = \frac{M_\mathrm{A}M_\mathrm{B}}{M_\mathrm{A}+M_\mathrm{B}}$$

Let $\omega_0 = \sqrt{\frac{k}{\mu}}$, $\lambda = \frac{2E}{\hbar\omega_0}$, $y = \sqrt{\frac{\mu\omega_0}{\hbar}}\cdot x$ then $\frac{\mathrm{d}^2}{\mathrm{d}y^2}\psi(y) + \left[\lambda - y^2\right]\psi(y) = 0$

The general solution is $\psi_n = c_n H_n(y) e^{-½ y^2}$

where the H_n are solutions of Hermite's Equation:

$$\frac{\mathrm{d}^2}{\mathrm{d}y^2}H_n(y) - 2y\frac{\mathrm{d}}{\mathrm{d}y}H_n(y) + (\lambda-1)y = 0$$

where $\lambda - 1 = 2n,$

$n = 0, 1, 2, \ldots$

$H_0 = 1$

$H_1 = 2y$

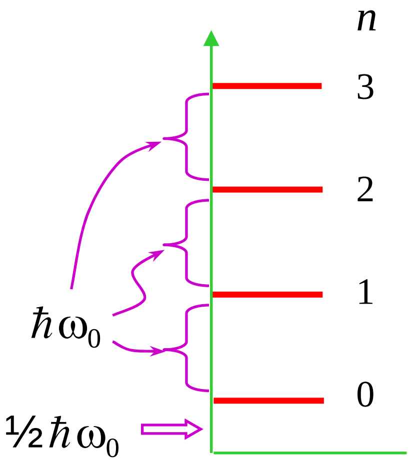
$H_2 = 4y^2 - 2$

$H_3 = 8y^3 - 12y$

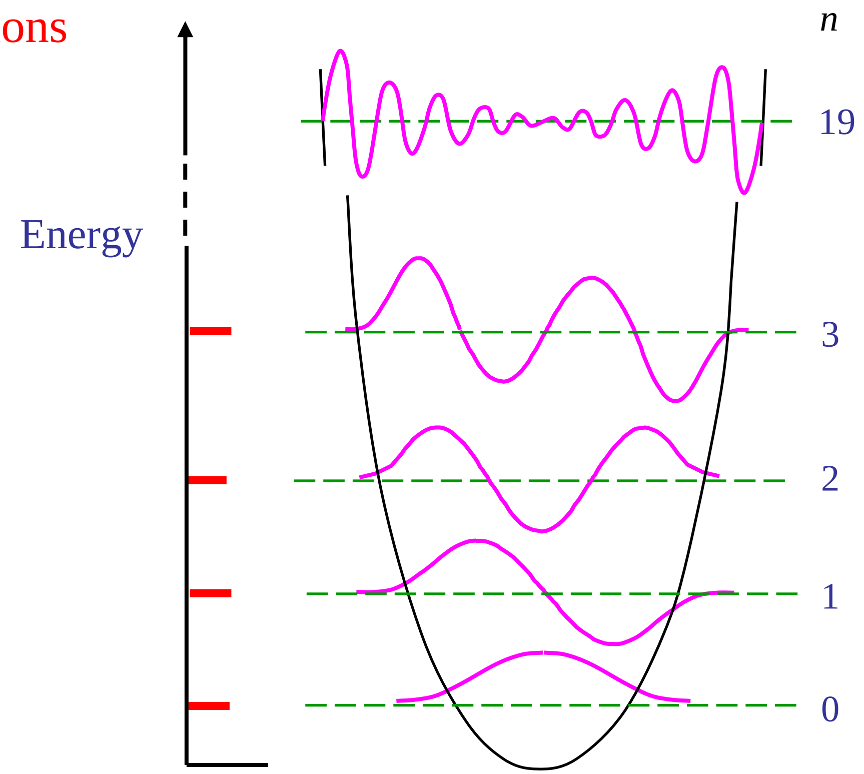
Simple Harmonic Oscillator – 2

Eigenvalues $E_n = (n + \tfrac{1}{2})\hbar\omega_0$

- The energy levels are equally spaced
- There is zero-point energy.



Eigenfunctions



Note the similarity to the particle in a box wavefunctions.

A new feature is the penetration of the potential at low n.

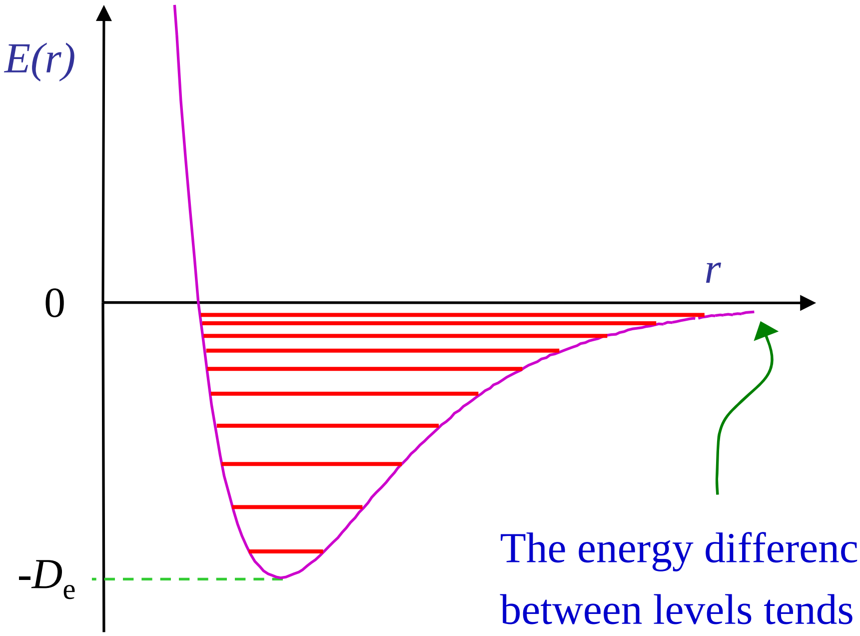
The Anharmonic Oscillator – 1

If the Schrödinger Equation is solved for the Morse potential the vibrational energy levels converge as the quantum number rises:

$$E_n = (n+½)\hbar\omega_\mathrm{e} - (n+½)^2 x_\mathrm{e}\hbar\omega_\mathrm{e} - D_\mathrm{e}$$

where the anharmonicity constant

$$x_\mathrm{e} = \frac{a^2\hbar}{2\mu\omega_\mathrm{e}}$$



The energy difference between levels tends to zero for large *r*.

Vibrational Spectra of Diatomic Molecules

Selection rules

- The vibration must *change* the dipole moment.
  Therefore, only *hetero*diatomics have IR spectra.
- $\Delta n = \pm 1$
  In a harmonic system this would give only one transition frequency: $\Delta E = \hbar\omega = h\nu$
  For anharmonic systems $\Delta E = h\upsilon = \hbar\omega[1 - 2x_e(n+1)]$
- The $\Delta n = \pm 1$ selection rule is relaxed in anharmonic systems;
  $\Delta n = \pm 2, \pm 3, \ldots$ are "partially" allowed.
  $\nu(0 \rightarrow 1)$ is called the fundamental.
  $\nu(0 \rightarrow 2)$ and $\nu(0 \rightarrow 3)$ are the first and second overtones.

Intensities

For typical molecules at room temperature $\Delta E_{\mathrm{vib}} \gtrsim 10 k_B T$ so most molecules are in the lowest vibrational state, and give a single strong fundamental absorption frequency. Overtone frequencies are much weaker.

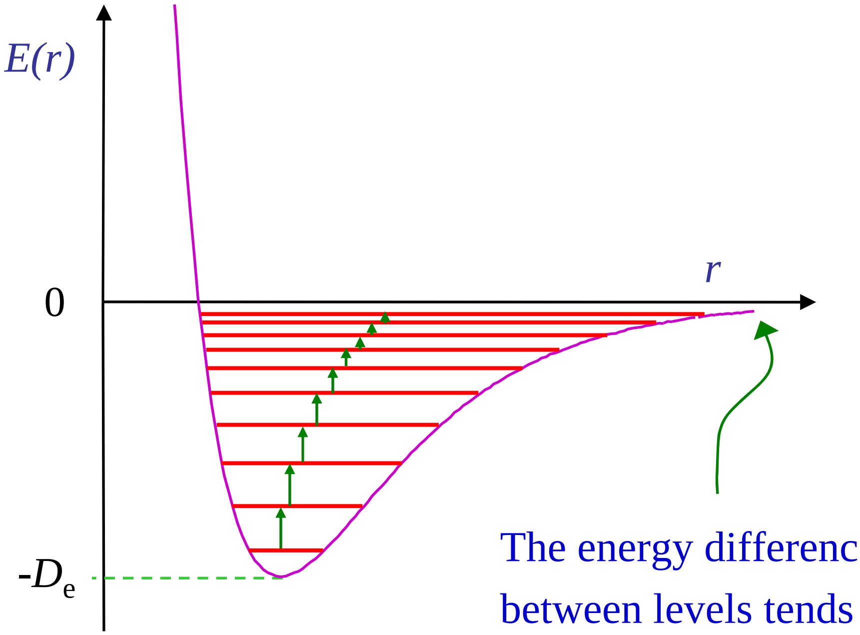
The Anharmonic Oscillator – 2

If the Schrödinger Equation is solved for the Morse potential the vibrational energy levels converge as the quantum number rises:

$$E_n = (n+½)\hbar\omega_e - (n+½)^2 x_e \hbar\omega_e - D_e$$

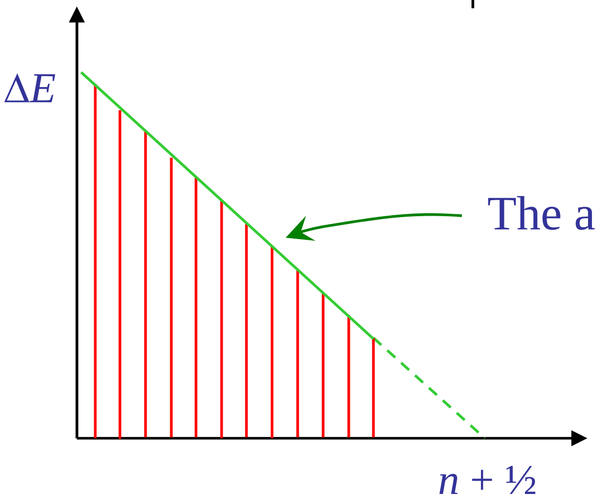
where the anharmonicity constant

$$x_e = \frac{a^2\hbar}{2\mu\omega_e}$$



The energy difference between levels tends to zero for large *r*.

Birge-Sponer plot



The area under this plot is

$$\sum_n \{E_{n+1} - E_n\} = D_e$$

Rotation-Vibration Spectra of Diatomics

$$\Psi_{\text{intra}} = \Psi_{\text{vib}}\Psi_{\text{rot}}$$

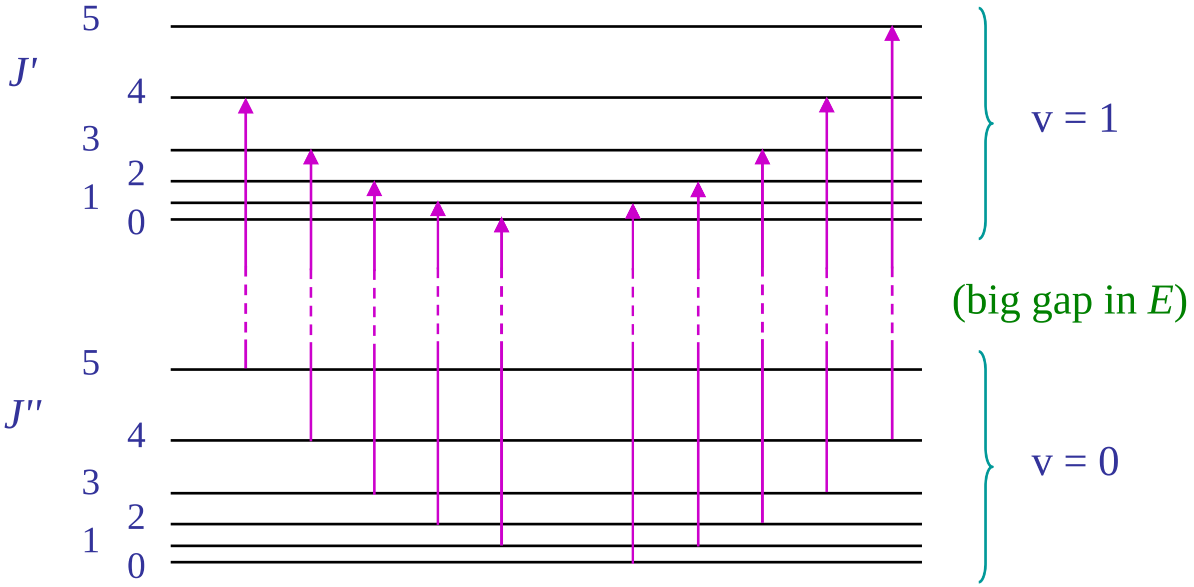
$$E_{\text{internal}} = E_{\text{vib}} + E_{\text{rot}}$$

$$E(\text{v},J) = (\text{v}+\tfrac{1}{2})\hbar\omega + BJ(J+1)$$

$$\Delta E = \Delta E_{\text{vib}} + \Delta E_{\text{rot}}$$

$$\text{v} = 0 \rightarrow 1 \qquad \Delta J = \pm 1$$

Energy levels



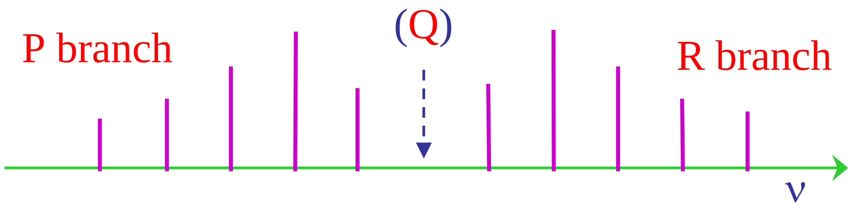
$\Delta J = -1$

$$\Delta E = \hbar\omega + B[(J-1)J - J(J+1)]$$
$$= \hbar\omega - 2BJ \qquad J = 1, 2, 3, \ldots$$

$\Delta J = +1$

$$\Delta E = \hbar\omega + B[(J+1)(J+2) - J(J+1)]$$
$$= \hbar\omega + 2B(J+1) \qquad J = 0, 1, 2, \ldots$$

Spectrum



Normal Modes

In general, the nuclei of a vibrating polyatomic molecule undergo complex movement about their equilibrium positions; but it is always possible to decompose this motion into a sum of vibrations – normal modes – for which the deviations are in phase.

Potential energy: $V = \frac{1}{2}\sum_{i\,j} k_{ij}\xi_i\xi_j$ $\xi =$ deviation from equilibrium

Generalized Force Constant: $k_{ij} = \left[\frac{\partial^2 V}{\partial\xi_i\partial\xi_j}\right]_0$

Evaluated at the equilibrium position

i and j both range from 1 to 3N.

Normal Coordinates are defined as the linear combinations

$$Q_i = \sum_k c_{ik} q_k = \sum_k c_{ik} m_k^{1/2} \xi_k$$

q = mass-weighted coordinate

such that $V = \frac{1}{2}\sum_i K_i Q_i^2 = \sum_i V_i$ and $T = \frac{1}{2}\sum_i m_i \dot{\xi}_i^2 = \frac{1}{2}\sum_i \dot{Q}_i^2$

i.e. the potential energy is diagonal just like the kinetic energy.

This general treatment applies to all 3N degrees of freedom,
but 3 of these are translational, 3 are rotational (2 for linear molecules).

Thus 3N-6 displacements correspond to vibrations (3N-5 for linear molecules).

Vibrational Spectra of Polyatomics

Once the complex vibrational motion of a molecule has been decomposed into normal modes the vibrational frequencies, zero-point energies, etc. associated with each mode can be treated to a good approximation as independent of each other.

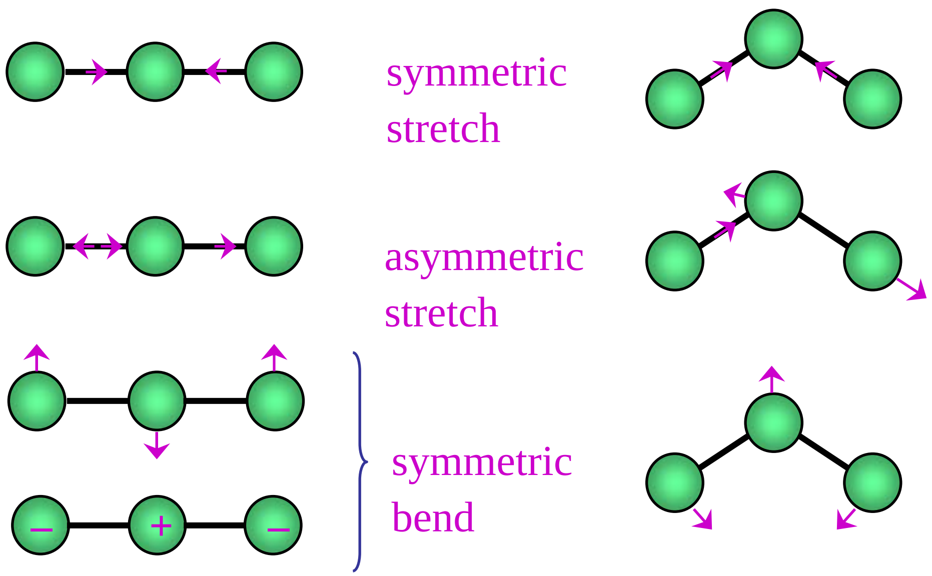
$$\hat{\mathrm{H}} = \sum_i \hat{\mathrm{H}}_i = \tfrac{1}{2}\sum_i \left\{ -\hbar^2 \frac{\partial^2}{\partial Q_i^2} + K_i Q_i^2 \right\} \qquad \Psi = \prod_{i=1}^{3N-6} \psi_i(Q_i) \qquad \hat{\mathrm{H}}_i\,\psi_i = E_i \psi_i$$

Each mode can be treated as a harmonic oscillator.

$$E = \sum_i \hbar\omega_i(\mathrm{v_i} + ½) \qquad \Delta E = \hbar\omega_i$$

Electric dipole transitions are only allowed for modes in which the dipole moment changes. Such modes are called IR active.

Normal modes for triatomic molecules



symmetric stretch

asymmetric stretch

symmetric bend