

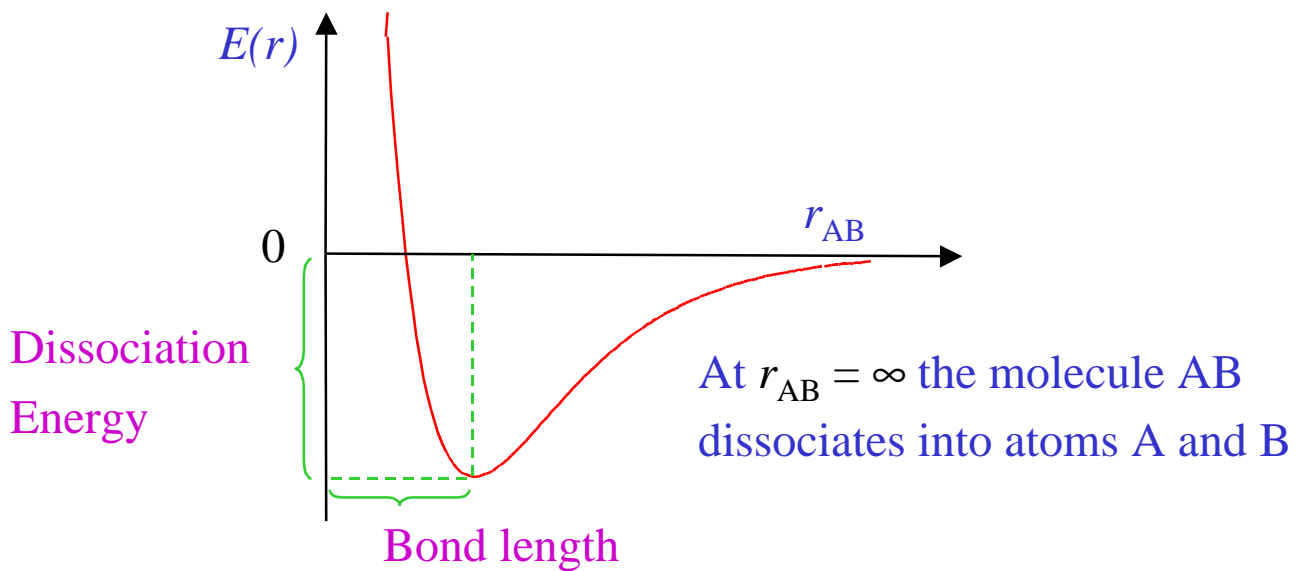
Molecular Vibrations

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:

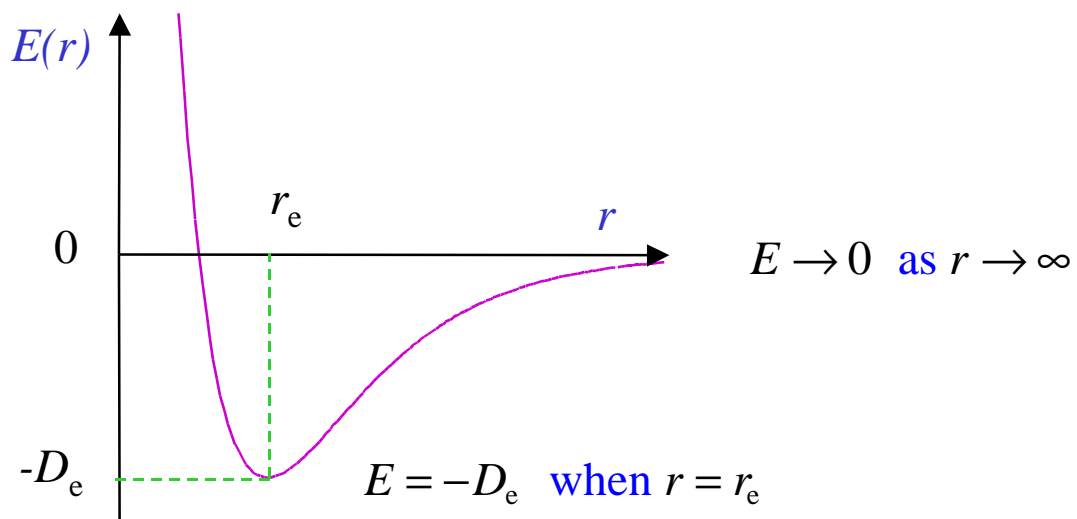


Near the minimum the curve is roughly parabolic, so bond vibrations are often treated as if **harmonic**.

The asymmetric distortion from the parabola is called **anharmonicity**.

The Morse Potential

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



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 $V(x) = \frac{1}{2}kx^2$

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

The Simple Harmonic Oscillator

A harmonic oscillator has a restoring force proportional to the deviation from equilibrium: $F = -kx$ k is the force constant.
Examples: simple pendulum, vibrating spring, bond vibration.

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 + V \qquad \mu = \frac{M_A M_B}{M_A + M_B}$$
$$= -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} k x^2$$

$$\frac{d^2 \psi}{dx^2} + \frac{2\mu}{\hbar^2} \left[E - \frac{1}{2} k x^2 \right] \psi = 0$$

Let $\omega_0 = \sqrt{\frac{k}{\mu}}$, $\lambda = \frac{2E}{\hbar\omega_0}$, $y = \sqrt{\frac{\mu\omega_0}{\hbar}} \cdot x$

then $\frac{d^2}{dy^2} \psi(y) + [\lambda - y^2] \psi(y) = 0$

The general solution is $\psi_n = c_n H_n(y) e^{-\frac{1}{2}y^2}$

where the H_n are solutions of Hermite's Equation:

$$\frac{d^2}{dy^2} H_n(y) - 2y \frac{d}{dy} H_n(y) + (\lambda - 1) H_n(y) = 0 \qquad \text{where } \lambda - 1 = 2n,$$
$$n = 0, 1, 2, \dots$$

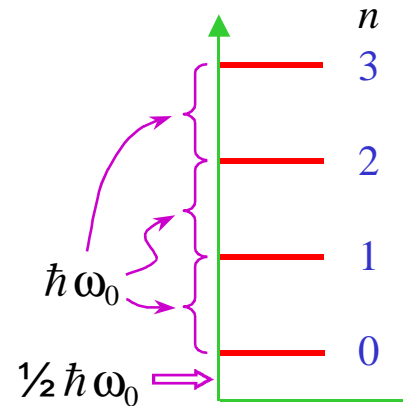
$$H_0 = 1 \qquad H_1 = 2y \qquad H_2 = 4y^2 - 2 \qquad H_3 = 8y^3 - 12y$$

Simple Harmonic Oscillator – 2

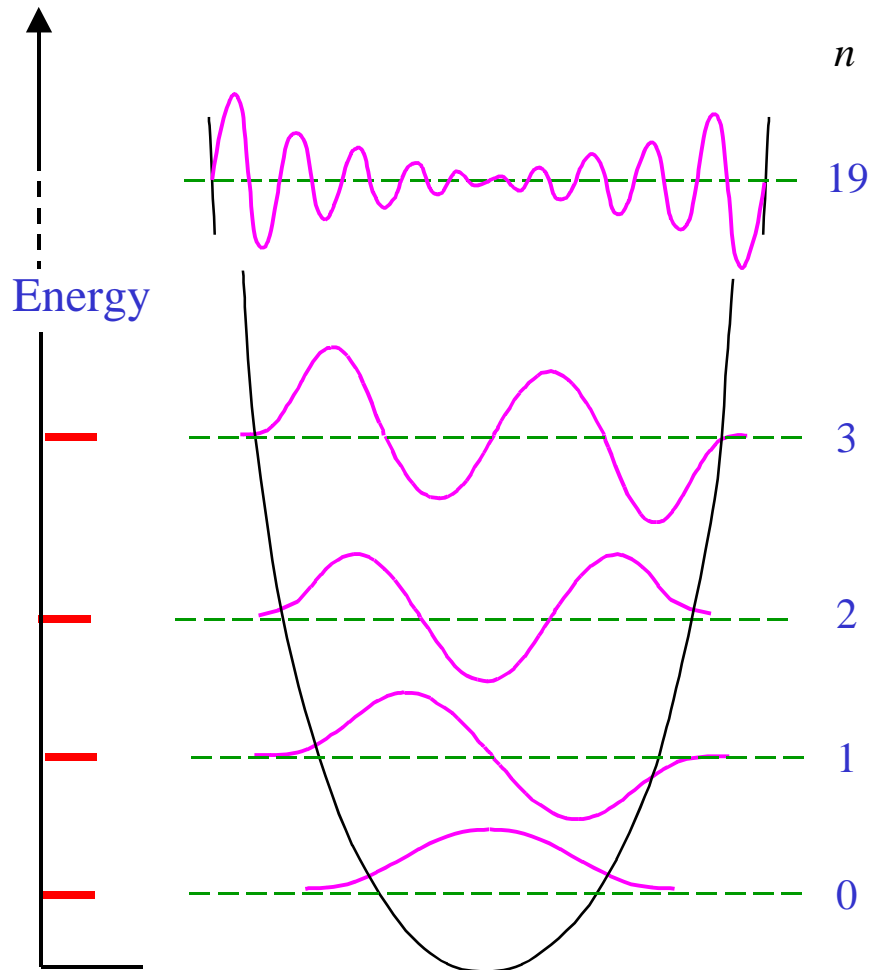
Eigenvalues

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

- The energy levels are equally spaced by $\hbar \omega_0$
- There is a zero-point energy of $\frac{1}{2} \hbar \omega_0$



Eigenfunctions



Note the similarity to the particle in a box wavefunctions.

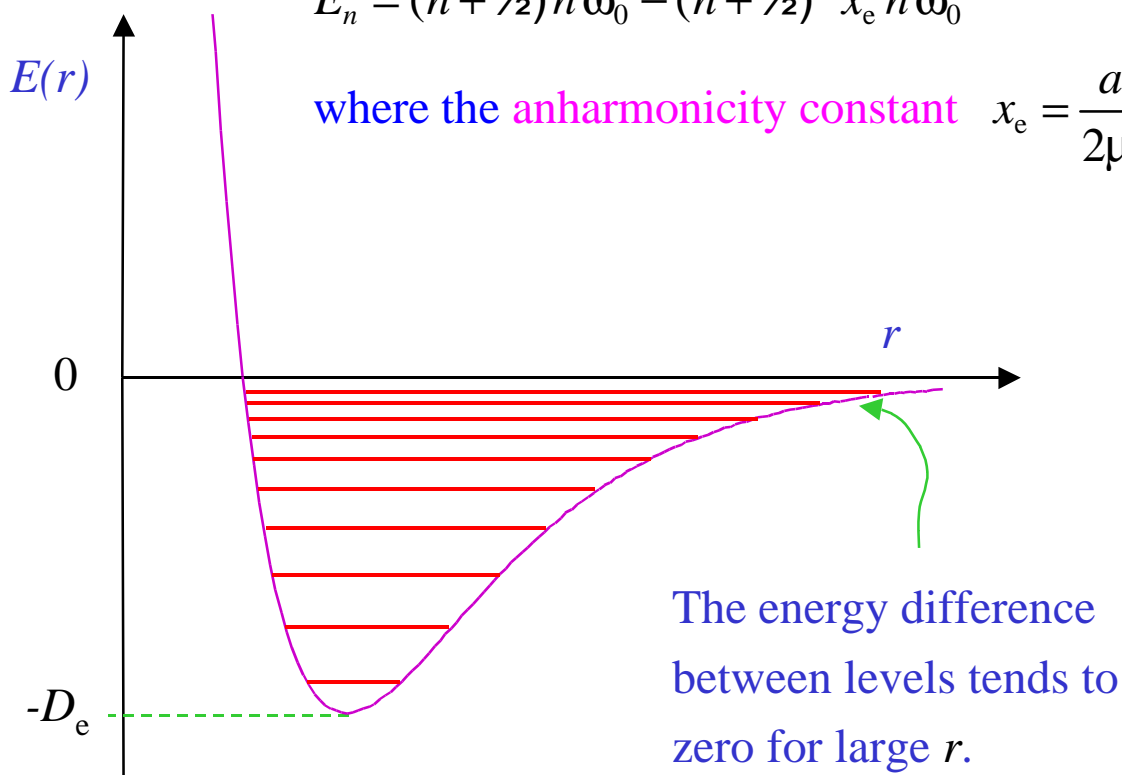
A new feature is the **penetration** of the potential at low n .

The Anharmonic Oscillator

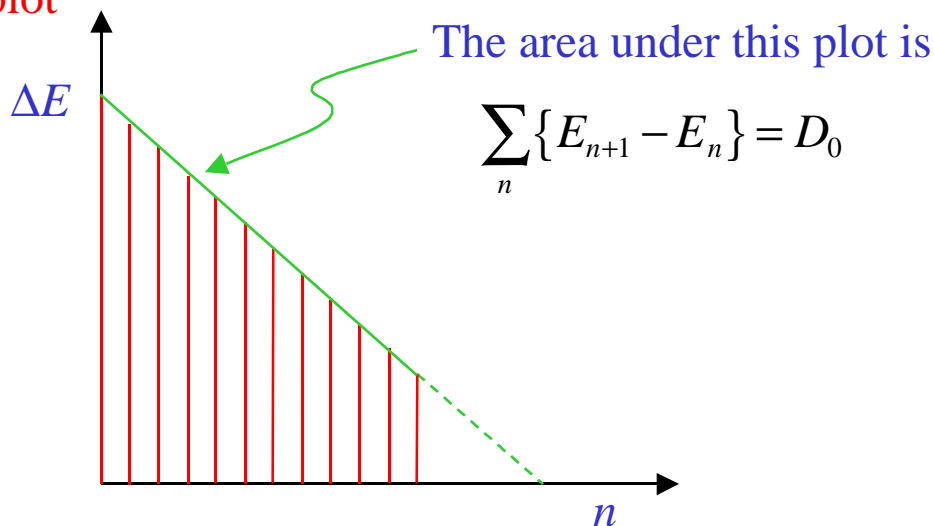
If the Schrödinger Equation is solved for the Morse potential the vibrational energy levels **converge** as the quantum number rises:

$$E_n = (n + 1/2)\hbar\omega_0 - (n + 1/2)^2 x_e \hbar\omega_0$$

where the **anharmonicity constant** $x_e = \frac{a^2\hbar}{2\mu\omega_e}$



Birge-Sponer plot



Vibrational Spectra of Diatomic Molecules

Selection rules

- The vibration must *change* the dipole moment.
Therefore, only *heterodiatomics* 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 $\Delta E = h\nu = \hbar\omega[1 - 2x_e(n + 1)]$

- The $\Delta n = \pm 1$ selection rule is relaxed in anharmonic systems; $\Delta n = \pm 2, \pm 3, \dots$ 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 $\Delta E_{\text{vib}} \geq 10k_{\text{B}}T$

so most molecules are in the lowest vibrational state,

and give a single strong fundamental absorption frequency.

Overtone frequencies are much weaker.

Rotation-Vibration Spectra of Diatomics

If intramolecular motion is treated as separable,

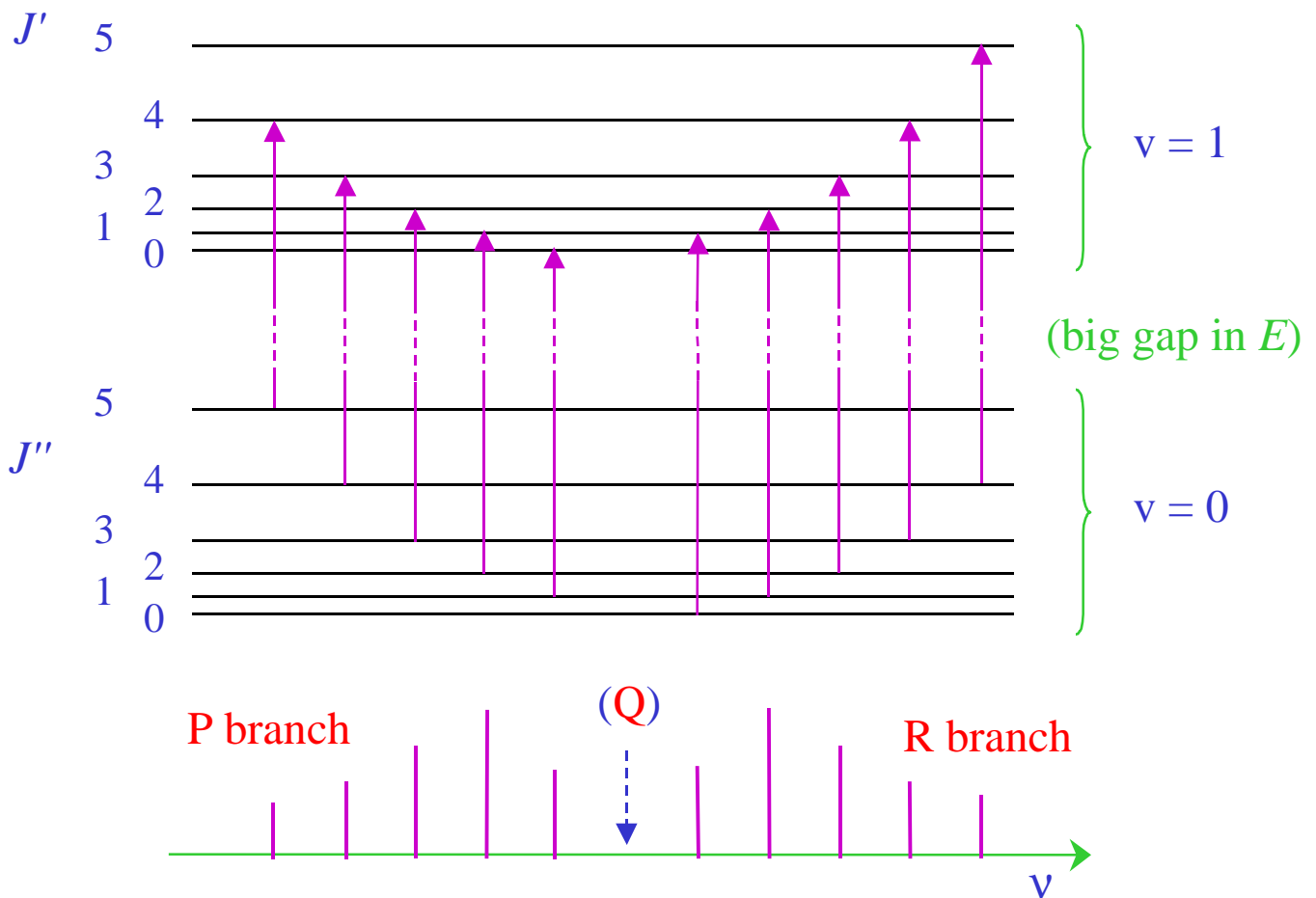
$$\Psi_{\text{intra}} = \Psi_{\text{vib}} \Psi_{\text{rot}} \quad E_{\text{internal}} = E_{\text{vib}} + E_{\text{rot}}$$

$$E(v, J) = (v + 1/2)\hbar\omega + BJ(J + 1)$$

Transitions $\Delta E = \Delta E_{\text{vib}} + \Delta E_{\text{rot}}$
 $v = 0 \rightarrow 1 \quad \Delta J = \pm 1$

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

R $\Delta J = +1 \quad \Delta E = \hbar\omega + B[(J + 1)(J + 2) - J(J + 1)]$
 $= \hbar\omega + 2B(J + 1) \quad J = 0, 1, 2, \dots$



Bracket Notation

Dirac proposed the bra-ket notation:

$$\langle \text{bra} | \text{c} | \text{ket} \rangle$$

$$|n\rangle = \text{ket} \equiv \psi_n$$

$$\langle m| = \text{bra} \equiv \psi_m^*$$

$$\langle m|n\rangle \equiv \int \psi_m^* \psi_n d\tau$$

$$\langle m|\hat{\Omega}|n\rangle \equiv \int \psi_m^* \hat{\Omega} \psi_n d\tau$$

Kets may be interpreted as vectors in Hilbert space.

Operators behave like matrices.

$\Omega_{mn} \equiv \langle m|\hat{\Omega}|n\rangle$ can be regarded as a matrix element.

Heisenberg developed a formulation of quantum mechanics using the language of matrix algebra.

Commutator Notation

Commutator $[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$