The separability implied by the Born-Oppenheimer (BO) wavefunction says that the electrons instantly adjust their state to the nuclear zero point motions.

The BO wavefunction is exactly true **only** if:

$$\nabla_\alpha^2 \Psi_{el,n}(q;Q_\alpha)\Phi(Q_\alpha) = \Psi_{el,n}(q;Q_\alpha)\nabla_\alpha^2 \Phi(Q_\alpha)$$

This is not quite true because $\nabla_\alpha^2 \Psi_{el,n}(q;Q_\alpha) \neq 0$

due to the atomic orbitals effectively floating along with the nuclear positions. The effect is, however, small most of the time.

The effect of the 2nd derivative on the electronic function with respect to nuclear positions is called *"Born-Oppenheimer breakdown"*, and
is responsible for excited state radiationless transitions such as the conversion of electron energy into nuclear kinetic energy (heat). (for example, internal conversion)

The Born-Oppenheimer wavefunction:

$$\Psi_{BO} = \Psi_{el,n}(q; Q_\alpha) \Phi_N(Q_\alpha)$$

says that **the electrons instantly adjust their state to the nuclear positions.**

It is interesting to view the Born-Oppenheimer wavefunction as a kind of linear combination of the $\Psi_{el}(q_i; Q_\alpha)$. A wavefunction can be thought of as a big vector of numbers, one for each point in space.

The B-O wavefunction has the amplitude for the electrons being at points in space when the nuclei are at Q_α multiplied by $\Phi_N(Q_\alpha)$, the amplitude for the nuclei to be at the points Q_α.

The probability density is therefore:
(probability density for a certain nuclear configuration) x *(probability density for the electrons when the nuclei are at that nuclear configuration)*

Matrix Elements Between B-O Vibronic States.

State functions of the B-O type are often called *vibronic* **states, because they describe both electronic and vibrational coordinates**
  We will want to know how to find matrix elements of the Hamiltonian that couple different molecular states because we shall see that:

1)perturbations such as vibrations can bring intensity into "forbidden transitions"
2)the **rate of transition** between states m and n is proportional to $|\mathbf{H_{mn}}|^2$

Consider a matrix element of the Hamiltonian (but it could be any other operator) coupling two B-O states m and n,

$$\mathbf{H_{mn}} = <\Psi_{el,m}(\mathbf{q_i};Q_\alpha)\,\Phi_{N,m}\,(Q_\alpha)\,|\,H\,|\,\Psi_{el,n}(\mathbf{q_i};Q_\alpha)\,\Phi_{N,n}(Q_\alpha)>$$

Since H= H(q_i,Q_α), and Ψ_N depends only on Q_α, we integrate first only over $\mathbf{q_i}$

$$H_{mn}(Q_\alpha)\quad = <\Phi_{N,m}\,(Q_\alpha)|\,<\Psi_{el,m}(\mathbf{q_i};Q_\alpha)|H|\,\Psi_{el,n}(\mathbf{q_i};Q_\alpha)>_{\mathbf{qi}}\quad|\Phi_{N,n}(Q_\alpha)>,$$

where the subscripts indicate the integration variable. This gives
$$H_{mn} = <\Phi_{N,m}\,(Q_\alpha)|\,H(Q_\alpha)\,|\Phi_{N,n}(Q_\alpha)>_{\mathbf{Q\alpha}}$$

$$H_{mn} = \langle \Phi_{N,m}(Q_\alpha) | H_{mn}(Q_\alpha) | \Phi_{N,n}(Q_\alpha) \rangle_{Q\alpha}$$

Very often $H_{mn}(Q_\alpha)$ is not very sensitive to Q_α, i.e., is essentially constant with the value at the equilibrium geometry, Q_e. (This is known as the **Condon Approximation**). Then it comes out of the integral to give:

$$H_{mn} = H_{mn}(Q_e) \langle \Psi_{N,m}(Q_\alpha) | \Psi_{N,n}(Q_\alpha) \rangle_{Q\alpha} \text{, so that}$$

$$|H_{mn}|^2 = |H_{mn}(Q_e)|^2 \langle \Phi_{N,m}(Q_\alpha) | \Phi_{N,n}(Q_\alpha) \rangle_{Q\alpha}|^2 = |H_{mn}(Q_e)^2 F_{mn}$$

The overlap integral squared of the nuclear wave functions for the two states **(in bold)** is called the **Franck-Condon** factor, F_{mn}.

$F_{mn} = 1$ only if the equilibrium nuclear positions and the force constants for stretching and bending bonds are the same in states m and n.

This is seldom the case because when electrons change state, e.g., during absorption of light or electron transfer, the electron densities in the bonds change, making the bond lengths and/or angles change.

The Independent Harmonic Oscillator Model for $\Phi_N(Q_\alpha)$: Normal Modes

Just as we take products of orbitals (independent electrons) as a starting point for the electronic wavefunction,
with more than two nuclei, we treat the 3N-6 vibrational coordinates as independent harmonic oscillators (3N-5 for linear molecules, which have only two rotational degrees of freedom).

In the limit of **harmonic** springs connecting neighboring atoms, one can diagonalize the mass weighted force-constant matrix and obtain eigenvectors **(normal modes of vibration,** which, describe concerted, correlated **independent** motion of the atoms).

3N-6 **independent** oscillators means the wavefunction must be written as the **product:**

$$\Phi_N(Q_\alpha) = \prod_{\alpha-1}^{3N-6} \varphi_{v\alpha}(Q_\alpha)$$

$$= \varphi_{v1}(Q_1)\varphi_{v2}(Q_2)\varphi_{v3}(Q_3)...\varphi_{v3N-6}(Q_{3N-6})$$

where $\varphi_{v\alpha}(Q_\alpha)$ is a harmonic oscillator energy eigenfunction for the vibrational coordinate Q_α ,
and v_α is a harmonic oscillator quantum number for the particular vibrational normal mode.

The Franck-Condon factor then separates into a product: $\mathbf{F_{mn} = \Pi\ f_{nm,\alpha}}$

where $\mathrm{f_{nm,\alpha}} = |<\varphi_{vm\alpha}(Q_\alpha)|\ \varphi_{v'n\alpha}(Q_\alpha)>|^2$

i.e., **the square of the overlap integral of the of the initial and final vibrational wavefunctions**

recall: $\varphi_{vm\alpha}(Q_\alpha)$ is a vibrational function of normal coordinate α

m and **n** label two **different electronic states**

v and **v'** label two **different vibrational states**

All about a single normal mode of vibration, α

The Franck-Condon factors are most sensitive to the difference in the equilibrium nuclear positions between the initial and final states, ΔQ_e as will be demonstrated in a figure below.

When the vibrational frequency difference is not very different between the final and initial states, the FC factors are dominated by ΔQ_e.

For the case of no frequency change it is seen that the ground vibrational wavefunction has an overlap =1.0 for the 0-0 transition, and exactly 0 for all other vibronic transitions due to the orthogonality the harmonic oscillator functions.
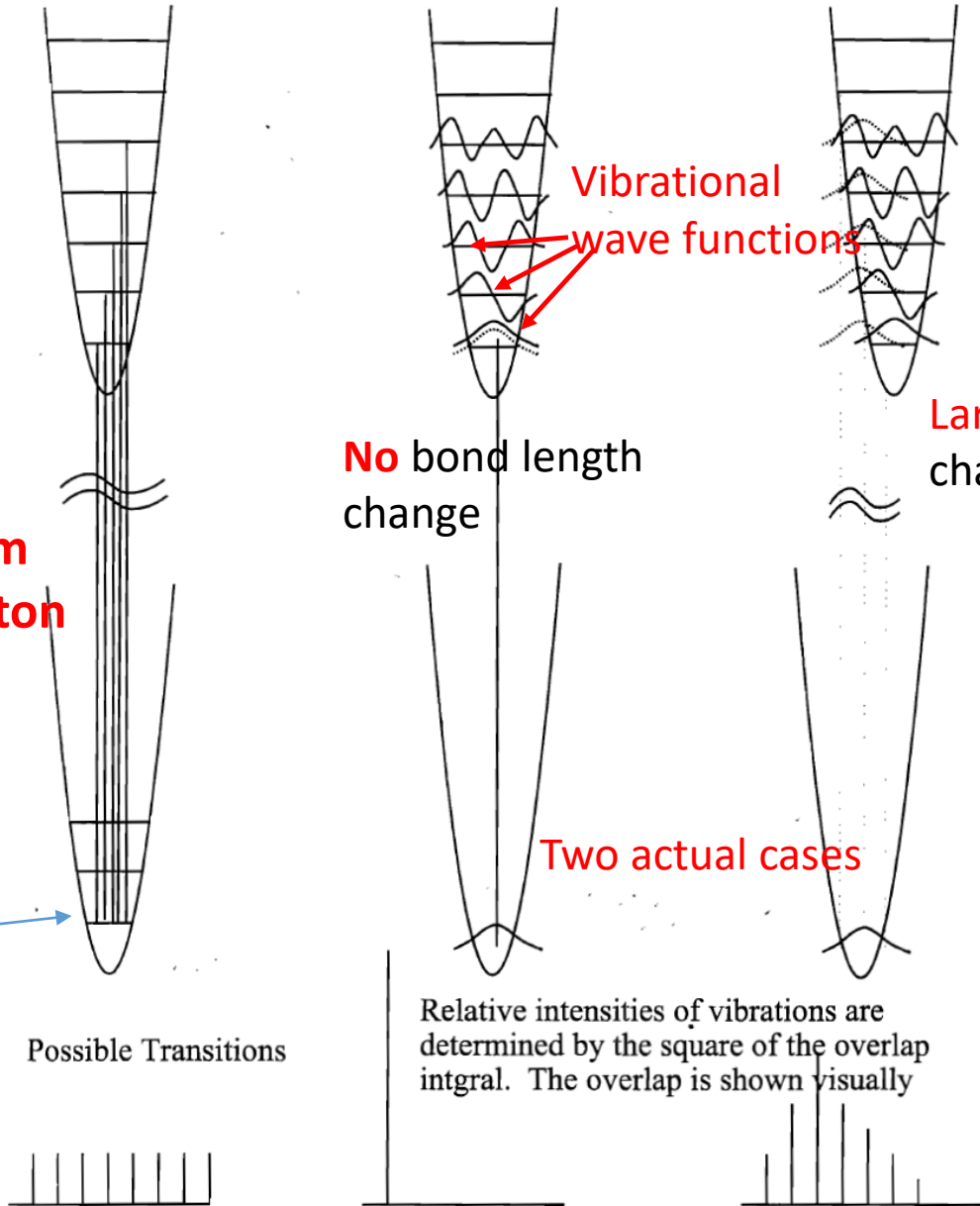
Frank - Condon Factors   ula Spongler.

Vibrational wave functions

No bond length change

Large bond length change

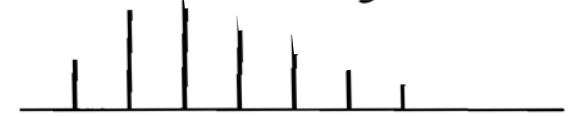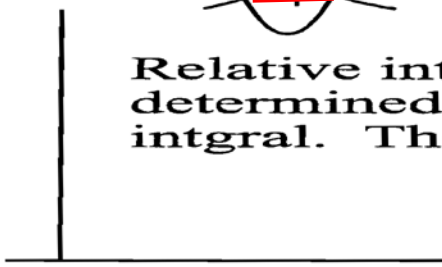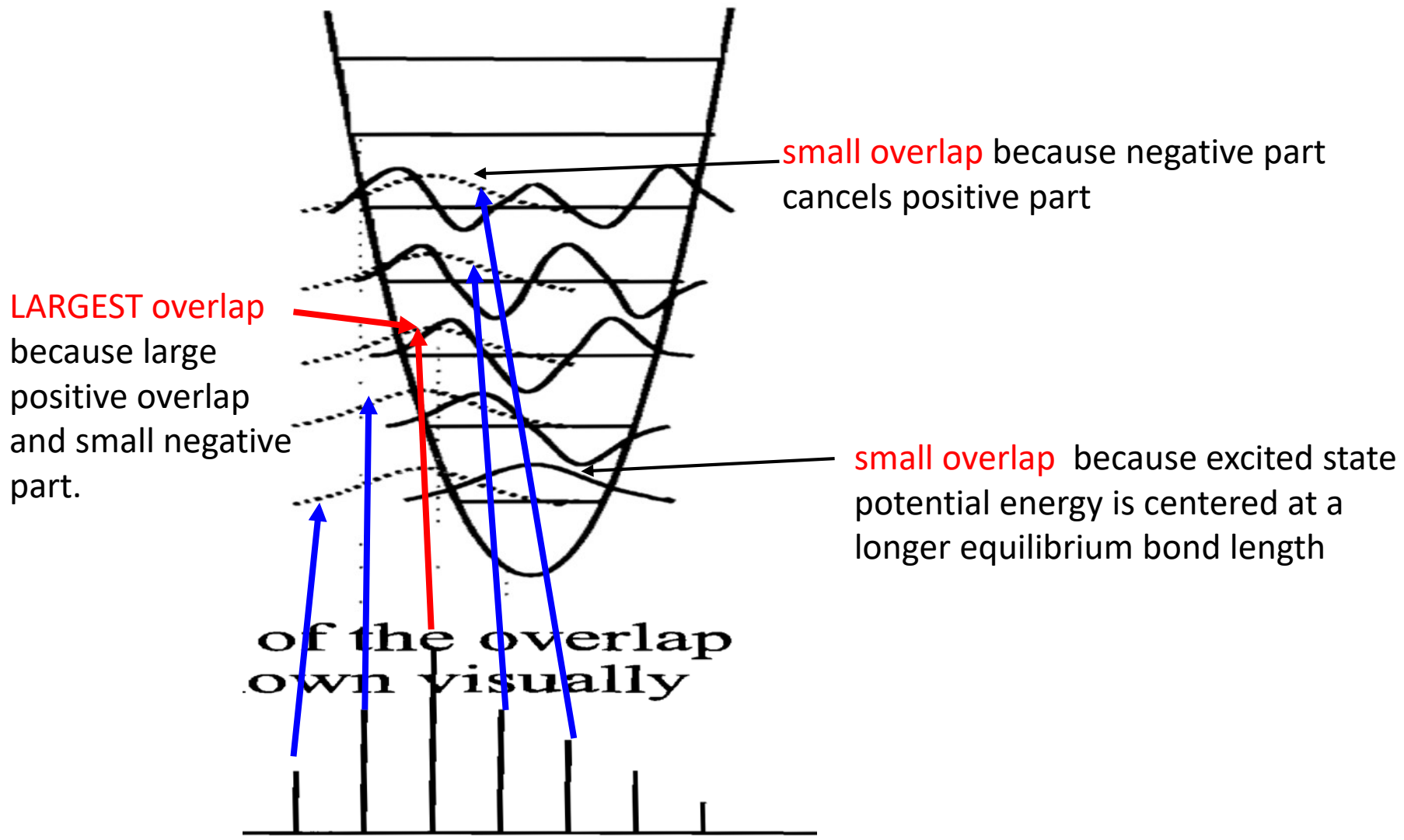"Vibronic" transitions from absorbing photon

0 Kelvin

Two actual cases

Possible Transitions
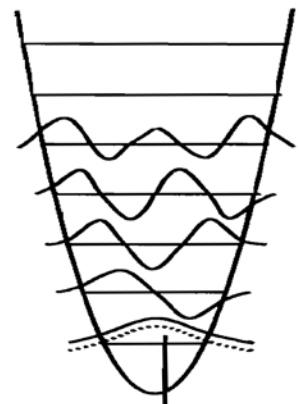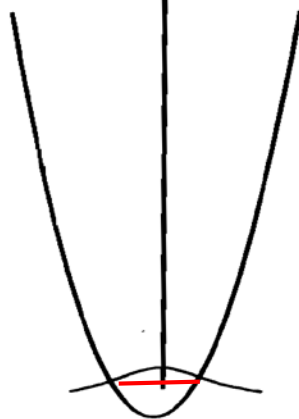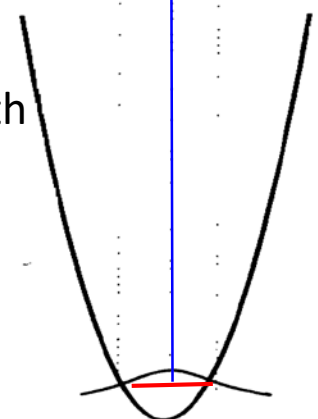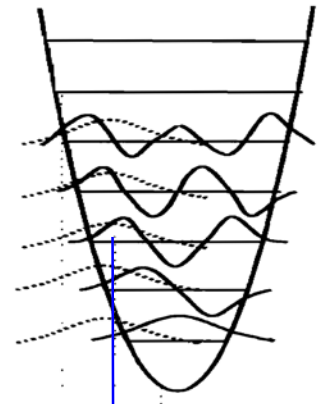
Relative intensities of vibrations are determined by the square of the overlap intgral. The overlap is shown visually

Frank – Condon Factors

small overlap because negative part cancels positive part

LARGEST overlap because large positive overlap and small negative part.

small overlap because excited state potential energy is centered at a longer equilibrium bond length

of the overlap
own visually