Photophysical requirements for absorption/emission

- For any photophysical process the following conservation laws must be followed:

  - ➢ *conservation of energy* ($E = h\nu$; $\Delta E = 0$)

  - ➢ *conservation of angular momentum* ($\Delta l = 0$)

    Electronic transitions must generate (abs) or destroy (emission) a node.

  - ➢ *finite interaction rule*

    the transition dipole moment (μ_{ge}) which determines the magnitude of light absorption must be finite.

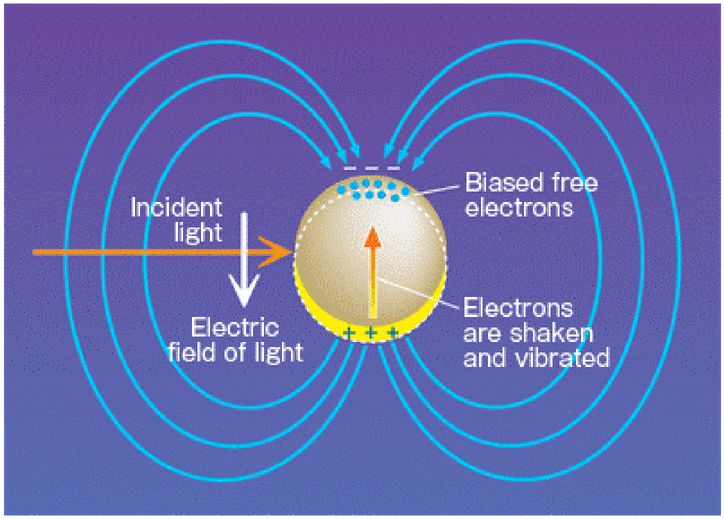
  - ➢ *frequency matching (resonance) rule* ($\nu = E / h$)

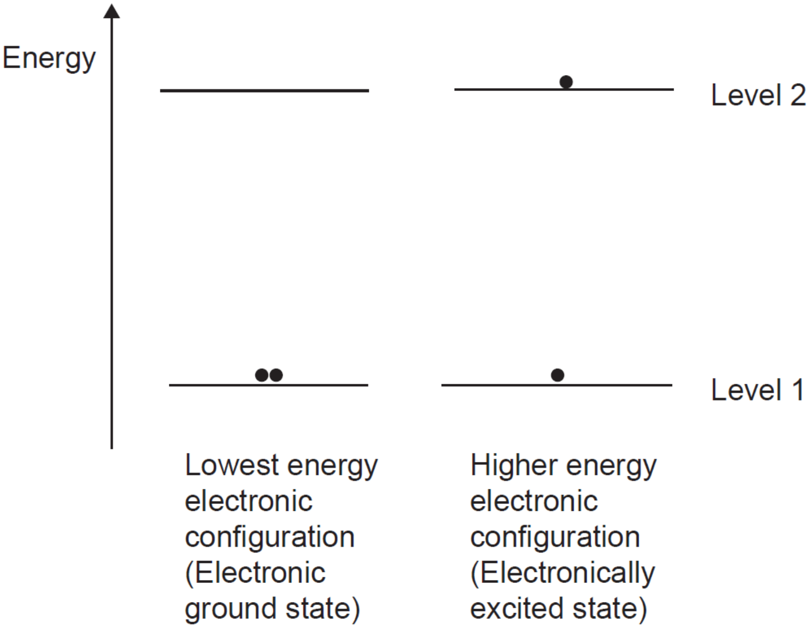
    there must be a matching of frequency (ν) of the oscillating light wave and a frequency that corresponds to the formation of a transition dipole moment.

Physical basis for light absorption

- When a photon, i.e. an oscillating electromagnetic field, encounters a chromophore possessing quantized electronic states it may be absorbed and its energy transferred to an electron to partake in an electronic transition.

$$E_{\text{photon}} = \Delta E_{\text{electronic transition}} = h\nu$$

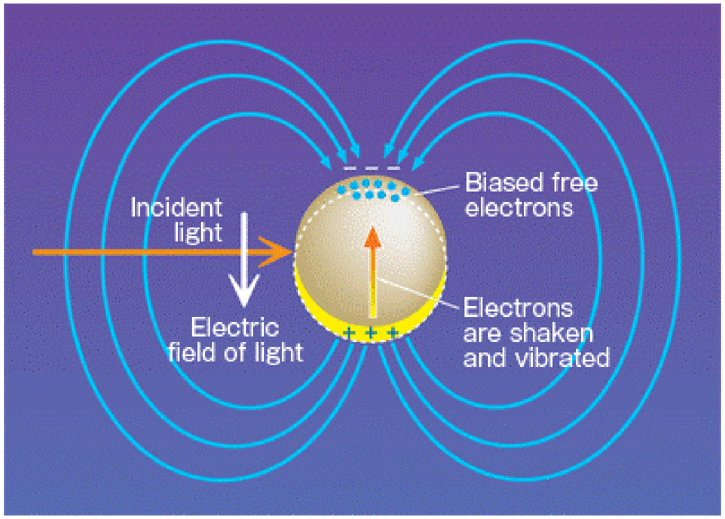




Classical description for light absorption (harmonic oscillator model)

- In the classical model the photon is considered an oscillating electromagnetic field.
- An excited state is considered as a harmonic oscillator, in essence an *oscillating electronic dipole*, e.g. HOMO-LUMO
- When both oscillations share the same frequency they are said to be in resonance with each other – one criteria for photon absorption.

$$E_{\text{photon}} = \Delta E_{\text{electronic transition}} = h\nu$$



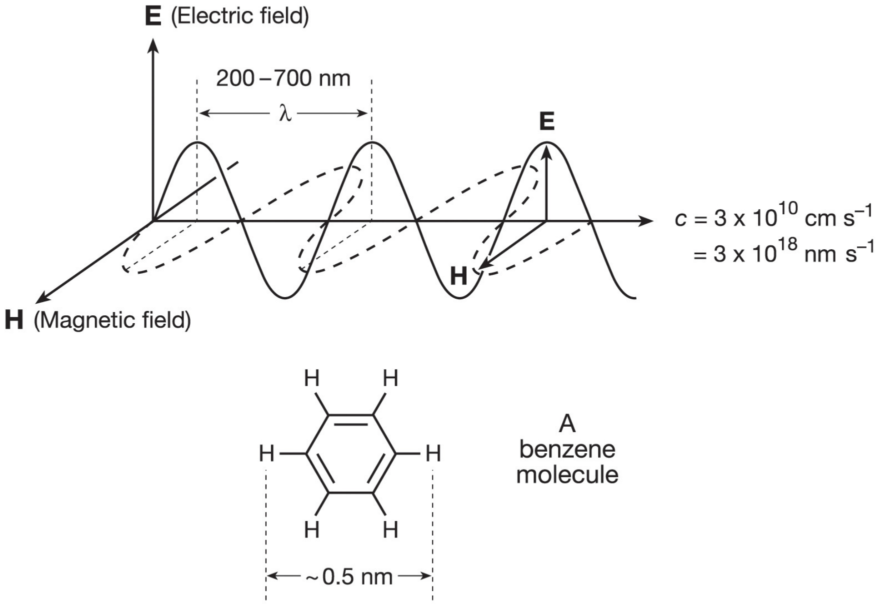


Figure 4.3 copyright 2009 University Science Books

- When resonance is met and an electronic transition occurs the photon energy is quantitatively absorbed.

- Perturbed electron density of the chromophore oscillates between both electronic states involved with a frequency of ν (barring some thermal loss) causing a change in the molecule's **dipole moment** ($\Delta\mu = \mu_{ee} - \mu_{gg}$)

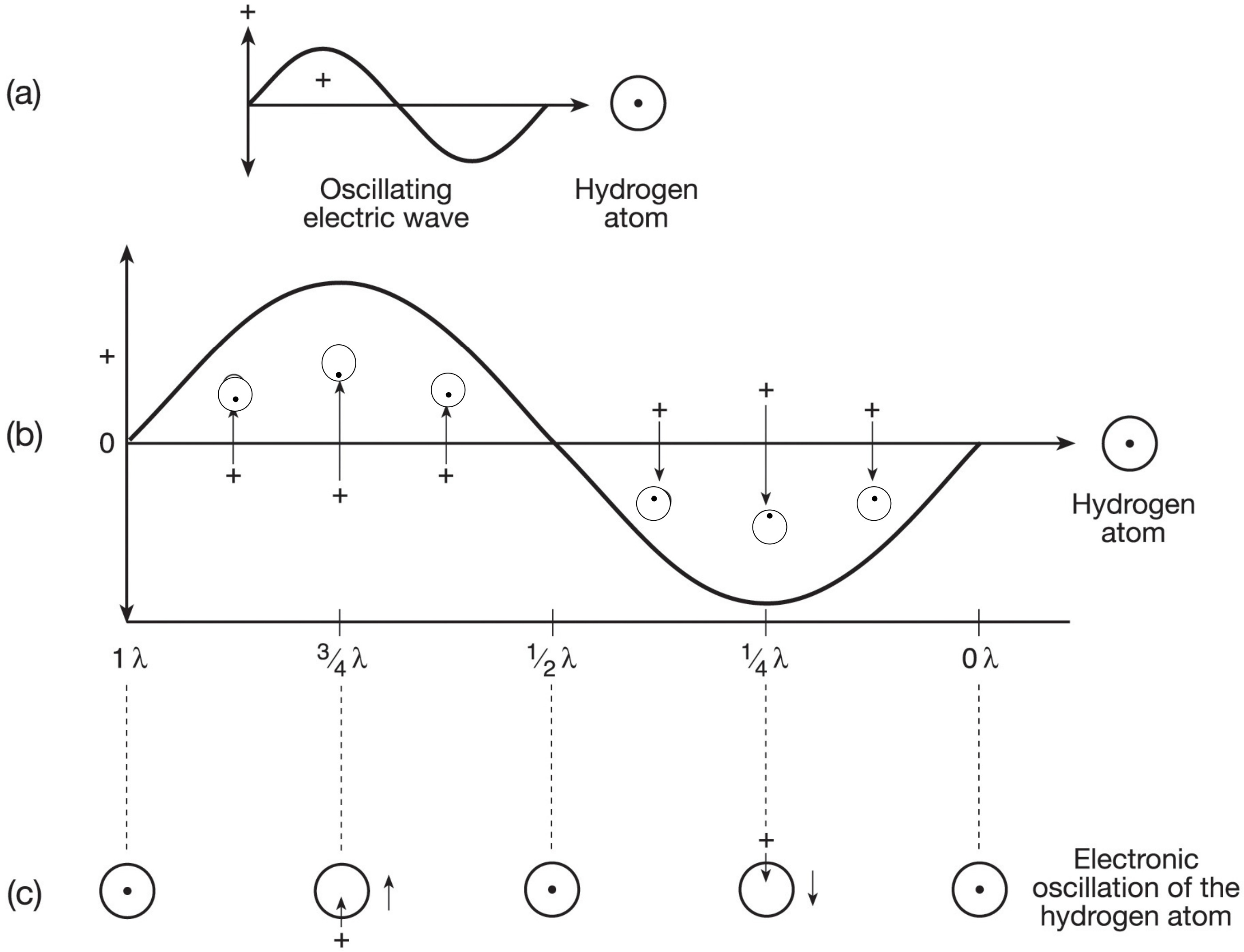
Photoexcited states are dynamic electronic states!

- It is the frequency of oscillation of the **transition dipole moment** (μ_{ge}) that is in resonance with the incident electromagnetic radiation. Classically described as a vibrating harmonic oscillator.

- The **transition dipole moment** (μ_{ge}) lasts only for the duration of the electronic transition and arises because of the process of electron displacement during the transition.

- The molar extinction coefficient (ε) is proportional to the square of the transition dipole moment.

$$\varepsilon \propto \mu_{ge}^2$$



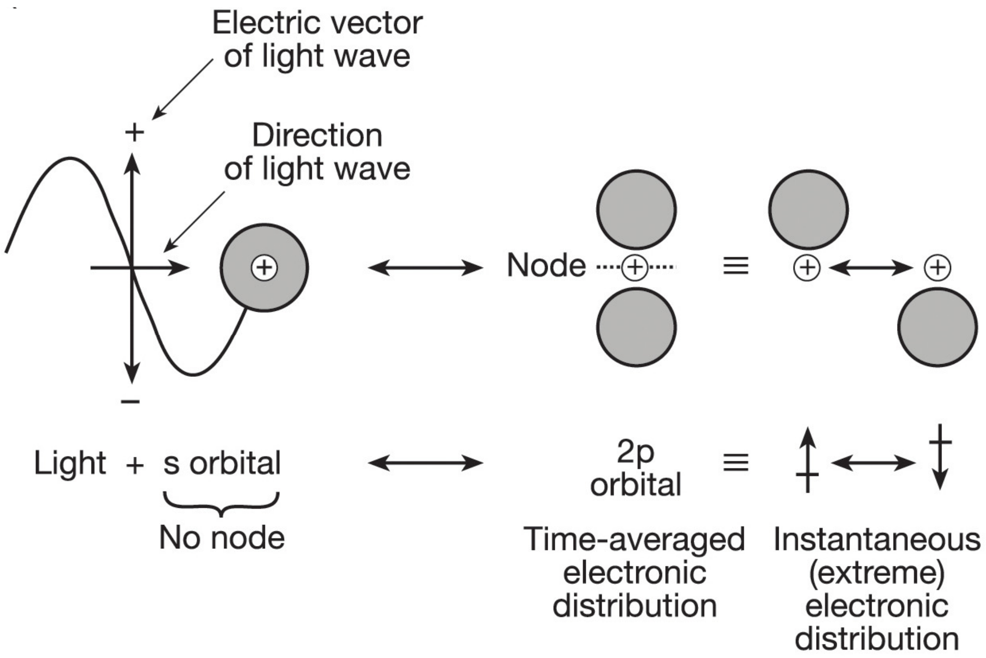
- Schematic of the electronic component of an electromagnetic wave interacting with the Bohr orbit of the H atom (classical model).

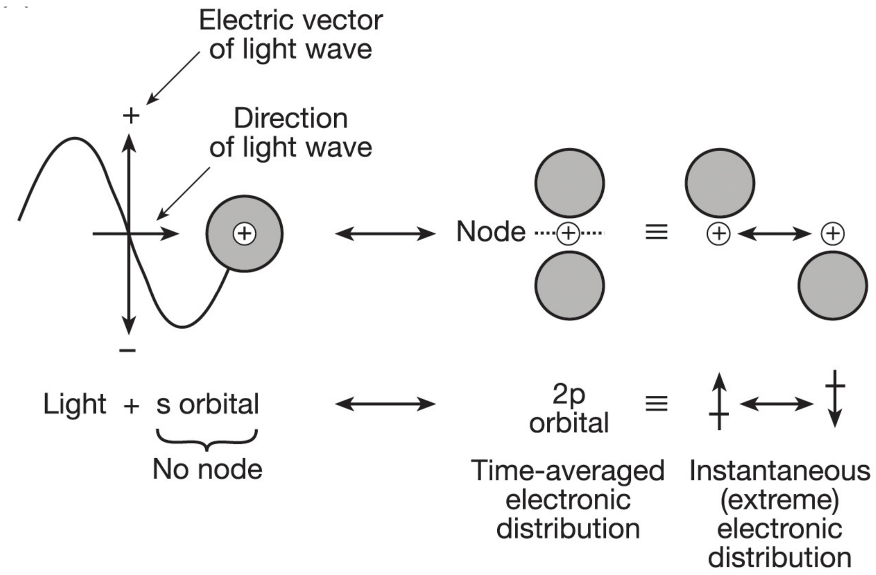
Physical basis for light absorption – Quantum model

- Considering again the H atom we now use the 1*s* wavefunction in our model which has R_3 symmetry and hence no net dipole when unperturbed.

- An electromagnetic wave may provide energy, providing it meets the resonance criteria, for the wavefunction to distort from its equilibrium position such that the electron density oscillates beyond its equilibrium position.

- This 1*s* oscillation corresponds to *"attractive and repulsive forces"*, according to the phase of the light wave, generating an appearance similar to that of a *p* orbital.





- In other words, upon absorption of a photon the angular momentum of the wavefunction changes from $l = 0$ to $l = 1$.

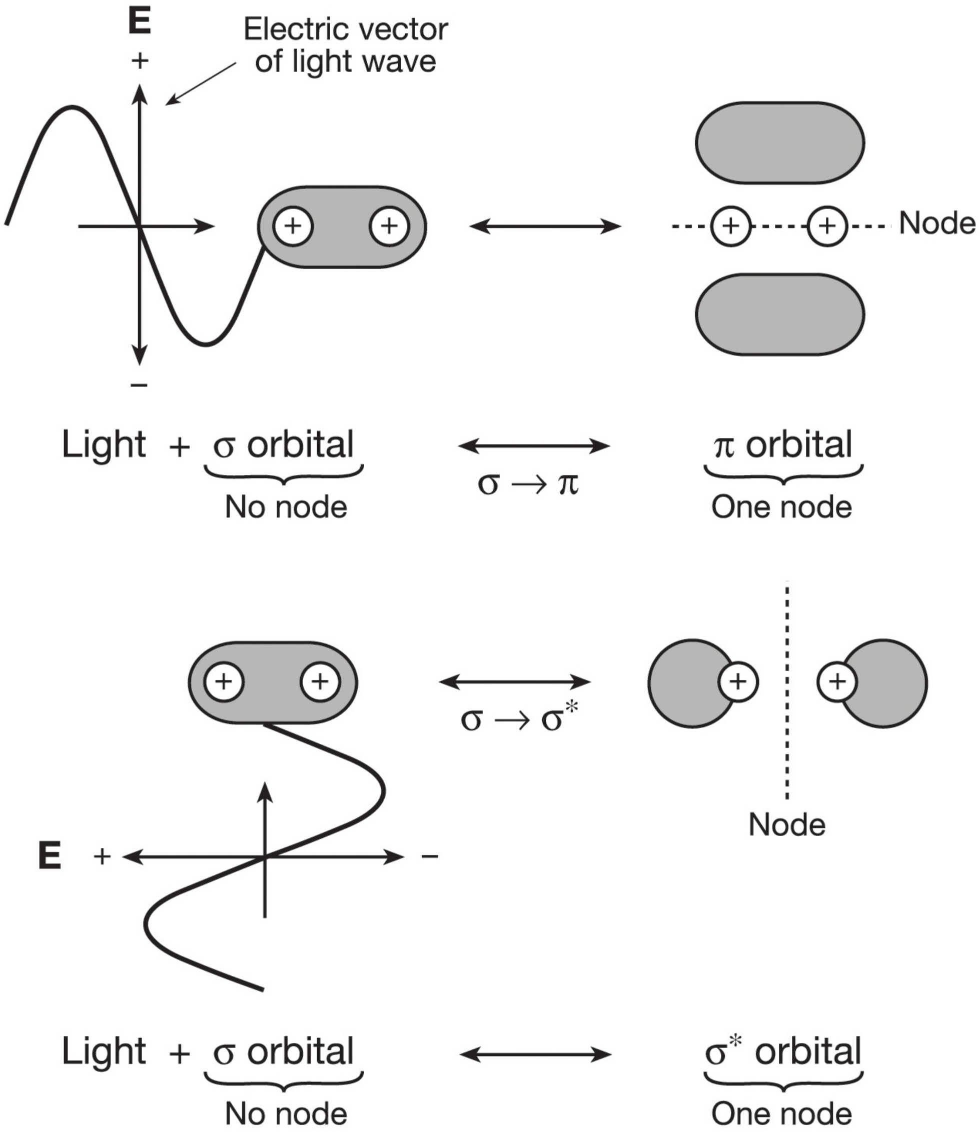
➢ It is important to note that a photon possesses one unit of spin angular momentum.

- Thus, this example shows how electronic excitation obeys two important requirements for a photochemical process:

  1) The conservation of energy ($\Delta E = 0$)
  2) The conservation of angular momentum($\Delta l = 0$)

Quantum model for the H–H molecule

- H_2 is cylindrically symmetrical ($D_{\infty h}$) which gives rise to axially parallel and perpendicular electronic excited state oscillations.
- This gives rise to σ^* and π orbitals each having one extra node, $\Delta l = +1$.
- The $\sigma \rightarrow \sigma^*$ electronic transition is perpendicular to the molecular axis.
- The $\sigma \rightarrow \pi$ electronic transition is parallel to the molecular axis.

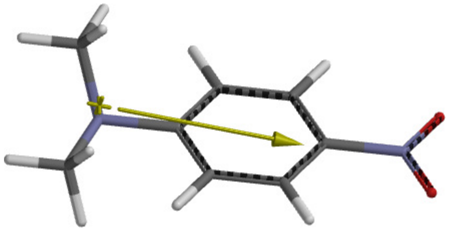


- Production of a single node in the wavefunction corresponds to the change of angular momentum (Δl = +1) by a single unit $\hbar$ (= $h/2\pi$)

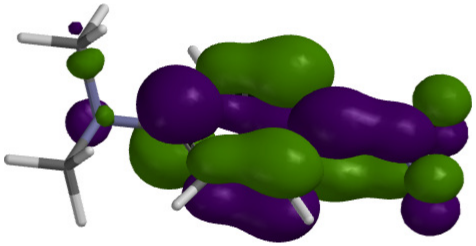
- The magnitude of charge separation, as the electron density is redistributed in an electronically excited state, is determined by the polarizability of the electron cloud (α) which is defined by the transition dipole moment (μ_{ge})

$$\alpha = \mu_{ge} / \boldsymbol{E}$$ (**E** = electrical force)

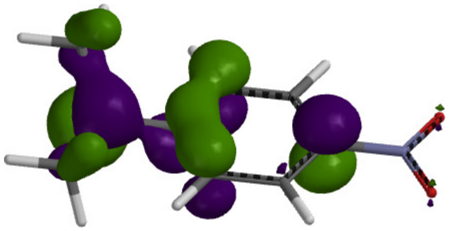
$$\mu_{ge} = e\,\mathbf{r}$$ (**e** = electron charge,
r = extent of charge displacement)



μ_{gg} = 5.95 D



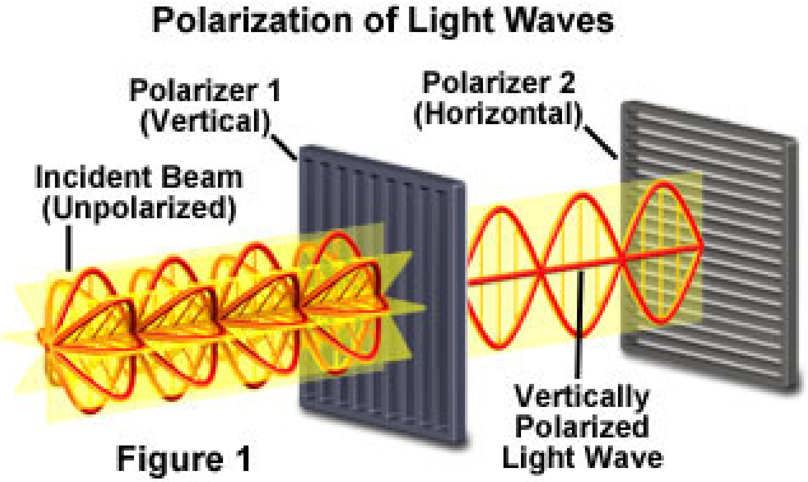
LUMO



HOMO

Absorption of polarized light

- The previous description allows us to introduce the selective absorption of polarized light by a chromophore.
- Upon photon absorption by the 1*s* wavefunction of the H atom the electron cloud oscillates in the same plane as the electromagnetic wave (also producing the nodal plane of a 2*p* orbital at 90º to this plane).
- The 1*s* wavefunction can be excited along any one of the three Cartesian axes producing one of three possible 2*p* orbitals (m_l = -1, 0, +1).



Absorption coefficient (α)

- Typically used for solid and gas phase samples

$$I = I_0 \, e^{-\alpha \, l}$$

$$T = \frac{I}{I_0} = e^{-\alpha \, l}$$

$$\alpha = N \, \sigma$$

$$T = e^{-N \, \sigma \, l}$$

$$A = \ln\left(\frac{1}{T}\right) = N \, \sigma \, l$$

α = absorption coefficient

I_0 = light intensity before incident on sample

I = light intensity after passing through sample

A = absorbance

T = transmission

c = concentration (M)

l = path length (cm)

N = atomic number density

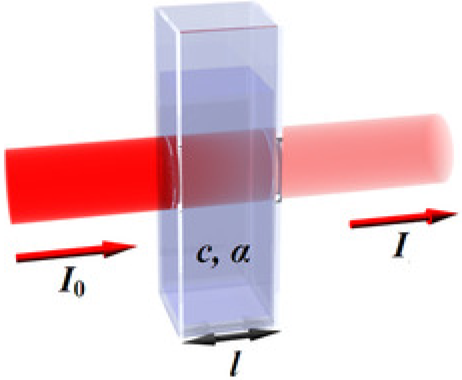
σ = optical cross section (α / N)

Transmission of light by a dilute solution

$$T = \frac{I}{I_0} = 10^{-\alpha\, l}$$

$$\alpha = \varepsilon\, c$$

$$T = \frac{I}{I_0} = 10^{-\varepsilon\, c\, l}$$



T = transmission

I_0 = light intensity before incident on sample

I = light intensity after passing through sample

c = concentration (M)

l = path length (cm)

α = absorption coefficient (constant)

ε = molar extinction coefficient (L mol^{-1} cm^{-1})

Beer-Lambert law

$$A = -\log T = -\log\left(\frac{I}{I_0}\right)$$

$$A = \log\left(\frac{1}{T}\right) = \log\left(\frac{I_0}{I}\right) = \log\left(10^{\varepsilon\ c\ l}\right)$$

$$A = \varepsilon\ c\ l$$

A = absorbance (aka *optical density* or *o.d.*)

T = transmission

I_0 = light intensity before incident on sample

I = light intensity after passing through sample

c = concentration (M)

l = path length (cm)

ε = molar extinction coefficient (L mol^{-1} cm^{-1})

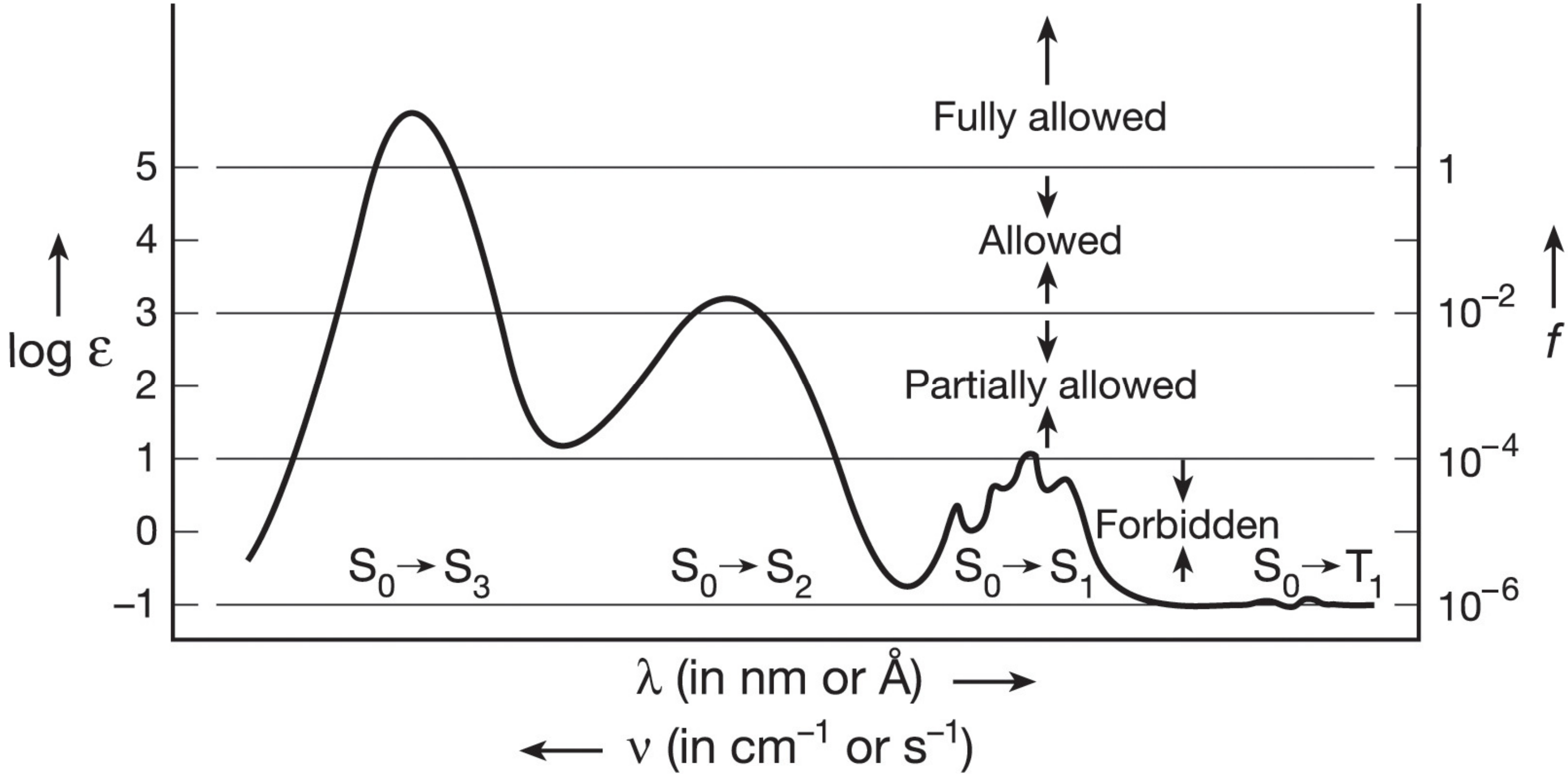
Beer-Lambert law

$$A = -\log T = -\log\left(\frac{I}{I_0}\right)$$

$$A = \log\left(\frac{1}{T}\right) = \log\left(\frac{I_0}{I}\right) = \log\left(10^{\varepsilon\ c\ l}\right)$$

$$A = \varepsilon\ c\ l$$

O.D.	% Transmission	% Absorption
0.1	99	1
1.0	10	90
2.0	1	99


Fully allowed
Allowed
Partially allowed
Forbidden
log ε
5
4
3
2
1
0
–1
1
10^{-2}
10^{-4}
10^{-6}
f
$S_0 \rightarrow S_3$
$S_0 \rightarrow S_2$
$S_0 \rightarrow S_1$
$S_0 \rightarrow T_1$
λ (in nm or Å) →
← ν (in cm⁻¹ or s⁻¹)

Eigenfunctions, eigenstates & eigenvalues

- Using the Schrödinger wave equation quantum mechanics provides an understanding of molecular structure, molecular energetics, and molecular dynamics based on computations that “operate” mathematically on the wavefunction Ψ

$$H\,\Psi = E\,\Psi$$

If the mathematical form of Ψ *is known precisely for a given molecule it is possible not only to compute the electronic, nuclear, and spin configurations of a molecule but also to compute the average value of any experimental observable property (electronic energy, dipole moment, nuclear geometry, electron spin energies, probabilities for transitions between electronic states, etc.) of any state of the molecule for an assumed set of initial conditions and interactions provided by internal and external forces.*

- In other words, for every measurable property of a molecular system there is a mathematical function H that operates on the wavefunction Ψ to produce an eigenvalue E that corresponds to an experimental measurement of that property of the system.

- The Schrödinger wave equation tells us that energy is quantized in discrete states, known as ***eigenstates*** *; eigen (deutsch)* = proper
- Each of these states corresponds to a specific wave function Ψ with a specific energy E
- The wavefunctions are called ***eigenfunctions*** and their corresponding energies are called ***eigenvalues*** of the operator H
- A complete eigenfunction Ψ represents the entire molecular structure (electronic, vibrational and spin)
- Therefore by choosing an appropriate Hamiltonian operator H the following eigenvalues may be determined
  - electronic, vibrational, spin structures and energies
  - electronic density distributions
  - probability of light absorption and light emission
  - rates of photophysical transitions
  - role of electron spin in determining excited state properties

- The mathematical operator *or* Hamiltonian $\boldsymbol{H}$ is related to the forces or interactions that determine the measurable properties of a system e.g., energy, dipole moment, angular momentum, transition probability etc.

- While quantum mechanics can predict discrete eigenvalue solutions $\boldsymbol{E}$ in reality, as experimentalists, we observe average eigenvalue distributions $\boldsymbol{E}_{\mathrm{av}}$ for large numbers of molecules…..known as the ***expectation value***.

- Expectation values for a molecular system are extracted from a wavefunction by applying the Hamiltonian operator and then computing what is know as the ***matrix element***

- The matrix element involves “normalization” of the component wavefunctions and integrating resultant values to give an approximate solution to the wave equation.

$$\underbrace{\boldsymbol{P}_{\mathrm{av}}}_{\textit{expectation value}} = \int \Psi\,\boldsymbol{P}\,\Psi = \underbrace{\langle \Psi | \boldsymbol{P} | \Psi \rangle}_{\textit{matrix element}}$$

- The expectation value of any observable molecular property of interest $\boldsymbol{P}$ (eigenstate, dipole moment, transition probability etc.) can be evaluated in terms of the *matrix element.*

Born-Oppenheimer approximation

$$\Psi = \Psi_{\text{electronic}} + \Psi_{\text{vibrational}} + \Psi_{\text{rotational}}$$

- The Born-Oppenheimer Approximation is the assumption that electronic, vibrational and rotational wavefunctions can be treated independently.

- This assumption is based upon the following premise

$$E_{\text{electronic}} >> E_{\text{vibrational}} >> E_{\text{rotational}}$$

- This approximation greatly simplifies solution of the Schrödinger wave equation as it allows an *approximate* wavefunction Ψ_0 to be independently solved determining approximate *eigenvalues (potential energy)* for any selected *static nuclear framework (*χ *, kinetic energy = 0)* and specified spin configuration ($\mathbf{S}$)

$$\Psi \cong \Psi_0 \, \chi \, \mathrm{S}$$

- This approximation breaks down in the presence of significant *vibronic coupling* or *spin-orbit coupling*.

Qualitative characteristics of wavefunctions (revision)

- Only the square of the wavefunction is subject to direct experimental observation (Ψ_0^2 , χ^2 or S^2)

- Ψ_0^2 , χ^2 and S^2 relate to the probability of finding the electrons, nuclei, and spins, respectively, at particular points in space in a molecular structure thus providing a means of pictorially representing electron density, nuclear geometry and spin.

- Ψ_0 , χ and S are subject to symmetry considerations which provide a basis for selection rules governing transitions between states.

- Wavefunctions of similar energies may "mix" , i.e. be in ***resonance*** with each other. Wavefunctions having identical energies are termed degenerate.

- Having a knowledge of

  (i) various state electronic, nuclear and spin configurations

  (ii) a qualitative ranking of their corresponding energies

  enables a ***state energy level (aka Jablsonki) diagram*** to be readily constructed.

Expectation values and matrix elements

$$\underbrace{\boldsymbol{P}_{\mathrm{av}}}_{\textit{expectation value}} = \int \psi\, \boldsymbol{P}\, \psi = \underbrace{\langle \psi | \boldsymbol{P} | \psi \rangle}_{\textit{matrix element}}$$

- ➢ The matrix element $<\Psi\,|\,\boldsymbol{P}\,|\,\Psi>$ is the quantum mechanical representation of the energy of an observable property $\boldsymbol{P}$ of a molecular system.

To avoid calculating the matrix element we visualize its components using constructs of classical mechanics to then deduce qualitative conclusions.

$$P_{av} = \langle \Psi_0\, \chi\, \mathrm{S}\, |P| \Psi_0\, \chi\, \mathrm{S} \rangle$$

$$P_{av} = \langle\, (\phi_1 \phi_2 \ldots \phi_n)\, \chi\, \mathrm{S}\, |P|\, (\phi_1 \phi_2 \ldots \phi_n\,)\chi\, \mathrm{S}\, \rangle$$

- In the ***zero-order approximation*** Ψ_0 is calculated as a product of one-electron molecular orbital wavefunctions ϕ_{n} for a one-electron molecule.

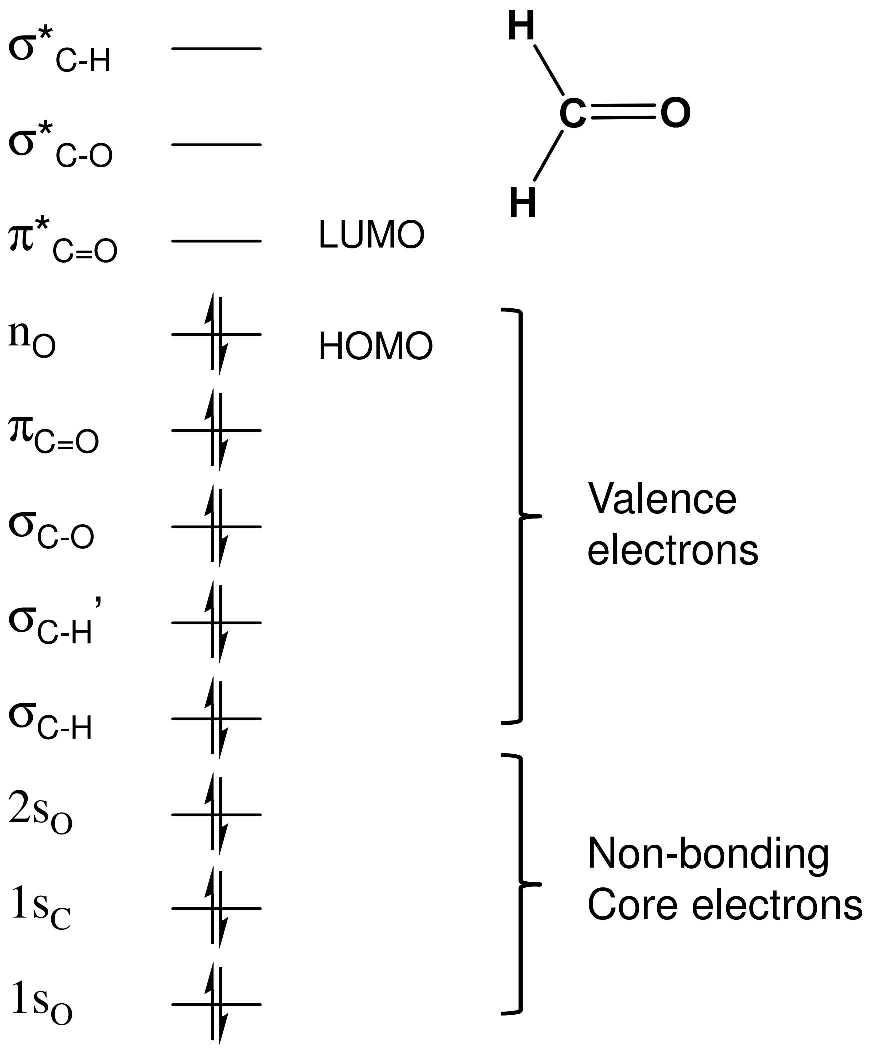
- The ***first-order approximation*** introduces electron-electron interactions by *mixing wavefunctions* to approximate $\boldsymbol{E}$ with more accuracy……***perturbation theory***!

Atomic orbitals, Molecular orbitals, electronic states and configurations, e.g. formaldehyde

- To visualize $\Psi_{electronic}$ we must approximate the structure of Ψ_0^2 as a configuration of overlapping, but non-interacting, one-electron occupied orbitals ϕ_n

- $H_2C{=}O$ has a total of 16 electrons. Using a classical approach for MO energies, # of electrons, Pauli and Aufbau principle we can build a basic MO diagram for the molecule.

- The electronic configuration on the right represents an approximation of the S_0 wavefunction for formaldehyde, i.e. $\Psi_0(S_0)$



$\sigma^*_{C\text{-}H}$

$\sigma^*_{C\text{-}O}$

$\pi^*_{C=O}$ LUMO

n_O HOMO

$\pi_{C=O}$

$\sigma_{C\text{-}O}$

$\sigma_{C\text{-}H}'$

$\sigma_{C\text{-}H}$

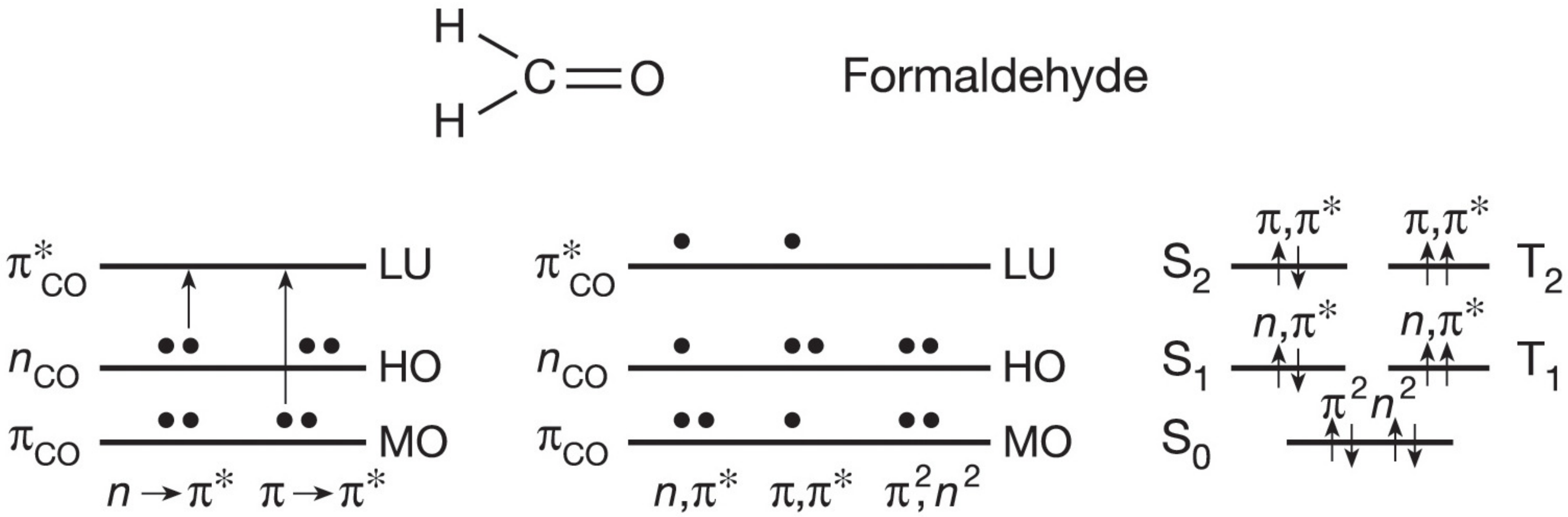
$2s_O$

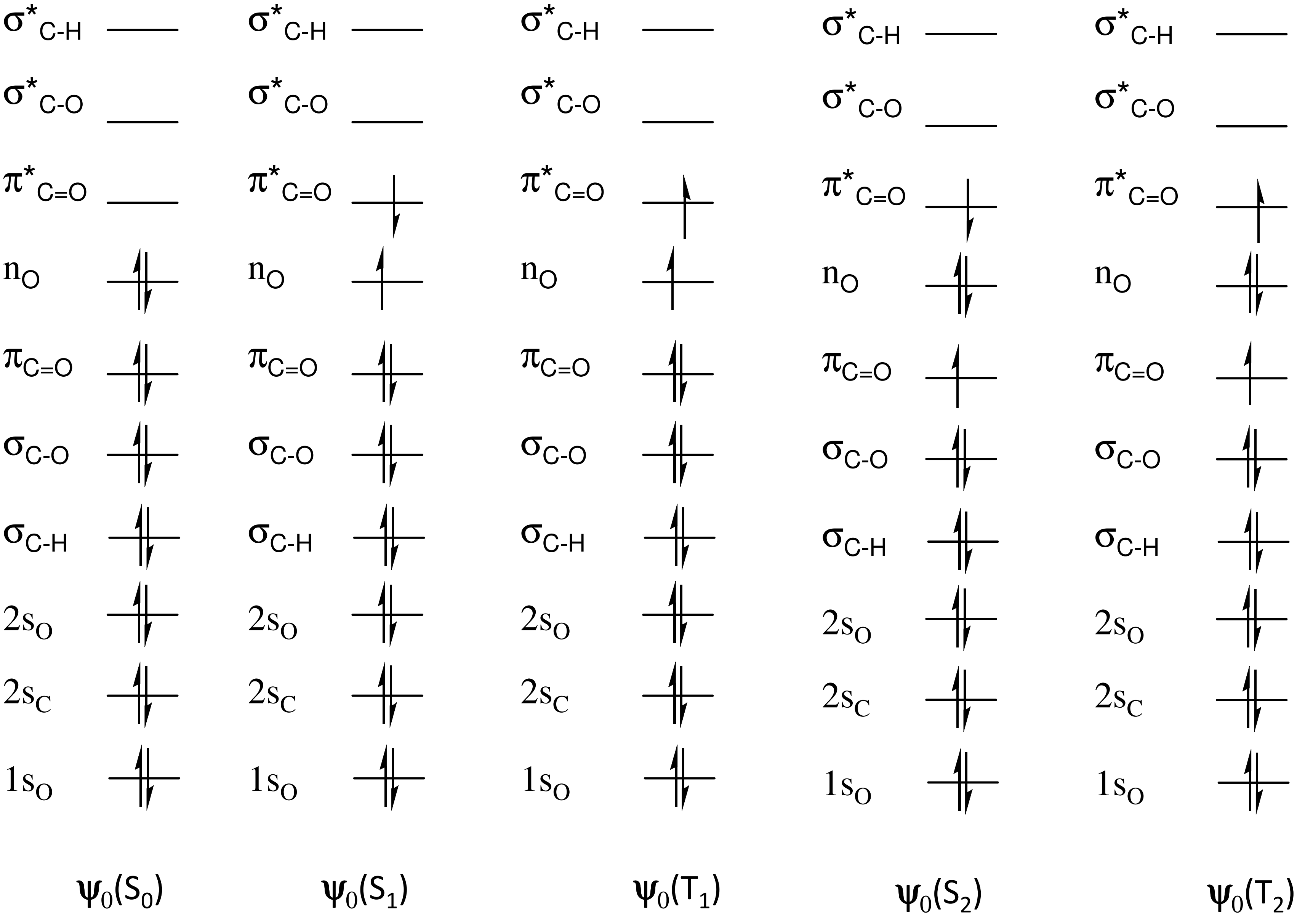
$1s_C$

$1s_O$

Valence electrons

Non-bonding Core electrons


Formaldehyde
H
H
C
O
π^*_{CO}
n_{CO}
π_{CO}
LU
HO
MO
$n \rightarrow \pi^*$
$\pi \rightarrow \pi^*$
π^*_{CO}
n_{CO}
π_{CO}
LU
HO
MO
n,π^*
π,π^*
π^2,n^2
S_2
S_1
S_0
T_2
T_1
π,π^*
π,π^*
n,π^*
n,π^*
π^2n^2


σ^*_{C-H}
σ^*_{C-O}
$\pi^*_{C=O}$
n_O
$\pi_{C=O}$
σ_{C-O}
σ_{C-H}
$2s_O$
$2s_C$
$1s_O$
$\psi_0(S_0)$
$\psi_0(S_1)$
$\psi_0(T_1)$
$\psi_0(S_2)$
$\psi_0(T_2)$

State	Characteristic orbitals	Characteristic spin electronic configuration	Shorthand description of state
S_2	π , π^*	$(\pi \uparrow)^1 (n)^2 (\pi^* \downarrow)^1$	$^1(\pi , \pi^*)$
T_2	π , π^*	$(\pi \uparrow)^1 (n)^2 (\pi^* \uparrow)^1$	$^3(\pi , \pi^*)$
S_1	n , π^*	$(\pi)^2 (n \uparrow)^1 (\pi^* \downarrow)^1$	$^1(n , \pi^*)$
T_1	n , π^*	$(\pi)^2 (n \uparrow)^1 (\pi^* \uparrow)^1$	$^3(n , \pi^*)$
S_0	π , n	$(\pi)^2 (n)^2 (\pi^*)^0$	$^1[(\pi)^2 (n)^2]$

- Each electronic state may be described in terms of a characteristic electronic configuration , which in turn may be described in terms of the HOMO and LUMO and in terms of a characteristic spin configuration, either singlet or triplet.

Electron correlation and exchange energy

Aufbau principle

Orbitals of lower energy are filled first and only then orbitals of higher energy are filled.

Madelung rule

Orbitals fill up on the order of the quantum number sum ***'n + l'***

Pauli exclusion principle

No two electrons can have the same four quantum numbers, i.e. if n, l, and m_l are the same, m_s must be different such that the electrons have opposite spins

Hunds rule of maximum multiplicity

For a given electron configuration, the maximum multiplicity term (2S + 1) has lower energy

- The Pauli exclusion principle and Hund's rules of maximum multiplicity dictate that the term with maximum multiplicity (2S + 1) has the lowest energy due reduced electron-electron repulsion.

$\mathbf{T_n < S_n}$ *always applies for the same electronic configuration !!!*

- In the zero-order approximation of $\Psi_0(S_n)$ electron-electron repulsions are ignored.

- In the first-order approximation of $\Psi_0(S_n)$ electron-electron repulsions are taken into account.

- Applying the *Born-Oppenheimer approximation* the nuclear geometry is fixed and attractive forces between the negatively charged electrons and the positively charged nuclei contribute a constant stabilization energy.

- The differences in energy between different states in this approximation are due entirely to electron-electron repulsions where the classical form of $\boldsymbol{H}$ is

$$\boldsymbol{H} = \frac{e^2}{r_{12}}$$

- The magnitude of electron-electron repulsion may be computed by integrating repulsive interactions (matrix element) over the entire molecular volume (assuming a fixed nuclear configuration)

  1. *Coulombic integral (K)* - electron repulsions due to electrostatic interactions
  2. *Electron exchange energy (J)* – a first-order quantum mechanical correction to *K* required by symmetry properties of Pauli's exclusion principle.

- The matrix element aka *electron exchange integral (J)* has the form

$$J \simeq \left\langle \Psi_1 \middle| \frac{e^2}{r_{12}} \middle| \Psi_2 \right\rangle$$

- The *electron exchange integral* (> 0) is a purely quantum mechanical phenomenon since it amounts to a quantum mechanical correction to the classical electronic distribution *(Pauli)*

- The *electron exchange integral* does note take into account the influence of electron spin angular momentum on electron-electron repulsion – only symmetry.

- Taking again $H_2C=O$ as an example, and restricting the calculation to the active MOs in the lowest energy transition:

$$E_S = E_0\,(\text{n}, \pi^*) + K\,(\text{n}, \pi^*) + J\,(\text{n}, \pi^*)$$

$$E_T = \underbrace{E_0\,(\text{n}, \pi^*)}_{\textit{zero-order}} + \underbrace{K\,(\text{n}, \pi^*)}_{\substack{\textit{first-order}\\ \textit{(classical)}}} - \underbrace{J\,(\text{n}, \pi^*)}_{\substack{\textit{first-order}\\ \textit{(quantum m)}}}$$

$$\textit{Electron exchange energy} \quad = \quad E_S - E_T \quad = \quad \Delta E_{ST} \quad = \quad 2\,J$$

Singlet-triplet splitting in $H_2C{=}O$

- Estimation of ΔE_{ST} for S_1/T_1 and S_2/T_2 in $H_2C{=}O$ requires qualitative evaluation of the magnitude of the electron exchange integrals for $J(n, \pi^*)$ and $J(\pi, \pi^*)$

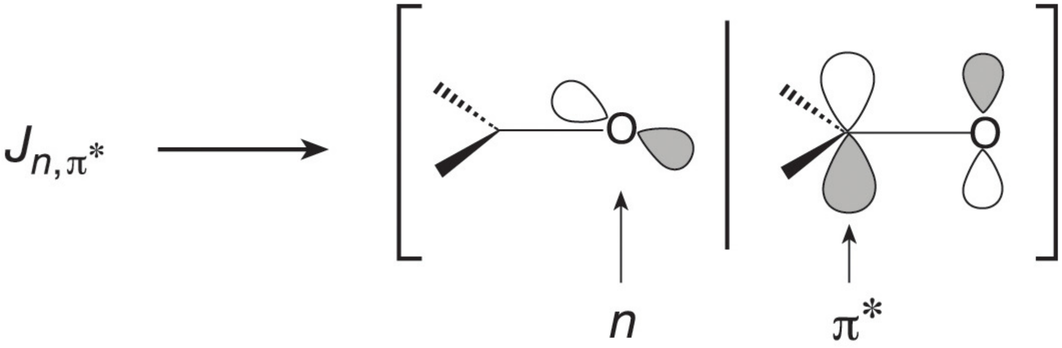
$$J(n,\pi^*) = \left\langle n(1),\pi^*(2) \left| \frac{e^2}{r_{12}} \right| n(2),\pi^*(1) \right\rangle$$

$$J(n,\pi^*) \sim \langle n(1),\pi^*(2) | n(2),\pi^*(1) \rangle \sim \langle n \mid \pi^* \rangle$$

- The ***orbital overlap integral*** $\langle n \mid \pi^* \rangle$ may be visualized as a measure of the mutual resemblance of the two wave functions (aka mixing/resonance).

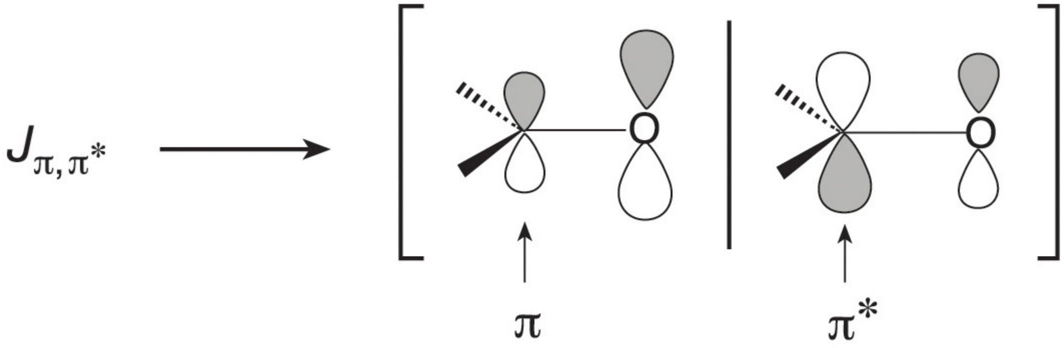
- If both wavefunctions are identical their normalized orbital overlap integral is unity, e.g. $\langle \pi \mid \pi \rangle = 1$

- If both wavefunctions are orthogonal the orbital overlap integral is zero.



Small orbital
overlap between
n and π*

$\langle n | \pi^* \rangle$ Small



Large orbital
overlap between
π and π*

$\langle \pi | \pi^* \rangle$ Large

- When the *orbital overlap integral* $\langle \phi_i | \phi_j \rangle = 0$, so does the *electron exchange integral* such that $J = 0$, $E_S = E_T$ and $\Delta E_{ST} = 0$

$$E_{S/T} = E_0\,(n, \pi^*) + K\,(n, \pi^*) \pm J\,(n, \pi^*)$$

$$J(n, \pi^*) \sim \langle n \,|\, \pi^* \rangle$$

- This is contradictory to our rule:

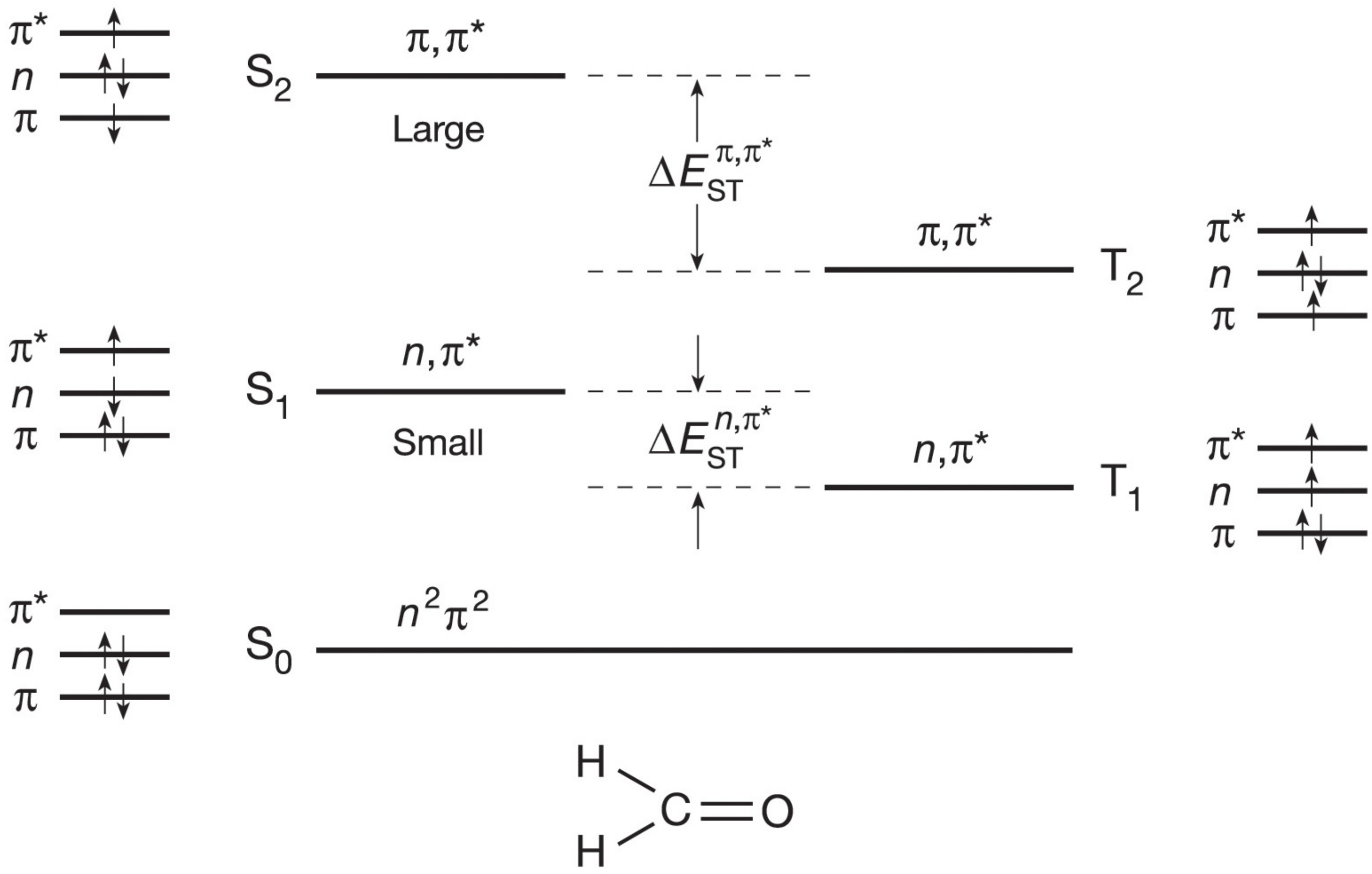
$T_n < S_n$ *always for the same electronic configuration !!!*

What does this mean for $\Psi(n, \pi^*)$ in $H_2C{=}O$?

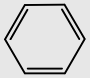
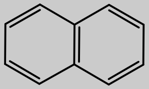
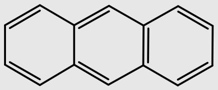
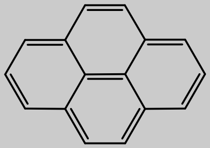
- We have effectively just derived a *selection rule* for singlet triplet energies of (n, π^*) excited states

- In contrast the value for $J(\pi, \pi^*)$ is finite and large.

- We can effectively conclude that $\Delta E_{ST}\,(n, \pi^*) < \Delta E_{ST}\,(\pi, \pi^*)$ in general because the overlap of a π with a π^* orbital will usually be greater than the overlap of a n and a π^* orbital.



A qualitative state energy diagram for formaldehyde, including singlet-triplet splittings and electronic configurations of states.

Molecule	Electronic configuration	ΔE_{ST} (kcal mol^{-1})
$H_2C{=}CH_2$	π, π*	70
$H_2C{=}CH{-}CH{=}CH_2$	π, π*	60
$H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2$	π, π*	48
	π, π*	52
	π, π*	38
	π, π*	34
	π, π*	30
$H_2C{=}O$	n, π*	10
$(CH_3)_2C{=}O$	n, π*	7
$Ph_2C{=}O$	n, π*	5

Increasing triplet yield ↓

- For electronic transitions between states of the different spin, such as $S_1 \rightarrow T_1$ the ***rate constant*** k_{obs} is limited by
- the zero-point electronic motion ($\sim 10^{15} - 10^{16}\ \text{s}^{-1}$)
- spin-orbit coupling between initial and final electronic states
- the square of vibrational overlap, i.e. the *Frank-Condon factor* $\langle \boldsymbol{\chi_1} | \boldsymbol{\chi_0} \rangle^{\mathbf{2}}$

$$k_{obs} = k^{0}_{max} \times \underbrace{\left[\frac{\langle \Psi(\mathrm{T_1})\,|P_{vib}|\,\Psi(\mathrm{S_0})\rangle}{\Delta E_{\mathrm{T1-S0}}}\right]^2}_{\substack{\textit{Vibrational}\\ \textit{coupling}}} \times \underbrace{\left[\frac{\langle \Psi(\mathrm{T_1})\,|P_{\mathrm{SO}}|\,\Psi(\mathrm{S_0})\rangle}{\Delta E_{\mathrm{T1-S0}}}\right]^2}_{\substack{\textit{Spin-orbit}\\ \textit{coupling}}} \times \underbrace{\langle \chi_{\mathrm{T1}} | \chi_{\mathrm{S0}} \rangle^2}_{\substack{\textit{Vibrational}\\ \textit{overlap}\\ \textit{Franck-Condon}\\ \textit{factors}}}$$

The classical harmonic oscillator model for vibrational wavefunctions

$$P_{av} = \langle \Psi_0\, \chi\, S\, |P| \Psi_0\, \chi\, S \rangle$$

$$P_{av} = \langle\, (\phi_1 \phi_2 \dots \phi_n)\, \chi\, S\, |P|\, (\phi_1 \phi_2 \dots \phi_n\,)\chi\, S\, \rangle$$

- To visualize χ a ***first order approximation of the vibrational wavefunction*** we often employ the classical harmonic oscillator model where the positive nuclei are viewed as oscillating back and forth in the potential field of the electron cloud.

- Vibrational wave functions are critical for determining the probability of both radiative and nonradiative transitions between different electronic states *(Franck-Condon principle)*

- A classical harmonic oscillator is described by Hooke’s law

$$F = -k\, \Delta r = -k\, \left| r - r_e \right|$$

$$F = -k\,\Delta r = -k\,\left| r - r_e \right|$$

- The potential energy varies directly with the magnitude of the force constant (k) and the square of the magnitude of displacement (Δr) from equilibrium (r_e)

$$PE = \frac{1}{2}k\,\Delta r^2$$

- The classical harmonic oscillator is a good zero-order approximation of a vibrating diatomic molecule.

- The frequency of oscillation ν (τ^{-1}), with one period occurring in time (τ) is related to the reduced mass (μ) of the displaced atoms

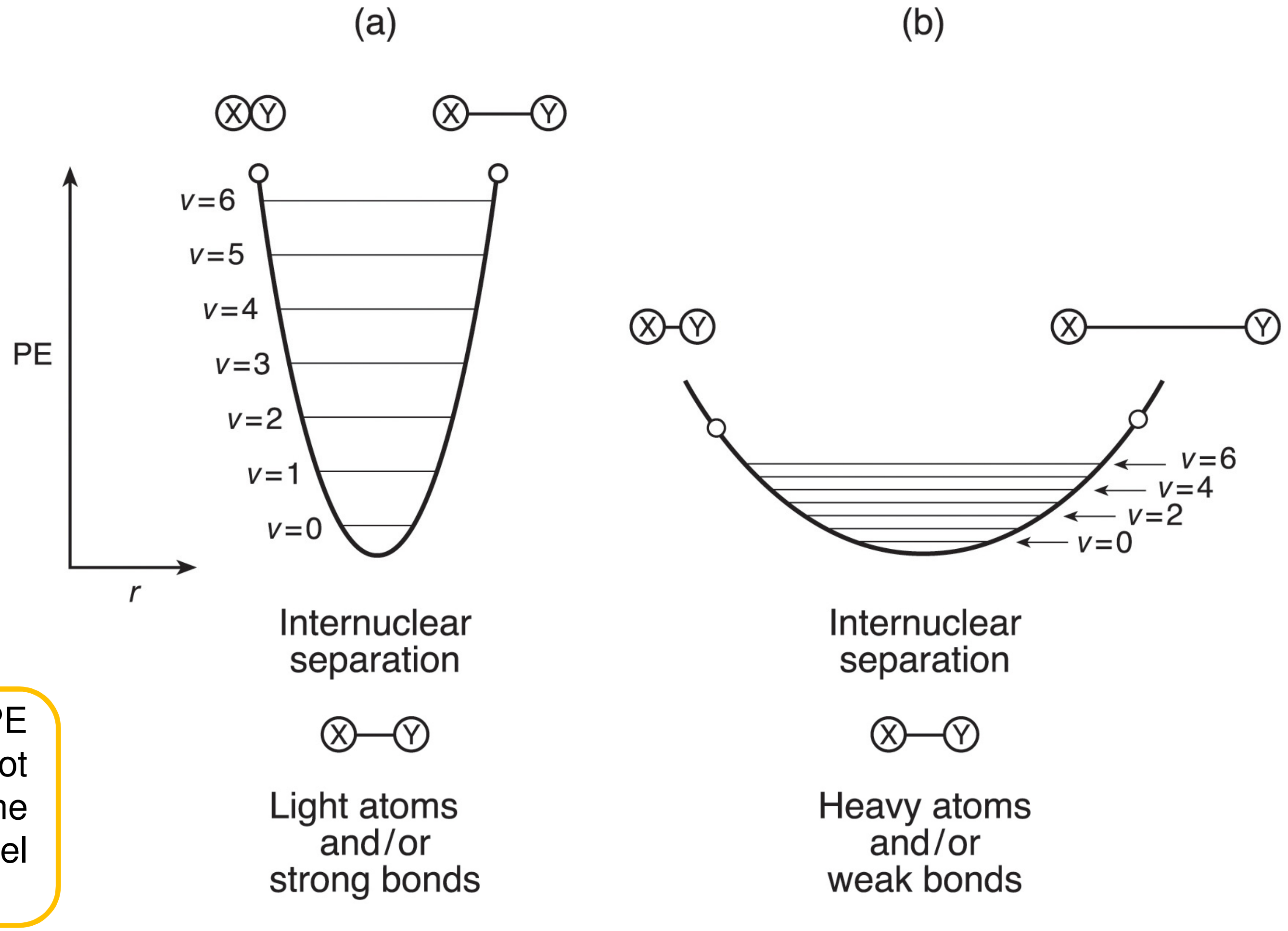
$$\upsilon = \left(\frac{k}{\mu}\right)^{1/2} \qquad \mu = \left(\frac{m_1 + m_2}{m_1 m_2}\right)^{1/2}$$

  - $\nu \propto k$
  - $\nu \propto \mu^{-1}$

- C-H bonds (90-100 kcal mol^{-1}) have a high frequency due to large k and small μ

- C-Cl bonds (60-80 kcal mol^{-1}) have a low frequency due to small k and large μ

$$PE = \frac{1}{2} k \, \Delta r^2$$



(a) Light atoms and/or strong bonds

(b) Heavy atoms and/or weak bonds

Note that PE displacement is not quantized in the classical model (independent of *v*)

- Classical PE curves (parabolas) with quantized levels superimposed
- Strong bonds with a large k and small change in r results in a large change in *PE*
- In contrast, weak bonds with a small k show much smaller changes in potential energy upon similar displacement.

Compare C-C to C=C to C≡C

The quantum harmonic oscillator model for vibrational wavefunctions

$$P_{av} = \langle \Psi_0 \chi \, \mathrm{S} \, | P | \Psi_0 \chi \, \mathrm{S} \rangle$$

$$P_{av} = \langle \, (\phi_1 \phi_2 \ldots \phi_n) \, \chi \, \mathrm{S} \, | P | \, (\phi_1 \phi_2 \ldots \phi_n \,) \chi \, \mathrm{S} \, \rangle$$

- **In the quantum model the vibrational wavefunction χ describes the instantaneous position and motion of the nuclei for a given electronic state (S_0, S_1, T_1 etc.) relative to its electron distribution.**

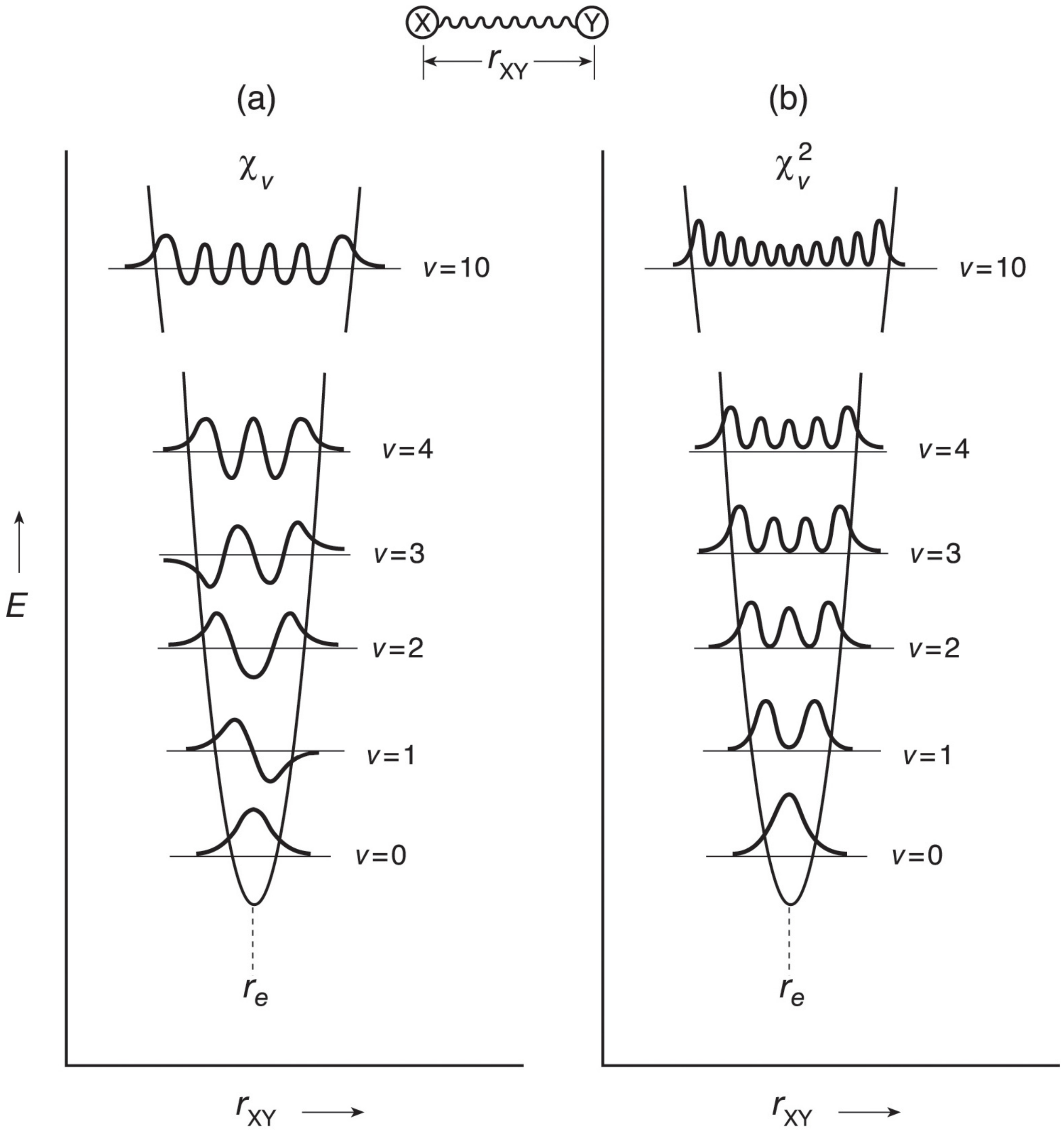
$$P_{av} = \langle \Psi_0 \, (\chi_1 \chi_2 \ldots \chi_n) \mathrm{S} \, | P | \Psi_0 \, (\chi_1 \chi_2 \ldots \chi_n) \mathrm{S} \, \rangle$$

- Visualization of χ can be conveniently achieved by beginning with a classical PE curve, then imposing quantization of the energy levels, and finally describing the appearance of the vibrational wave functions of the quantized energy levels.

- Solving the wave equation according to Hooke's law reveals the quantization of vibronic energy levels characterized by the *vibrational quantum number* $\boldsymbol{v}$ (0, 1, 2, 3,…)

$$PE_v = h\nu\ (\boldsymbol{v} + 0.5)$$

- ➢ PE_v is now quantized with levels separated by units $h\nu$
- ➢ $PE_{\mathrm{v}=0}$ is non-zero ($h\nu/2$)
- ➢ Unstoppable zero-point energy (PE) and motion (KE) are essential features of every quantum particle. Quantum particles are always in oscillation as a consequence of the uncertainty principle (***zero-point motion energy***)
- ➢ At the turning points, the total energy of the oscillator is pure potential energy, because the two masses have stopped vibrating in one direction and are starting to vibrate back in the reverse direction.
- ➢ PE_v and KE_v vary continuously during the oscillation but total energy E_v is constant.



Quantum mechanical description of a vibrating diatomic molecule.

- A closer inspection of sine-wave quantum mechanical solutions for the vibrational wavefunction χ provides valuable insight that is essential in the interpretation of both radiative and nonradiative electronic transitions.

  - ➢ The number of nodal points for χ_v corresponds to the value of v while χ_v changes phase as it passes through the energy-level line.

  - ➢ Overlap of two χ_v wavefunctions can result in *constructive interference* or *destructive interference*.

  - ➢ This is akin to mixing of states, in other words resonance.

  - ➢ According to $(\chi_v)^2$ the electron density spends a majority time at the turning points on the *PE* curve. χ_v wavefunctions approach the classical model at high values of v, *PE* greatest at turning points

  - ➢ Furthermore χ_v wavefunctions have a tendency to spread out in space beyond the boundary of the classical *PE* curve – a phenomenon which gives rise to tunnelling.

The Franck-Condon principle

The Franck-Condon principle

Because nuclei are much larger than electrons (~1000:1) an electronic transition from one orbital to another takes place instantaneously while the higher-inertia nuclei are essentially stationary.

The *Born-Oppenheimer approximation*

Assumes that electron motion (~ 10^{-15}–10^{-16} s) is so much faster than nuclear motion (~ 10^{-13}–10^{-14} s) that photoexcitation leads to electronic transitions across a fixed molecular geometry

- For electronic transitions between states of the same spin, the rate constant k_{obs} is limited by resonance of both Ψ_{i} and Ψ_{f} .

$$k_{obs} = k^0_{max} \times \left[\frac{\langle \Psi_i \,|P_{vib}|\Psi_f\rangle}{\Delta E_{f-i}}\right]^2 \times \langle \chi_i|\chi_f\rangle^2$$

- Accordingly conversion of electronic energy from the photoexcited transition state ***(Franck-Condon state)*** to vibrational energy resulting in a thermally equilibrated excited state ***(thexi state)*** is the rate limiting step between wavefunctions of significantly different molecular geometries.

Franck-Condon factor and transitions between electronic states

- A state energy diagram or Jablonski diagram displays the ***time-independent energies*** for the electronic states of a molecule.

- We have already discussed one time-dependent transition in absorption of a photon. Here we will focus on a time-dependent emissive decay from $S_1 \rightarrow S_0$ but ***the same principles apply to any electronic transition***.

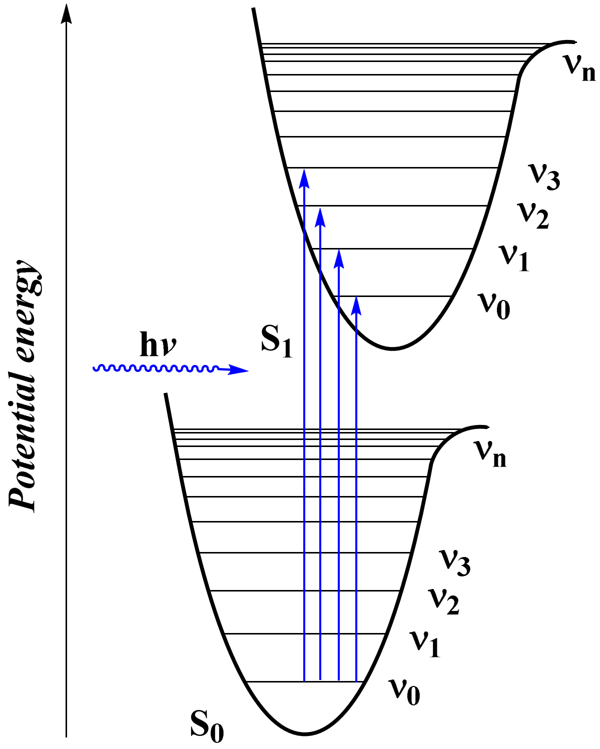
- The ***rate constant*** (k) for a transition between two electronic states, e.g. emission from $S_1 \rightarrow S_0$ (k_{fl}), can be calculated from the square of the matrix element for k_{fl} if the operator $P(S_1 \rightarrow S_0)$ and wavefunctions $\Psi(S_0)$ and $\Psi(S_1)$ are known

$$P(S_1 \rightarrow S_0) \sim \langle \Psi(S_1) | P(S_1 \rightarrow S_0) | \Psi(S_0) \rangle^{\mathbf{2}}$$

- In this case the function of the mathematical operator $P(S_1 \rightarrow S_0)$ is to calculate the probability of “mixing” (aka resonance) of both wavefunctions $\Psi(S_0)$ and $\Psi(S_1)$ which is required to trigger the transition between both electronic states.

- The mathematical form of the operator is derived from classical mechanics, adapted for quantum mechanical models to include quantization (quantum numbers) which provides the basis for *spectroscopic selection rules*.

- At room temperature, most molecules will be in the ν_0 vibrational state of the electronic ground state S_0 (Boltzmann distribution)
- Each vibrational level has an associated wavefunction, the square of which (χ^2) relates to the most probable nuclear configuration.



$$\frac{N_n}{N_0} = e^{\left(-\Delta E/_{\mathrm{RT}}\right)}$$

N_0 = population of ν_0 vibrational state

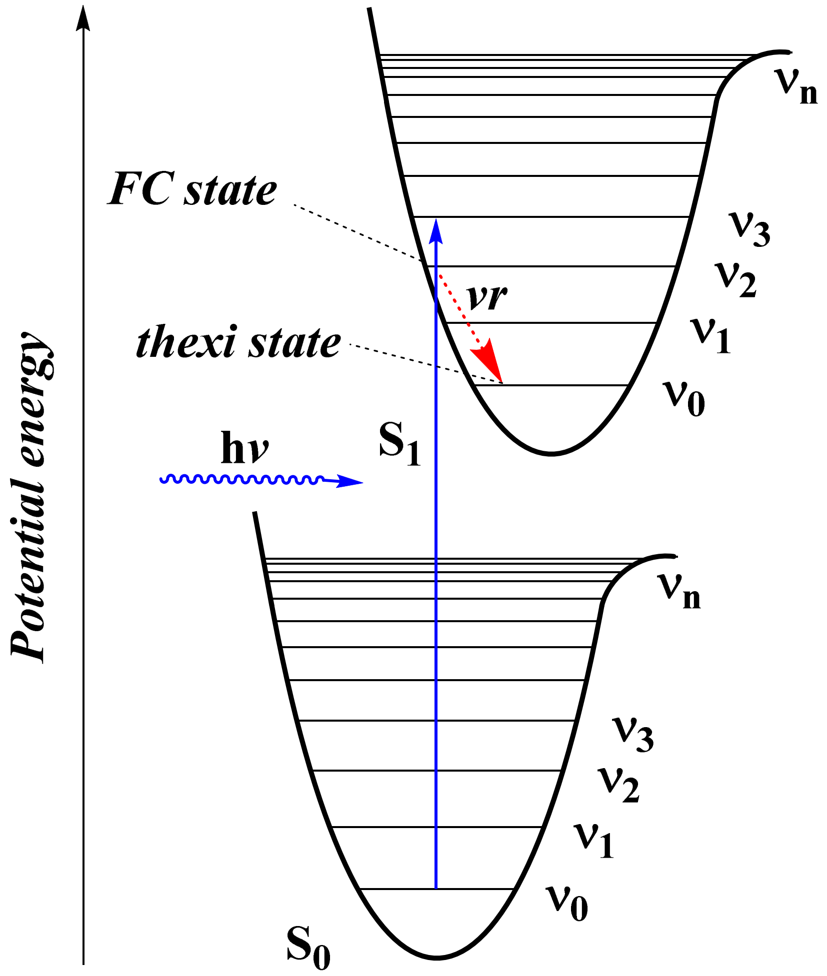
N_n = population of ν_n vibrational state

$\Delta E = E(\nu_n) - E(\nu_0)$

R = gas constant (8.314 J K^{-1} mol^{-1})

T = absolute temperature (K)

- The ***Franck–Condon principle*** is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment.
  (re. Born-Oppenheimer approximation)
- The resulting state is called a ***Franck–Condon state***, and the transition involved, a vertical transition.
- *Transition intensities are proportional to the square of the overlap integral between the vibrational wavefunctions of the two electronic states involved in the transition.*
  - ➢ the *Frank-Condon factor* $\langle \chi_1 | \chi_0 \rangle^2$



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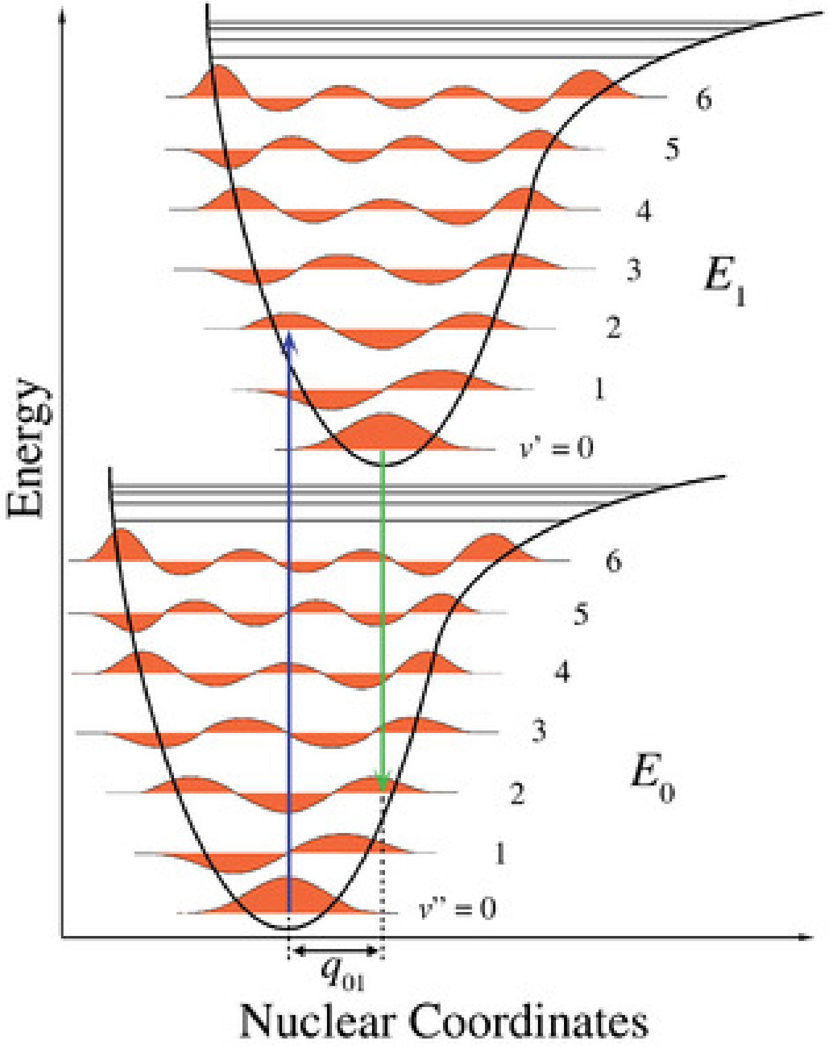


What dictates the rate of radiative or nonradiative excited state decay?

Transitions are faster when there is minimum quantum mechanical reorganization of wavefunctions. This reorganization energy includes the energy required to change both electronic structure and nuclear geometry. i.e. the closer the resemblance of $\Psi(\mathrm{S}_0)$ and $\Psi(\mathrm{S}_1)$ *the larger the rate constant* k_{fl} *and shorter the radiative lifetime* ${}^1\tau$

- In ***perturbation theory***, weak perturbations are applied to distort the zero-order wavefunction Ψ_0 and give a more accurate estimate of the transition probability, *for example:*

$$\Psi(\mathrm{S}_1) + P(\mathrm{S}_1 \rightarrow \mathrm{S}_0) \quad \rightarrow \quad \underbrace{\Psi(\mathrm{S}_1) \pm \lambda[\Psi(\mathrm{S}_0)]}_{\lambda\text{, resonance mixing coefficient}} \quad \rightarrow \quad \Psi(\mathrm{S}_0)$$

$$\lambda = \frac{strength\ of\ perturbation}{energy\ of\ separation} = \frac{\langle\Psi(\mathrm{S}_1)|P(\mathrm{S}_1 \rightarrow \mathrm{S}_0)|\Psi(\mathrm{S}_0)\rangle}{\Delta E(\mathrm{S}_1 \rightarrow \mathrm{S}_0)}$$

➢ Transition probability is dependent upon the resonance between states and the transition energy

- Rates of “fully allowed” transitions are limited only by the zero-point electronic motion (~ $10^{15} – 10^{16}$ s^{-1})

- If nuclear or spin configurations of S_1 and S_0 are not equal, mixing of $\Psi(S_0)$ and $\Psi(S_1)$ is poor, and electron transition is rate-limited by the time needed for vibrational and/or spin reorganization *(e.g. molecular rigidity, phosphorescence)*

- Vibrational and spin reorganization may act as bottlenecks in electronic transitions.

$$k_{\mathrm{obs}} \quad = \quad k^{0}_{\mathrm{max}} \quad \mathrm{x} \quad (f_{\mathrm{e}}\ f_{\mathrm{v}} f_{\mathrm{s}})$$

k_{obs} = observed rate constant

k^{0}_{max} = zero-point motion limited rate-constant (~ $10^{15} – 10^{16}$ s^{-1})

f_{e} = orbital configuration change factor (e.g. ΔE and # nodal planes)

f_{v} = vibrational configuration change factor

f_{s} = spin configuration change factor

- *Fermi’s golden rule:* $k_{obs} \sim \rho\langle\Psi(\mathrm{S}_1)\ |P(\mathrm{S}_1 \rightarrow \mathrm{S}_0)|\Psi(\mathrm{S}_0)\rangle^{\mathbf{2}}$

  *where ρ represents the **density of states** capable of mixing* $\Psi(S_0)$ and $\Psi(S_1)$ and the matrix element corresponds to the transition dipole moment.

- For electronic transitions between states of the same spin, such as $S_1 \rightarrow S_0$ the rate constant k_{obs} is limited by the time it takes for
    - the electronic wavefunction $\Psi(S_1)$ to distort so that it can mix with $\Psi(S_0)$
    - or for the vibrational wavefunction $\chi(S_1)$ to distort so that it can mix with $\chi(S_0)$
- The most important perturbation for "mixing" electronic wavefunctions is vibrational nuclear motion that is coupled to the electronic oscillation of the transition dipole (*vibronic coupling*)

$$k_{obs} = k_{max}^{0} \times \left[\frac{\langle \Psi(\mathrm{T_1})\ |P_{vib}|\ \Psi(\mathrm{S_0})\rangle}{\Delta E_{\mathrm{T1-S0}}}\right]^2 \times \langle \chi_{\mathrm{T1}} | \chi_{\mathrm{S0}} \rangle^2$$

- The matrix element here includes the vibrational operator P_{vib} that mixes $\Psi(S_1)$ and $\Psi(S_0)$.
- Strong perturbation corresponds to a strong resonance between $\Psi(S_1)$ and $\Psi(S_0)$ such that the rate limiting factor is dependent upon the square of vibrational overlap, i.e. the *Frank-Condon factor* $\langle \boldsymbol{\chi_1} | \boldsymbol{\chi_0} \rangle^2$
- The *Frank-Condon factor* $\langle \boldsymbol{\chi_1} | \boldsymbol{\chi_0} \rangle^2$ is a measure of vibronic coupling between initial and final states in an electronic transition.

- For electronic transitions between states of the different spin, such as T_1→S_0 the rate constant k_{obs} is further limited by spin-orbit coupling between between initial and final electronic states, e.g. limited by the time it takes for

$$k_{obs} = k_{max}^{0} \times \underbrace{\left[\frac{\langle \Psi(\mathrm{T}_1)\ |P_{vib}|\ \Psi(\mathrm{S}_0)\rangle}{\Delta E_{\mathrm{T1-S0}}}\right]^2}_{\substack{\textit{Vibrational}\\ \textit{coupling}}} \times \underbrace{\left[\frac{\langle \Psi(\mathrm{T}_1)\ |P_{\mathrm{SO}}|\ \Psi(\mathrm{S}_0)\rangle}{\Delta E_{\mathrm{T1-S0}}}\right]^2}_{\substack{\textit{Spin-orbit}\\ \textit{coupling}}} \times \underbrace{\langle \chi_{\mathrm{T1}} | \chi_{\mathrm{S0}} \rangle}_{\substack{\textit{Vibrational}\\ \textit{overlap}\\ \textit{Franck-Condon}\\ \textit{factors}}}{}^2$$

Transition probabilities

- A *spin-allowed* transition between two electronic states, e.g. absorption from $S_0 \rightarrow S_1$ has a rate constant k_{fl} determined by the equation

$$k_{obs} = k^0_{max} \times \left[\frac{\langle \Psi(S_0)\,|P_{vib}|\,\Psi(S_1)\rangle}{\Delta E_{1-0}}\right]^2 \times \langle \chi_0 | \chi_1 \rangle^2$$

What if the symmetry dictates that the matrix element P_{vib}= 0 ?

- In this case the electronic transition is ***forbidden*** *(…zero-order approximation)*
- All *allowed* transitions have a finite value of $P_{vib} > 0$
  …..we will discuss magnitude of P_{vib} and absorption coefficient ε shortly
- In the *first order approximation perturbation of* matrix elements P_{vib} and P_{SO} (vibronic and spin-orbit coupling) may overcame the zero-order forbidden transition character.
- If the transition probability is still small (< 1%) the process is ***"weakly allowed"*** , i.e. the transition rate k_{obs} is too slow to compete with ***"strongly allowed"*** *transitions*

Vibronic coupling…summary

- How do vibrational wave functions χ influence the rate of radiative and nonradiative spin-allowed transitions?

- The *Franck-Condon factor* $<\chi_0|\chi_1>^2$ is a measure of the similarity of the vibrational wavefunctions for Ψ_0 and Ψ_1 and are critical in determining whether a transition is allowed or forbidden.

$$k_{obs} \sim \langle \chi_0 | \chi_1 \rangle^2$$

- The *Born-Oppenheimer approximation* allows a zero-order approximation of electronic structure & energy of an electronic state with a fixed nuclear *(nonvibrating)* and spin configuration

$$\Psi \cong \Psi_0 \chi S$$

To appreciate vibronic coupling and its influence on electronic transitions we must consider the effect of nuclear vibrational motion on the electronic structure & energy of a molecule and the perturbation it provides allowing resonance of difference electronic state wavefunctions.

- Molecular vibrations are constantly active, opening the possibility of mixing electronic states, should perturbation of the resonance mixing coefficient distort the initial electronic wavefunction to resemble that of the final state

$$\Psi(S_0) \pm \lambda[\Psi(S_1)]$$

- The energy of a these weak vibronic perturbations E_{vib} are defined as

$$E_{vib} = \frac{\langle \psi(\mathrm{S}_0)\ |P_{vib}|\ \psi(\mathrm{S}_1)\rangle^2}{\Delta E_{0-1}}$$

- Applying Fermi's golden rule:

$$k_{obs} \sim \rho\langle \psi(\mathrm{S}_0)\ |P_{vib}|\ \psi(\mathrm{S}_1)\rangle^{\mathbf{2}}$$

where ρ represents the ***density of states*** *capable of mixing* $\Psi(S_0)$ and $\Psi(S_1)$

$$\lambda \sim \frac{1}{\Delta E}$$

- *Large band-gap → small resonance mixing coefficient ≡ a low density of states*
- *Small band-gap → high resonance mixing coefficient ≡ high density of states*

$$E_{vib} = \frac{\langle \psi \, |P_{vib}| \, \psi \rangle^2}{\Delta E}$$

- Consider low band-gap organic chromophore, with and absorption maximum at λ = 600 nm. This corresponds to ΔE_{0-1} = 48 kcal mol^{-1}
  - C–H stretch ~ 3000 cm^{-1} ; E_{vib} = 8.58 kcal mol^{-1}
  - C≡C stretch ~ 2180 cm^{-1} ; E_{vib}= 6.23 kcal mol^{-1}
  - C=O stretch ~ 1700 cm^{-1} ; E_{vib}= 4.86 kcal mol^{-1}
  - C=C stretch ~ 1660 cm^{-1} ; E_{vib}= 4.75 kcal mol^{-1}
  - C=N stretch ~ 1650 cm^{-1} ; E_{vib}= 4.72 kcal mol^{-1}

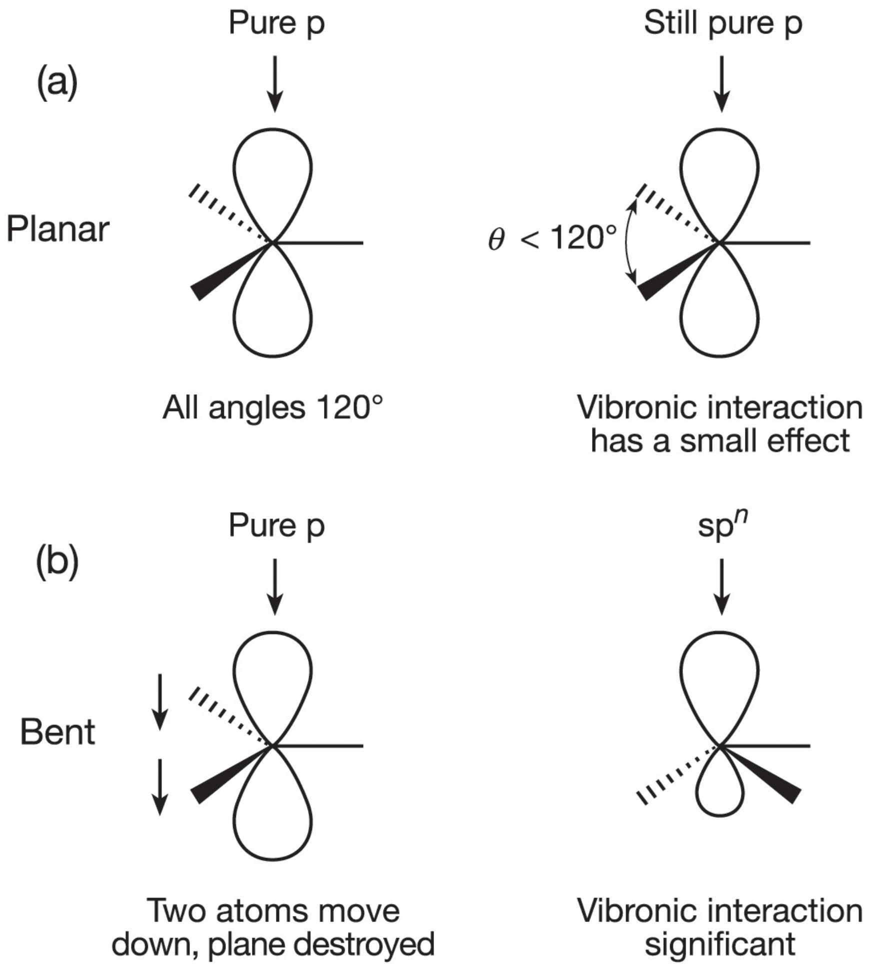
Vibronic coupling between ground and excited states is very weak due to large Δ*E* however excited state energy gaps are much smaller and vibronic coupling becomes very important. C–H stretches are very effective in mixing electronically excited states

- Born-Oppenheimer approximation only works well for ground state molecules where ground state vibrations do not mix with electronically excited states effectively.

- Radiative and nonradiative electronic transitions depend upon the ability of vibrations (distortion of the molecular geometry) to couple the initial electronic wavefunction to vibrations of the final electronic wavefunction, particularly for electronic excited states.

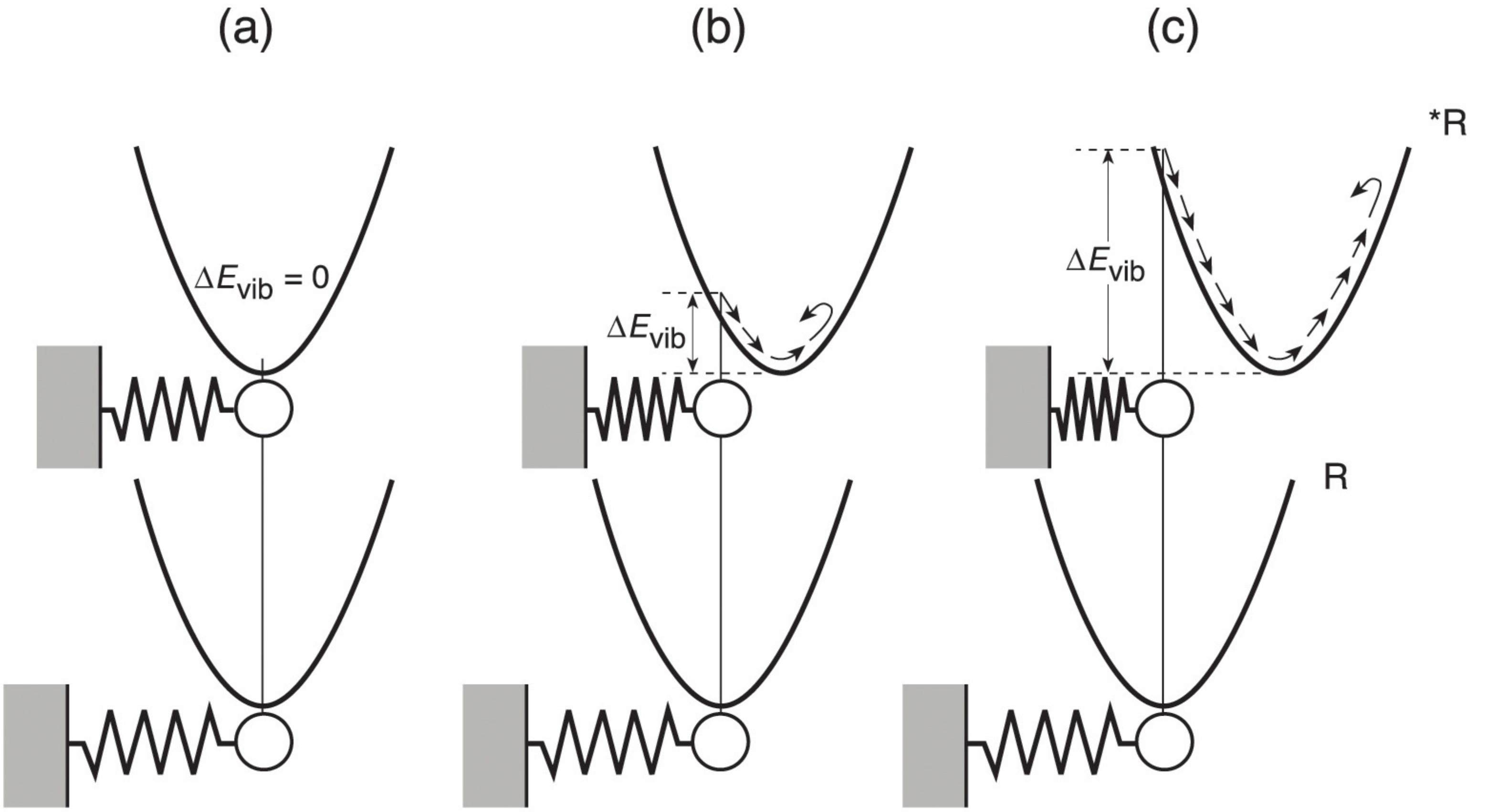
a) "weak vibronic coupling"
In-plane symmetric stretching for an *sp*^{2} hybridized C atom has no effect of the spatial distribution of the *p* orbital. This vibrational stretch is *decoupled* from the electronic wavefunction.

b) "strong vibronic coupling"
Asymmetric stretching causes the atom to re-hybridize to *sp*^{3} illustrating distortion of the electronic wavefunction for the molecule whose energy will change (lower) accordingly.



Classical harmonic oscillator model of the Franck-Condon principle: radiative transitions

- Consider three different situations (a, b & c) for a heteronuclear diatomic molecule with $m_1 >> m_2$ e.g. C–H



- The timescale for photoabsorption is on the order of ~ 10^{-15} – 10^{-16} s such that the geometry produced at the instance of the electronic transition to the upper surface by a radiative transition, e.g. fro S_0 to S_1, is governed by the relative positions of the PE surfaces controlling the vibrational motion.

- Assuming both PE curves have similar shapes (i.e. identical bond order) the most favored transitons are predicted to be

  a) $S_0(v_0) + h\nu \rightarrow S_1(v_0)$

    - typical of extensively conjugated cyclic π systems, e.g. anthracene

  b) $S_0(v_0) + h\nu \rightarrow S_1(v_n)$ $n > 0$

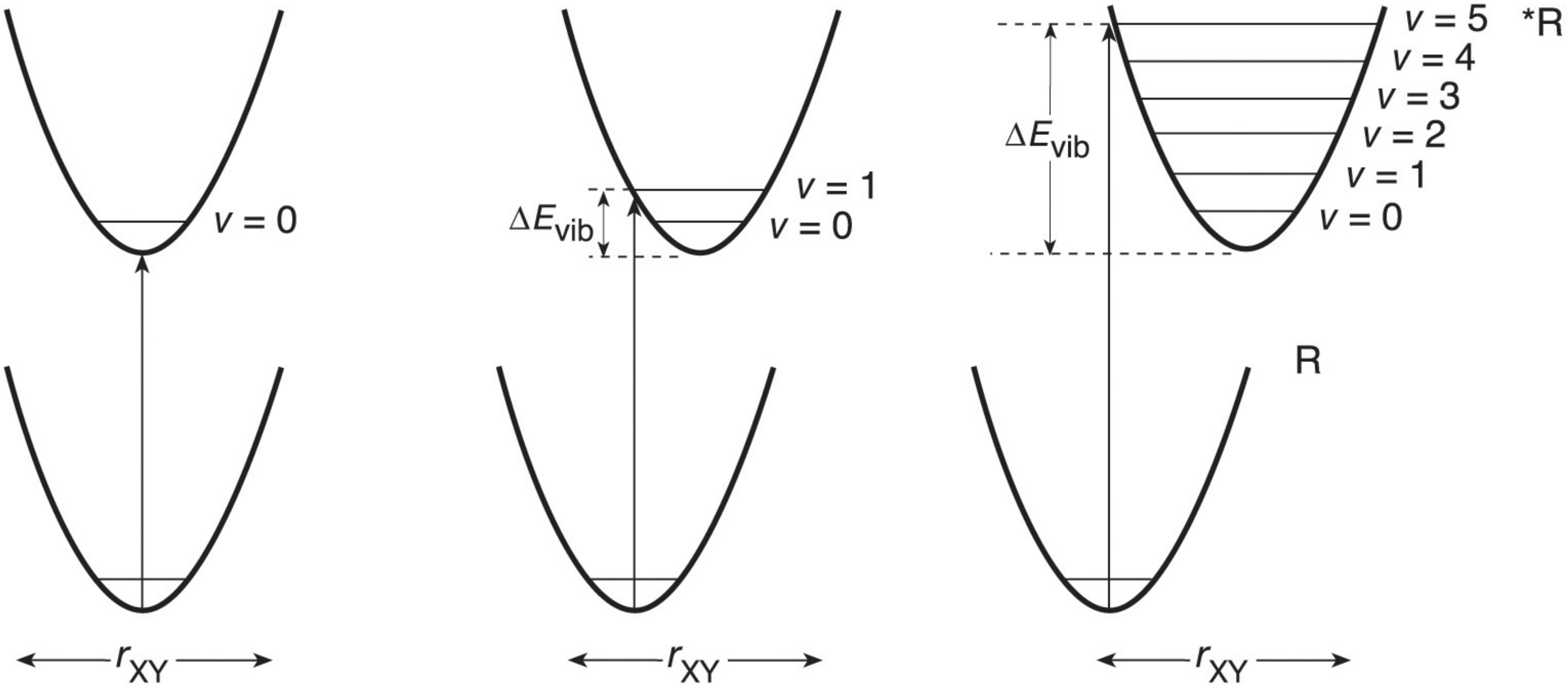
    - typical of n→π* systems, e.g $Ph_2C{=}O$

  c) $S_0(v_0) + h\nu \rightarrow S_1(v_x)$ $x > n$

    - typical conjugated acyclic π systems with vibrational freedom

- It follows that the original nuclear geometry of the ground state is a turning point of the new vibrational motion in the excited state, and that vibrational energy is stored by the molecule in the excited state.

- In a semi-classical model where we impose quantization on the classical harmonic oscillator, radiative transitions from $v = 0$ are not initiated from a single geometry but from a range of geometries that are explored during the zero-point motion of the vibration.



Quantum mechanical harmonic oscillator model of the Franck-Condon principle: radiative transitions

- Expressed in quantum mechanical terms the Franck-Condon principle states that *the most probably transitions between electronic states occur when the wave function of the initial vibrational state* (χ_i) *most closely resembles the wave function of the final vibrational state* (χ_f)*.*

- Mathematically we represent the vibrational wavefunction overlap integral as

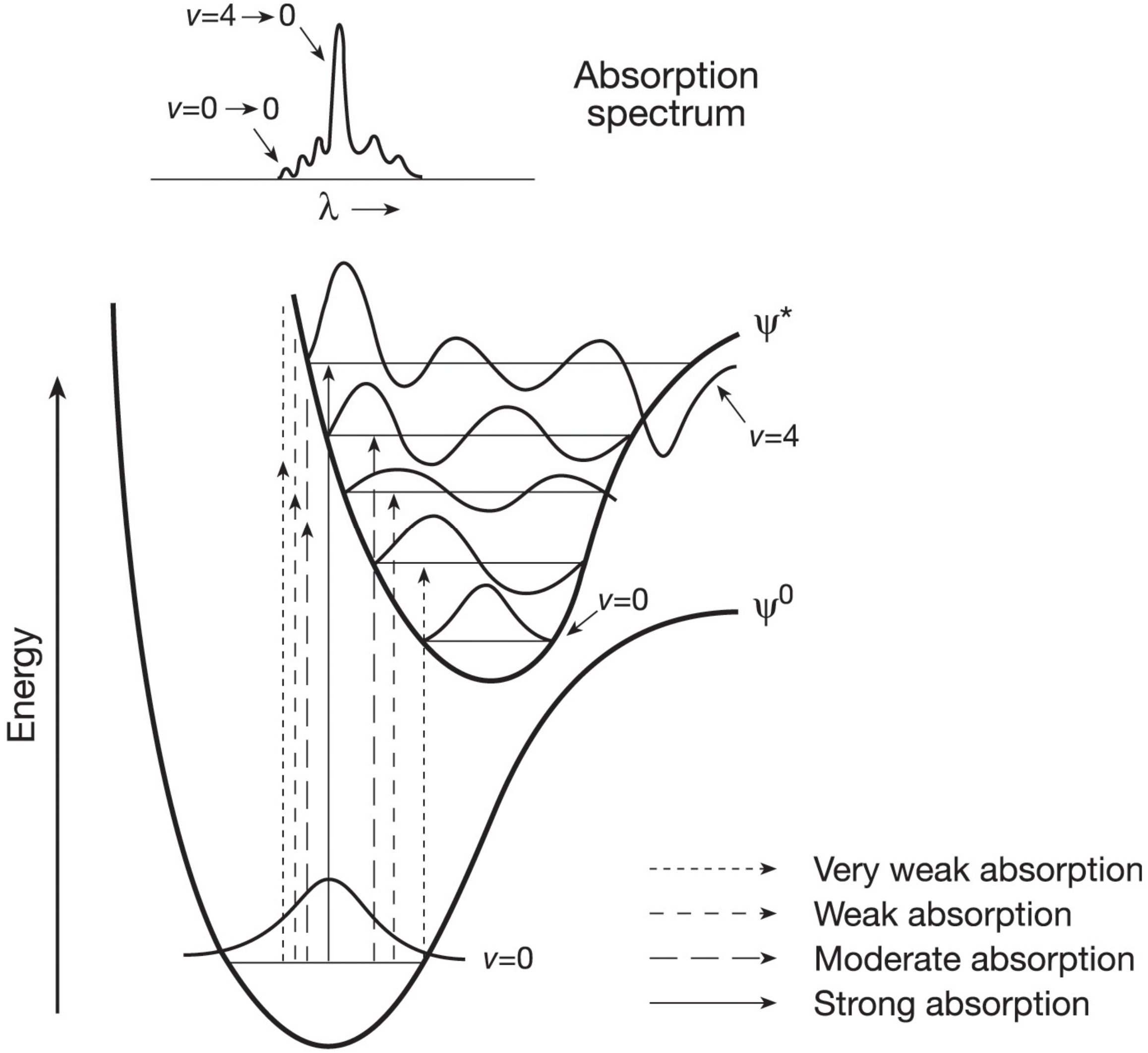
$$<\chi_0|\chi_1>$$

- Hence the term ***Franck-Condon factor***

$$k_{obs} = k^0_{max} \times \underbrace{\left[\frac{\langle \Psi_i \,| P_{vib} | \Psi_f \rangle}{\Delta E_{f-i}}\right]^2}_{\textit{Vibrational coupling}} \times \underbrace{\left[\frac{\langle \Psi_i \,| P_{\mathrm{SO}} | \Psi_f \rangle}{\Delta E_{f-i}}\right]^2}_{\textit{Spin-orbit coupling}} \times \underbrace{\langle \chi_i | \chi_f \rangle^2}_{\textit{Franck-Condon factor}}$$

- The Franck-Condon principle provides a useful visualization of both radiative and noradiative transitions

- The larger the FC factor $<\chi_0|\chi_1>^2$ the greater constructive overlap of vibrational wavefunctions the smaller the nuclear reorganization the more probable the electronic transition.



- **The FC factor provides a selection rule for electronic transitions and governs the relative intensities of radiative transitions (absorption and emission).**

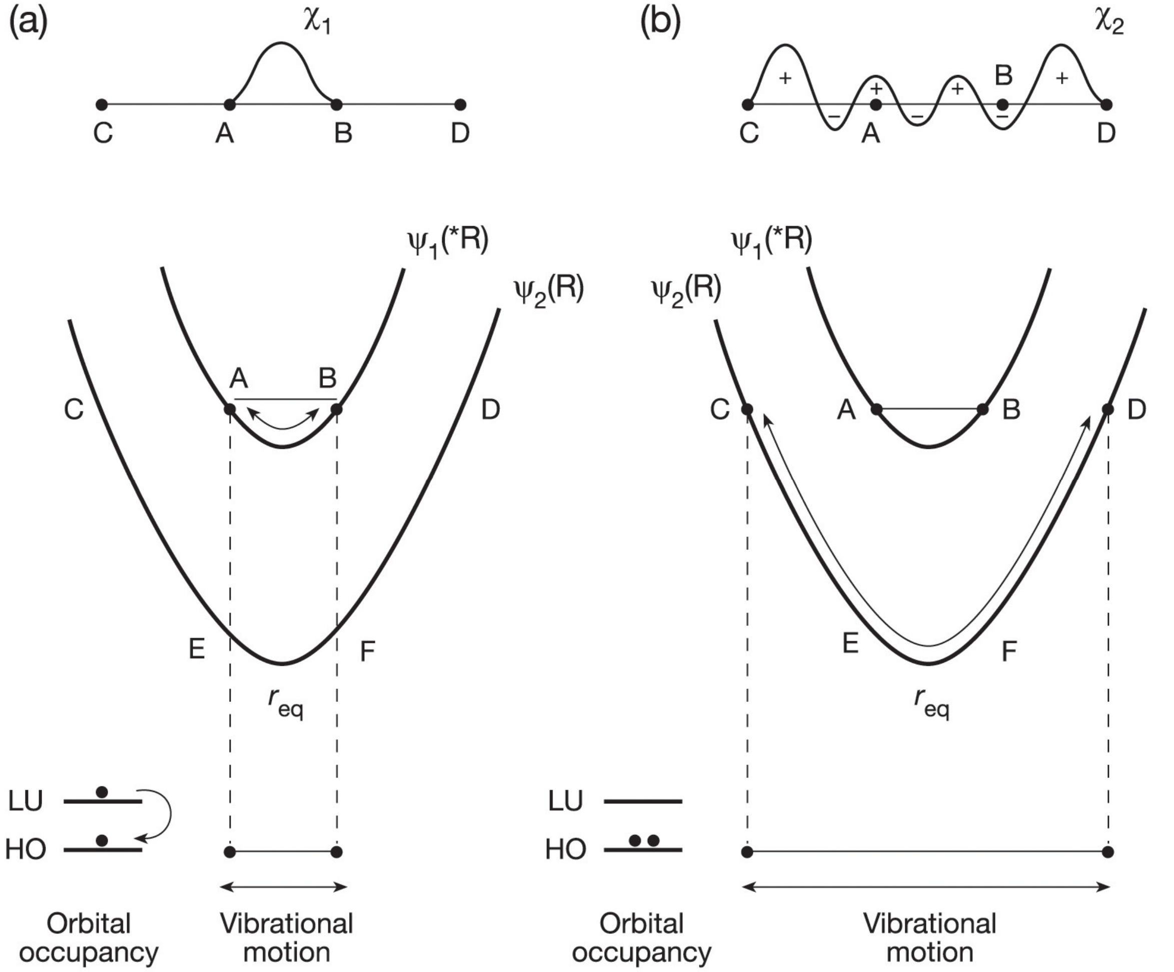
- For emissive processes the critical overlap is between the χ corresponding to $S_1(v_0)$ and the various vibrational levels (v_n) of S_o

Nonradiative transitions & the Franck-Condon principle

- For a radiationless transition, the initial and “final” electronic states must have the same energy and the same nuclear geometry.
- Typically a small amplitude vibration (usually v_0) of a higher electronic state couples vibronically with a higher amplitude vibrational state v_n of a lower energy electronic state.
- Subsequent equilibration of the v_n state of the lower energy electronic state results in dissipation of heat to the molecules local environment (solvent).

$$S_1(v_0) \rightarrow [\ S_0(v_n)\ ] \rightarrow S_0(v_0)\ \ + \text{heat}$$

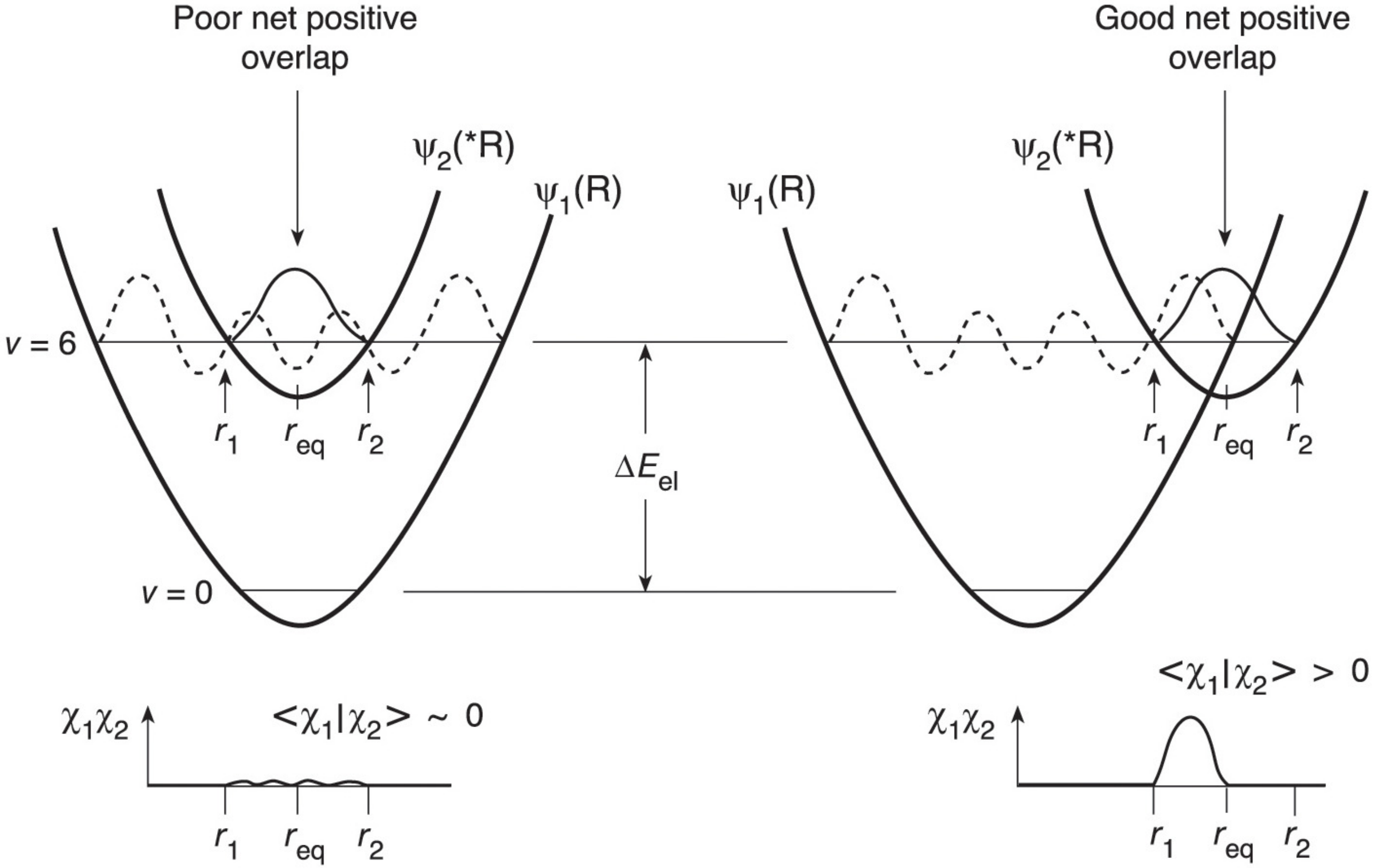
- Only at the crossing point of two wavefunctions does each state have the same energy.
- For a radiationless transition, e.g. from S_1 to S_0 , ***energy and momentum must be conserved.***



(a) Clasical model (b) Quantum mechanical model

- A→C (or B→D) conserves energy but requires a change in geometry. A direct transition here at points A and B will conserve geometry at the expense of an increase in amplitude of the vibrational wavefunction
- A → E (or B→F) conserves geometry but requires a change in energy
- Such transitions with large reorganization energies have a negligible overlap integral of vibrational wavefunctions $<\chi_0|\chi_1>$ and are implausible.

- Radiationless transitions are most probable when two PE curves for a vibration cross (or come very close to one another). In this scenario the energy, motion, and phase of the nuclei are conserved during the transition.



- If there is a spin change associated with the horizontal transition the transition is strictly forbidden in a zero-order approximation.

- Mixing of spin states requires a change in spin angular momentum.

- Total angular momentum must be conserved however so any change in spin angular momentum is here associated with a change in orbital angular momentum…this defines *spin-orbit coupling.*

- A first order approximation invokes spin-orbit coupling which enables resonance between, e.g. singlet and triplet states, making *intersystem crossing* possible.

Oscillator strength (*f*): classical model

- ***f*** , absorption oscillator strength, is a measure for the integrated intensity of electronic transitions. In classical terms; the ratio of light intensity absorbed by a chromophore relative to an electron which behaves as a perfect harmonic oscillator (***f*** = 1).

- For ***f*** = 1, every photon of the appropriate frequency that interacts with the electron will be absorbed.

- The oscillator strength ***f*** may be related to the molar absorption coefficient ε assuming that the harmonic oscillating electronic excited state is unidimensional, i.e. an oscillating dipole.

$$f = 4.3 \times 10^{-9} \int \varepsilon \, d\bar{\nu}$$

- The integral component corresponds to the area under the absorption curve on a plot of molar absorptivity vs. wavenumber (ε vs. $\bar{\nu}$). As ε is characteristic for each frequency, line intensity is sufficient here without integration.

- Classical theory fails to explain the wide variation in oscillator strengths

Oscillator strength (f): quantum mechanical model

- For an electronic transition to occur an oscillating dipole must be induced by interaction of the molecules electric field with electromagnetic radiation.
- To understand the absorption coefficient a knowledge of dipole moments is required.
- In fact both ε and k^0 can be related to the transition dipole moment (μ_{ge})
- If two equal and opposite electrical charges (e) are separated by a vectorial distance (**r**), a dipole moment (μ) of magnitude equal to e**r** is created.

$$\mu = e\,\mathbf{r}$$

(e = electron charge,
r = extent of charge displacement)

- The magnitude of charge separation, as the electron density is redistributed in an electronically excited state, is determined by the polarizability of the electron cloud (α) which is defined by the transition dipole moment (μ_{ge})

$$\alpha = \mu_{\mathrm{ge}} / \boldsymbol{E}$$

(***E*** = electrical force)

$$\mu_{\mathrm{ge}} = e\,\mathbf{r}$$

- The magnitude of the oscillator strength (f) for an electronic transition is proportional to the square of the transition dipole moment produced by the action of electromagnetic radiation on an electric dipole.

$$f \propto \boldsymbol{\mu}_{\mathrm{ge}}{}^2 = (e\,\mathbf{r})^2$$

- The dipole strength of an electronic transition is equal to e**r** which can be viewed as the average size of the transition dipole moment where **r** is the dipole vector length.

- Combining the classical oscillator strength with the quantization of the oscillation of electrons we have an expression relating f and $\boldsymbol{\mu}_{\mathrm{ge}}$

$$f = \left(\frac{8\,\pi\,m_e\,\bar{\upsilon}}{3\,h\,e^2}\right)\boldsymbol{\mu}_{ge}^2 \;\cong\; 10^{-5}\,\bar{\upsilon}\,\left|e\mathbf{r}_{ge}\right|^{\,2}$$

- This equation may be rewritten to express f in terms of the matrix element of initial and final electronic state wave functions which are responsible for the transition dipole moment

$$f = \left(\frac{8\,\pi\,m_e\,\bar{\upsilon}}{3\,h\,e^2}\right)\langle\Psi_1|\boldsymbol{P}|\Psi_2\rangle^{\,2}$$