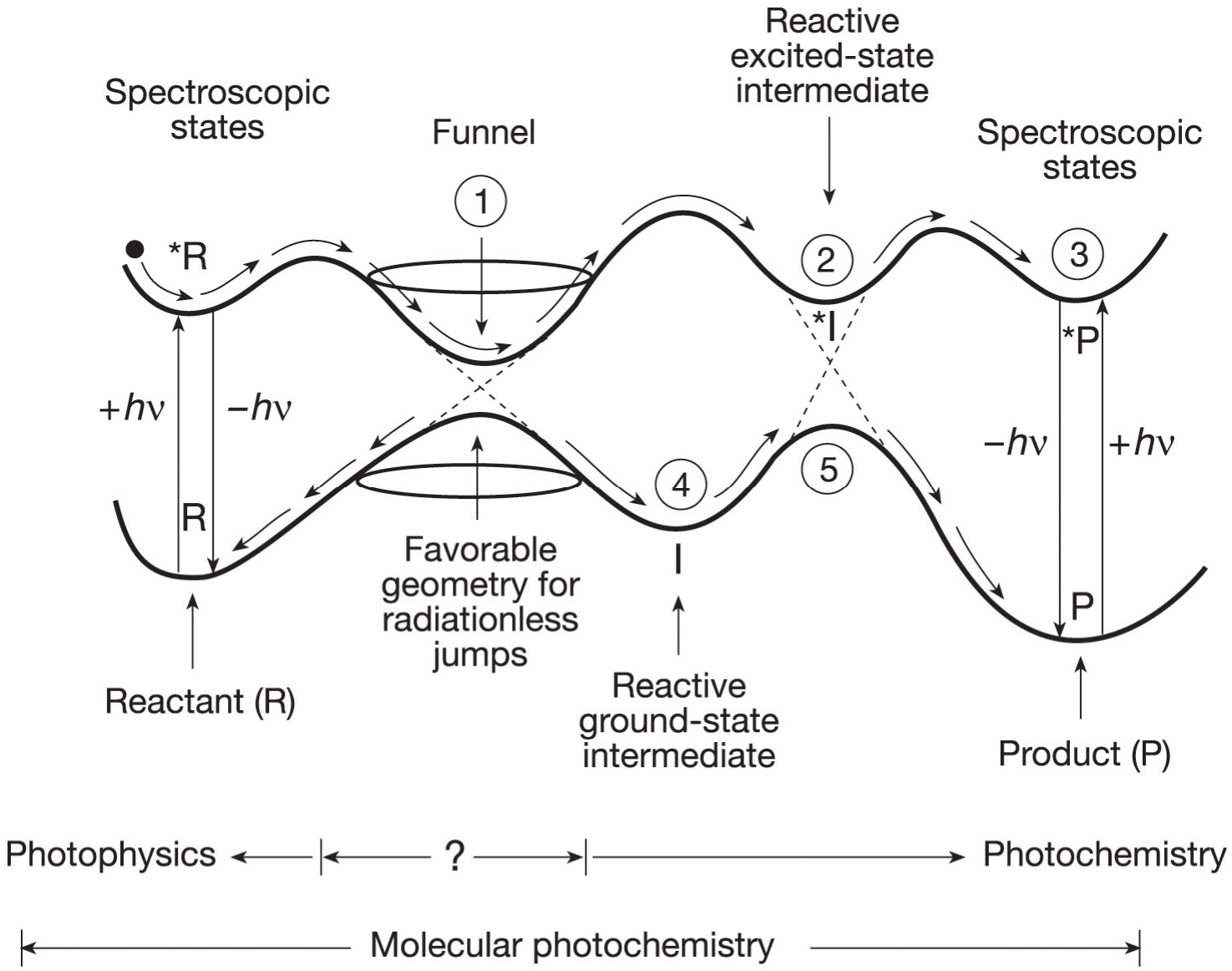
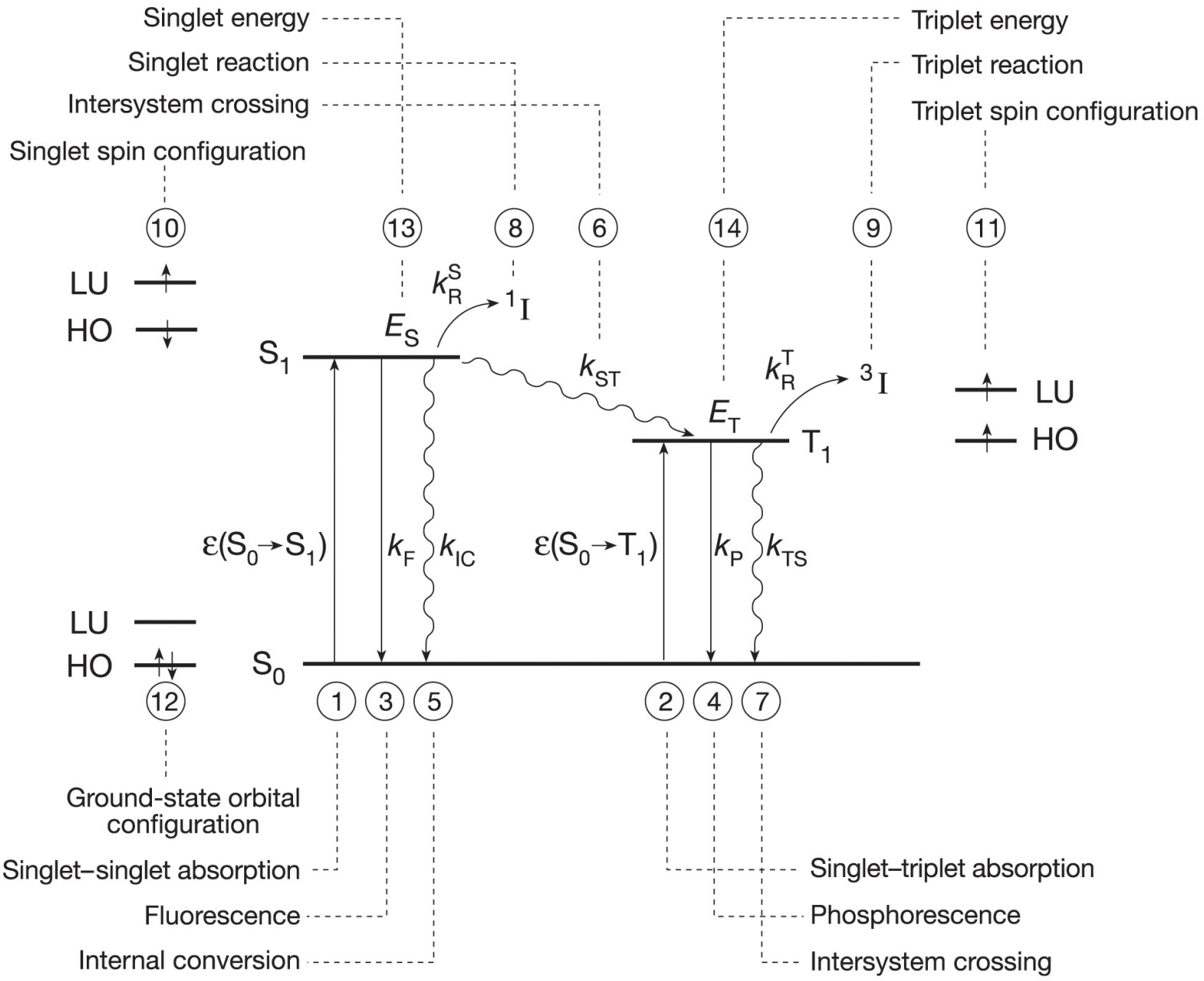
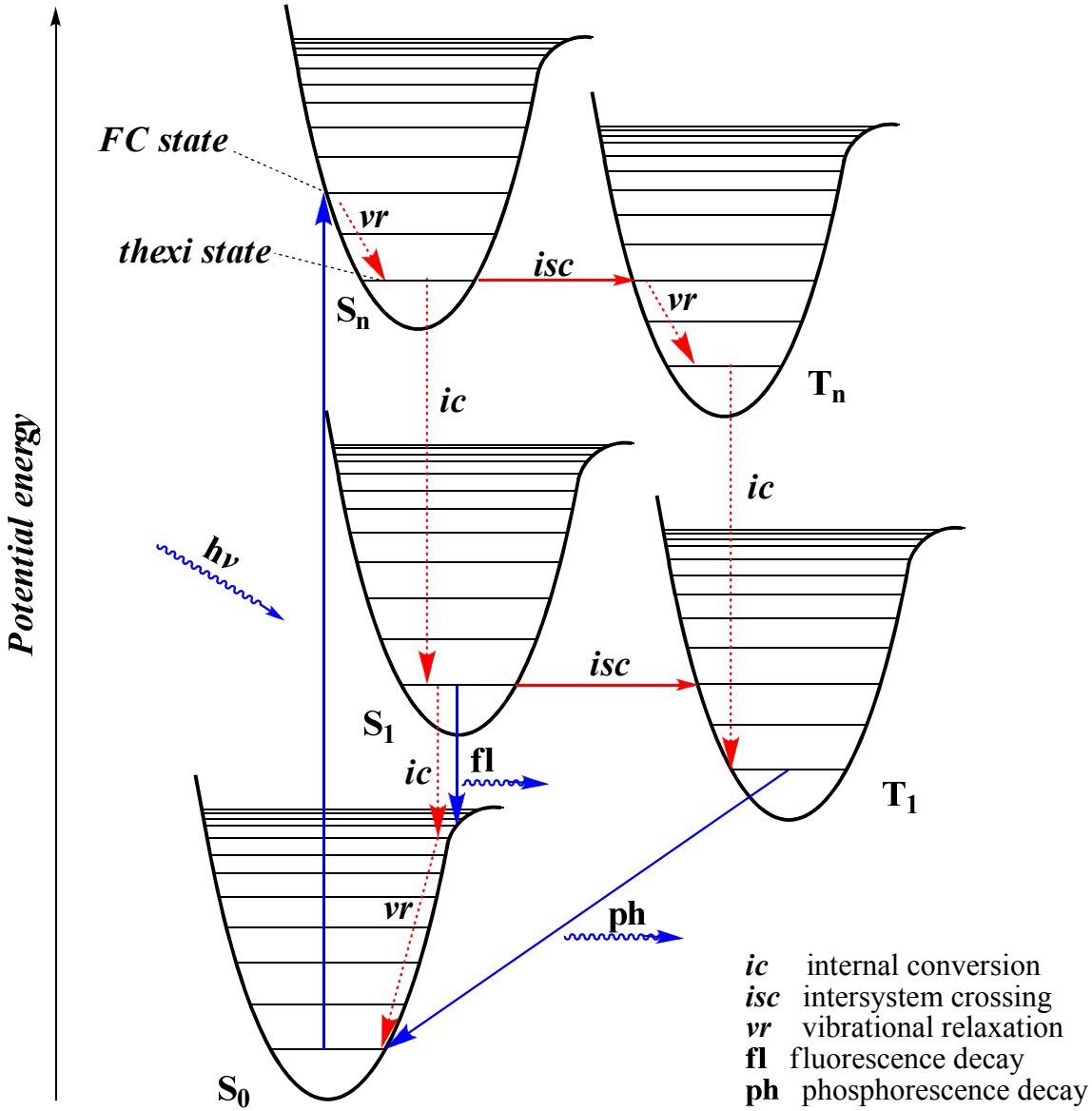

Spectroscopic states
Funnel
Reactive excited-state intermediate
Spectroscopic states
1
2
3
*R
*I
*P
+hν
−hν
−hν
+hν
R
4
5
Favorable geometry for radiationless jumps
I
P
Reactant (R)
Reactive ground-state intermediate
Product (P)
Photophysics
?
Photochemistry
Molecular photochemistry


Singlet energy
Singlet reaction
Intersystem crossing
Singlet spin configuration
Triplet energy
Triplet reaction
Triplet spin configuration
10
13
8
6
14
9
11
LU
HO
k_R^S
^1I
E_S
S_1
k_{ST}
k_R^T
^3I
E_T
T_1
LU
HO
$\varepsilon(S_0 \rightarrow S_1)$
k_F
k_{IC}
$\varepsilon(S_0 \rightarrow T_1)$
k_P
k_{TS}
LU
HO
S_0
12
1
3
5
2
4
7
Ground-state orbital configuration
Singlet–singlet absorption
Fluorescence
Internal conversion
Singlet–triplet absorption
Phosphorescence
Intersystem crossing

Scheme 1.4

Jablonski diagram



Basic concepts

- wave-particle duality of photons/electrons
- quantization and atomic and molecular structures
- Schrödinger wave equation $H\psi = E\psi$
- principle (n), angular momentum (l), magnetic (m_l) and spin (m_s)
- ψ^2 = the probability of finding the electron at a particular location in space
- Pauli exclusion principle - no two e^-s share the same quantum numbers
- Total spin = Σm_s multiplicity m = 2s + 1

Basic concepts

- Planck's law; $E = h\nu = hc/\lambda$ where h is Planck's constant (6.626×10^{-34} Js)
- wavelength uses units of nm (10^{-9} m) or Å (10^{-10} m)
- wavenumber (ν) uses units of cm^{-1} (= 10^7/nm)
- 1 einstein = 1 mol photons = $N(hc/\lambda)$ J
- 1 eV = 1.602×10^{-19} J
- Frequency uses units of Hz (= s^{-1}).

Colour	λ/nm	$\nu/10^{14}$ Hz	$\bar{\nu}/10^4$ cm^{-1}	E/kJ mol^{-1}	eV
red	700	4.3	1.4	170	1.77
orange	620	4.8	1.6	193	1.99
yellow	580	5.2	1.7	206	2.14
green	530	5.7	1.9	226	2.34
blue	470	6.4	2.1	254	2.64
violet	420	7.1	2.4	285	2.95
ultraviolet	<300	>10.0	>3.3	>400	>4.13

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.

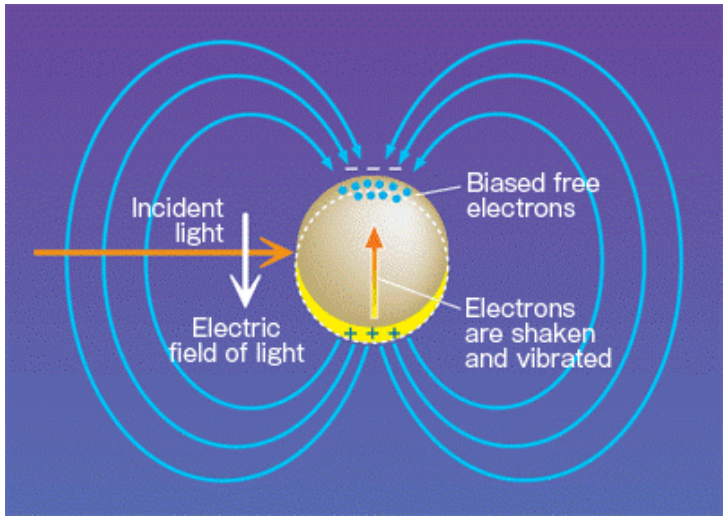
  - *frequency matching (resonance) rule* ($\nu = E / h$)

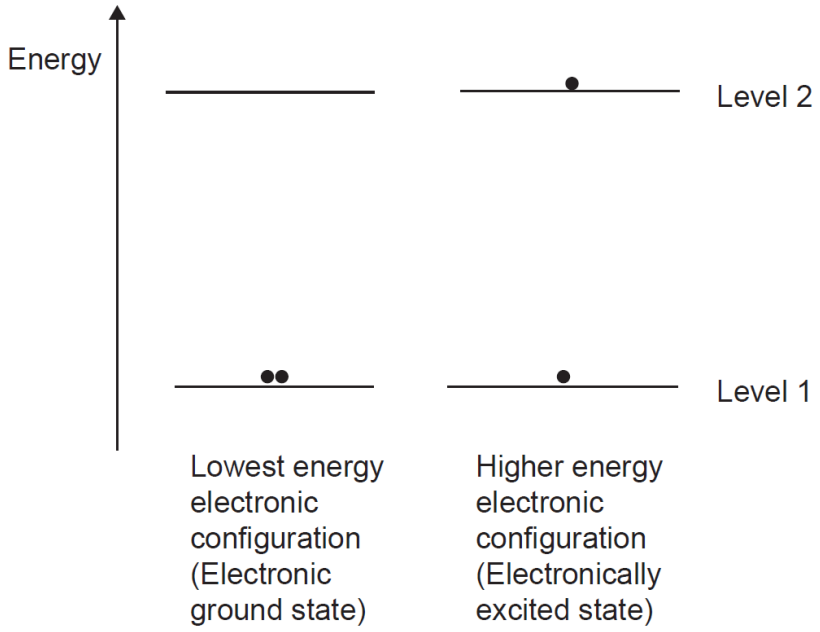
    there must be a matching of frequency (ν) of the oscillating light wave and a frequency that corresponds to the formation of a transition dipole moment.

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.

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

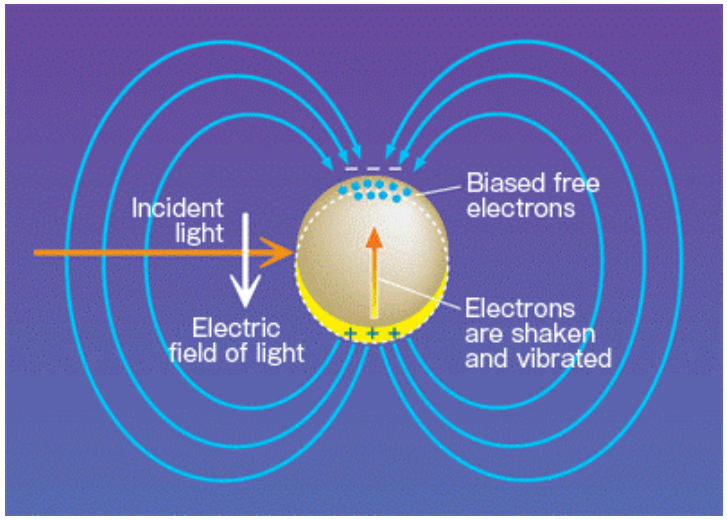




Classical description for light absorption (harmonic oscillator model)

- 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.

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



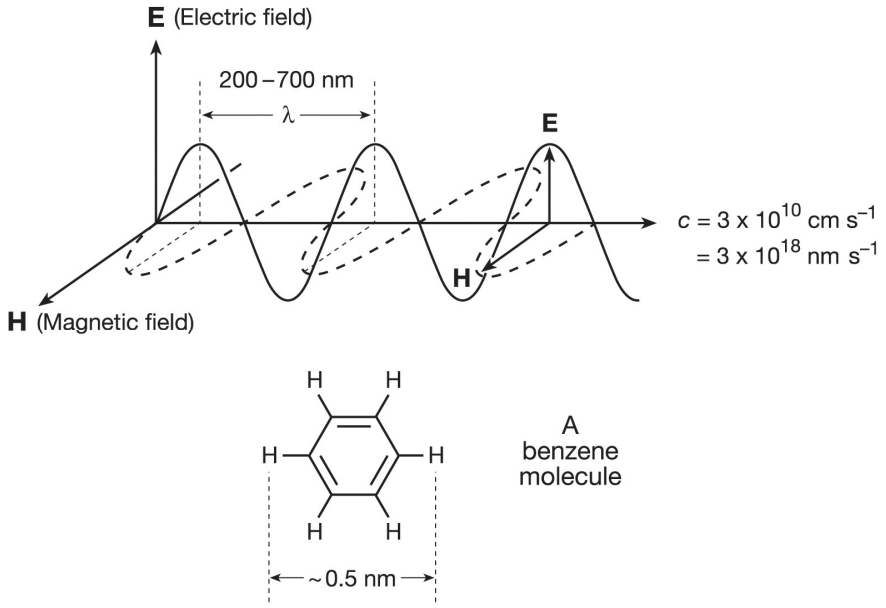


Figure 4.3 copyright 2009 University Science Books

- 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** ($\Delta\mu = \mu_{ee} - \mu_{gg}$)

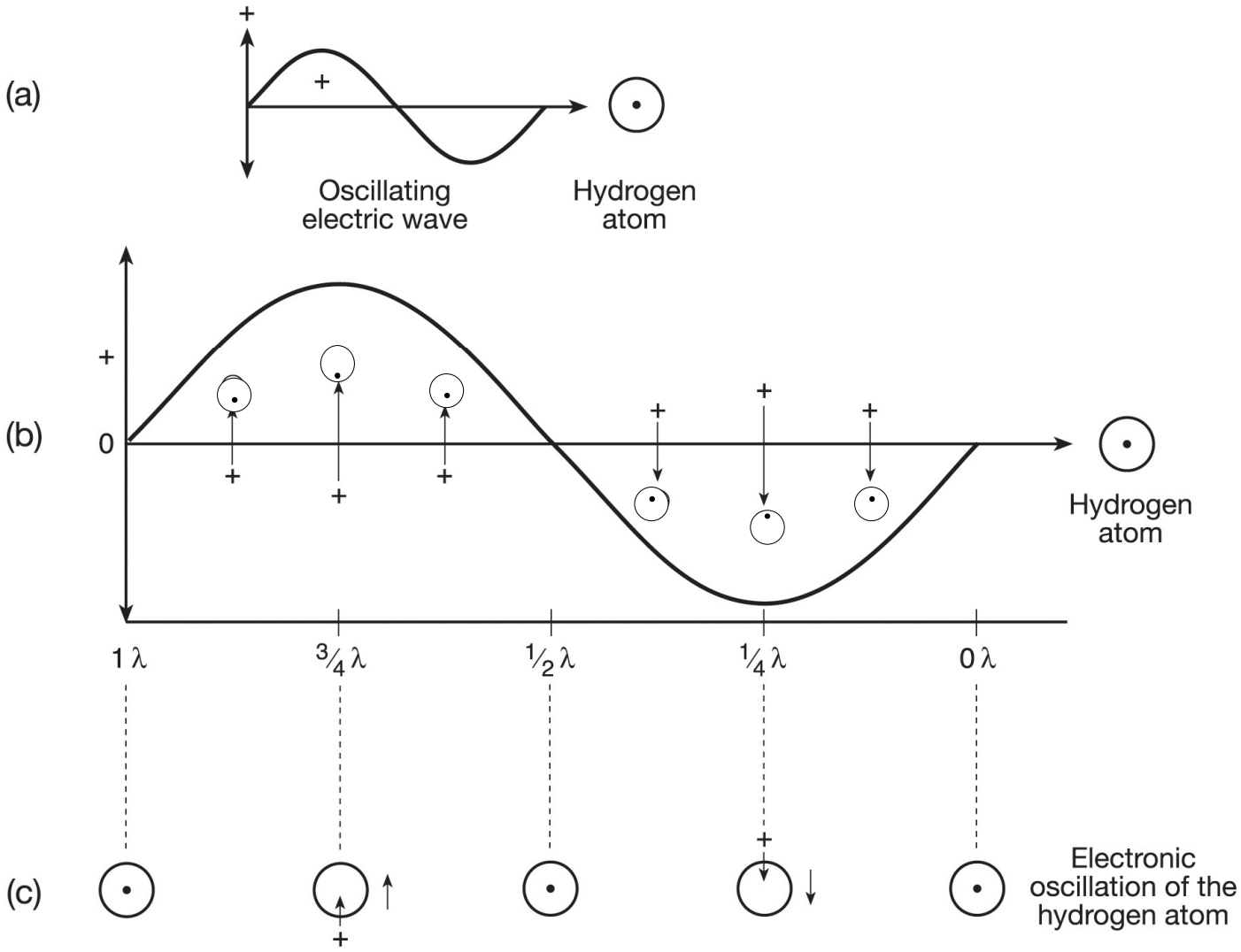
Photoexcited states are dynamic electronic states!

- 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.

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



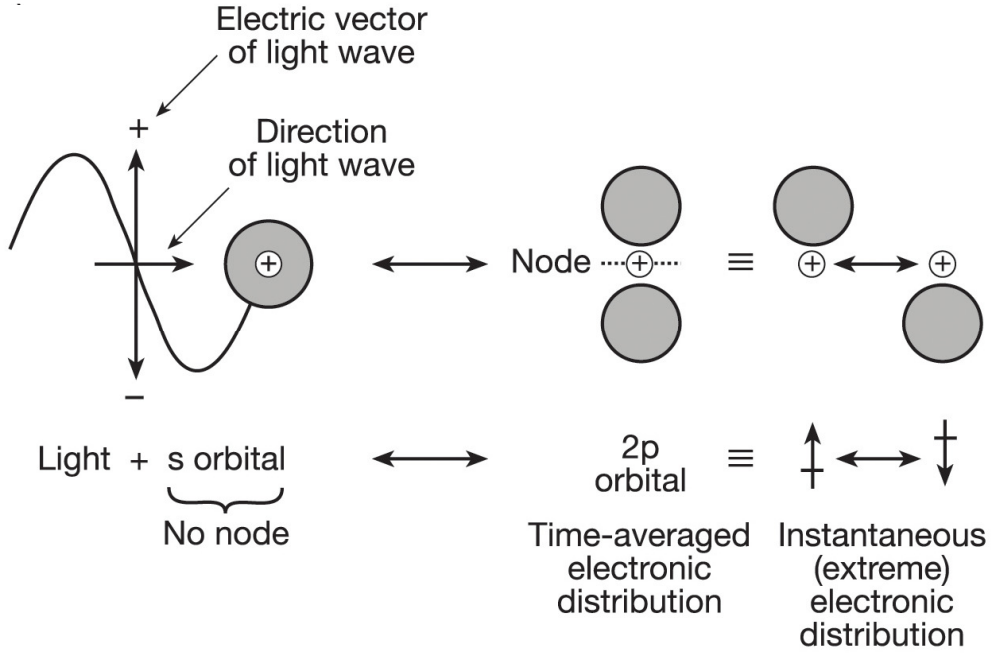
- Schematic of the electronic component of an electromagnetic wave interacting with the Bohr orbit of the H atom (classical model).

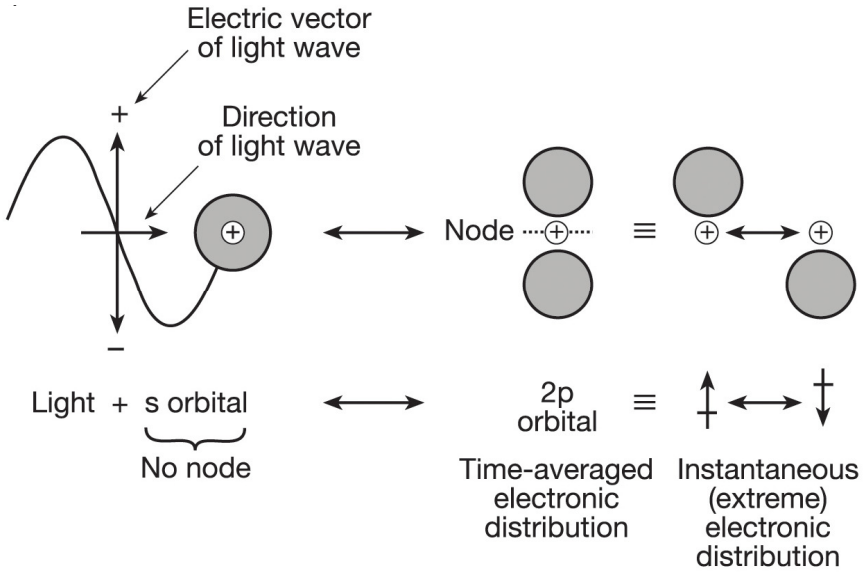
Physical basis for light absorption – Quantum model

- 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.

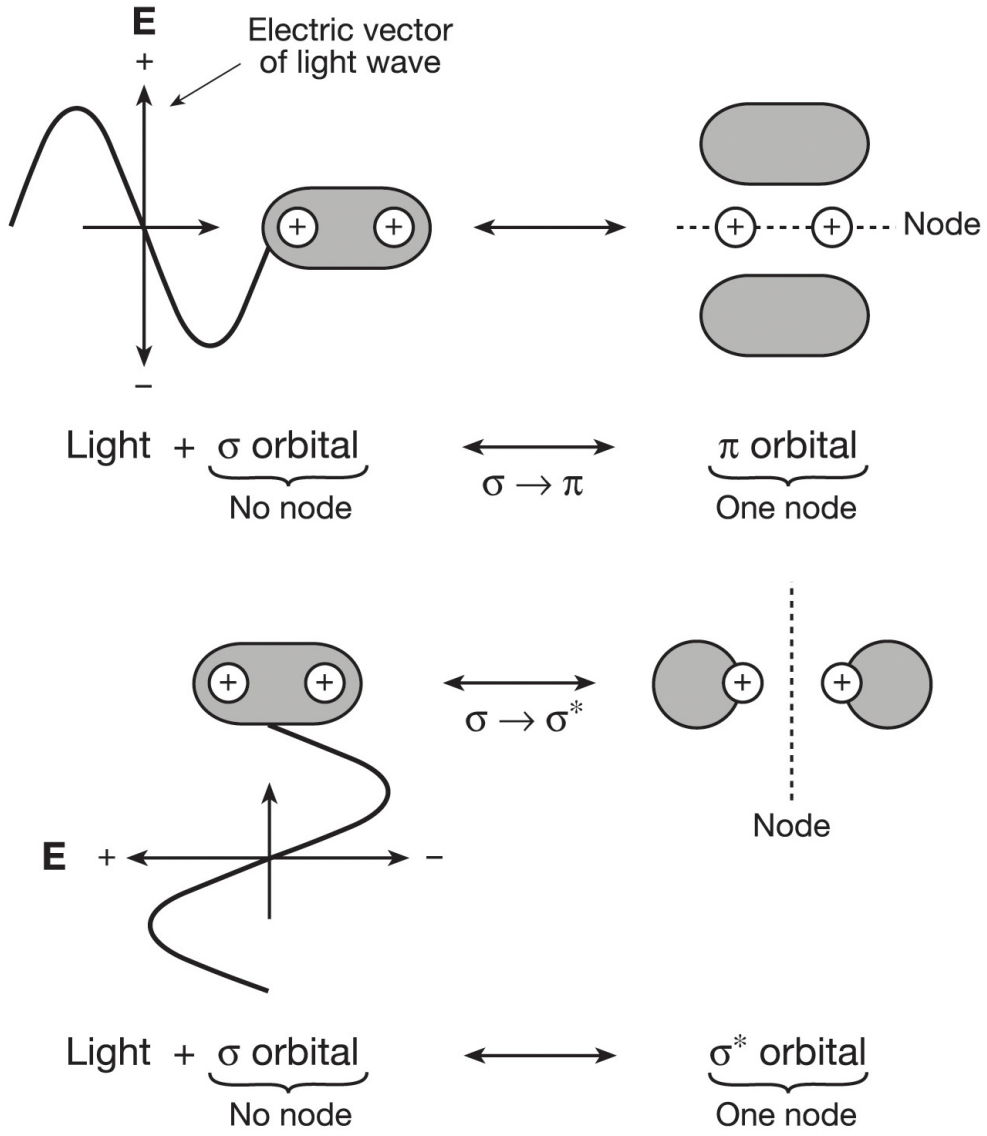
- Thus, this example shows how electronic excitation obeys two important requirements for a photochemical process:

1) The conservation of energy (ΔE = 0)

2) The conservation of angular momentum(Δl = 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.

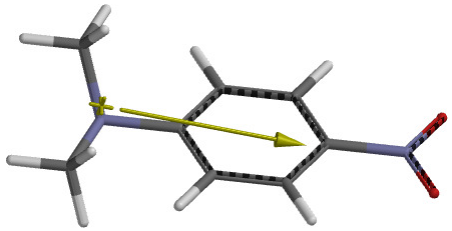


- Production of a single node in the wavefunction corresponds to the change of angular momentum (Δl = +1) by a single unit $\hbar$ (= $h/2\pi$)

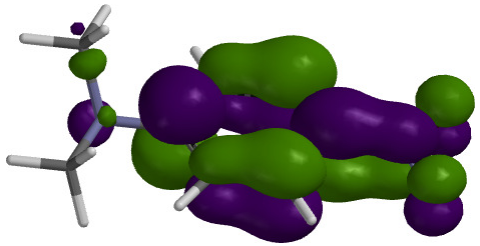
- The magnitude of charge separation, as the electron density is redistributed in an electronically excited state, is determined by the polarizability of the electron cloud (α) which is defined by the transition dipole moment (μ_{ge})

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

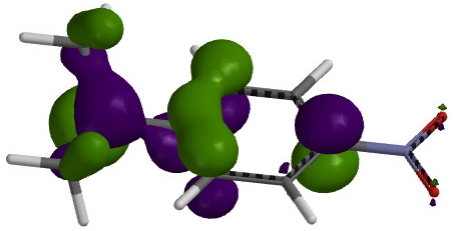
$$\mu_{ge} = e\,\mathbf{r}$$ (**e** = electron charge, **r** = extent of charge displacement)



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 90° 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).

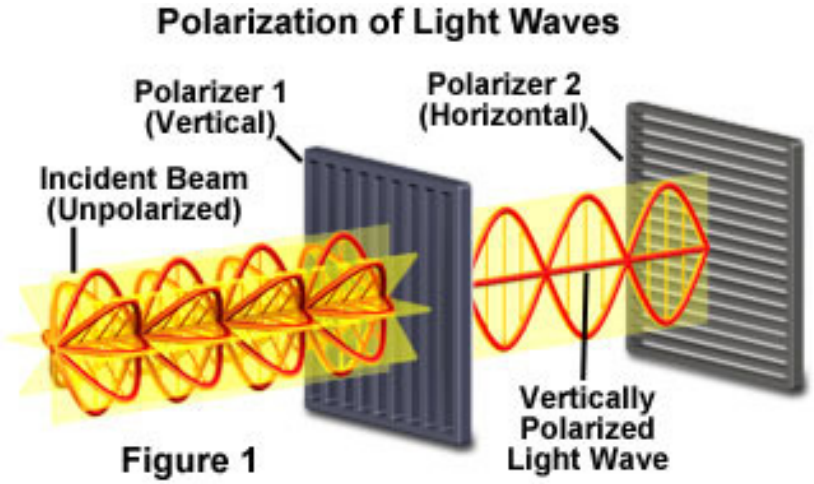


Figure 1

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

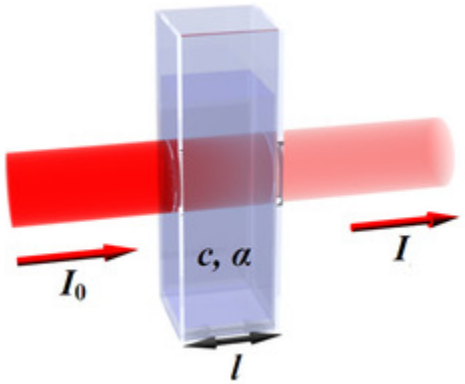
σ = optical cross section (α / N)

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})

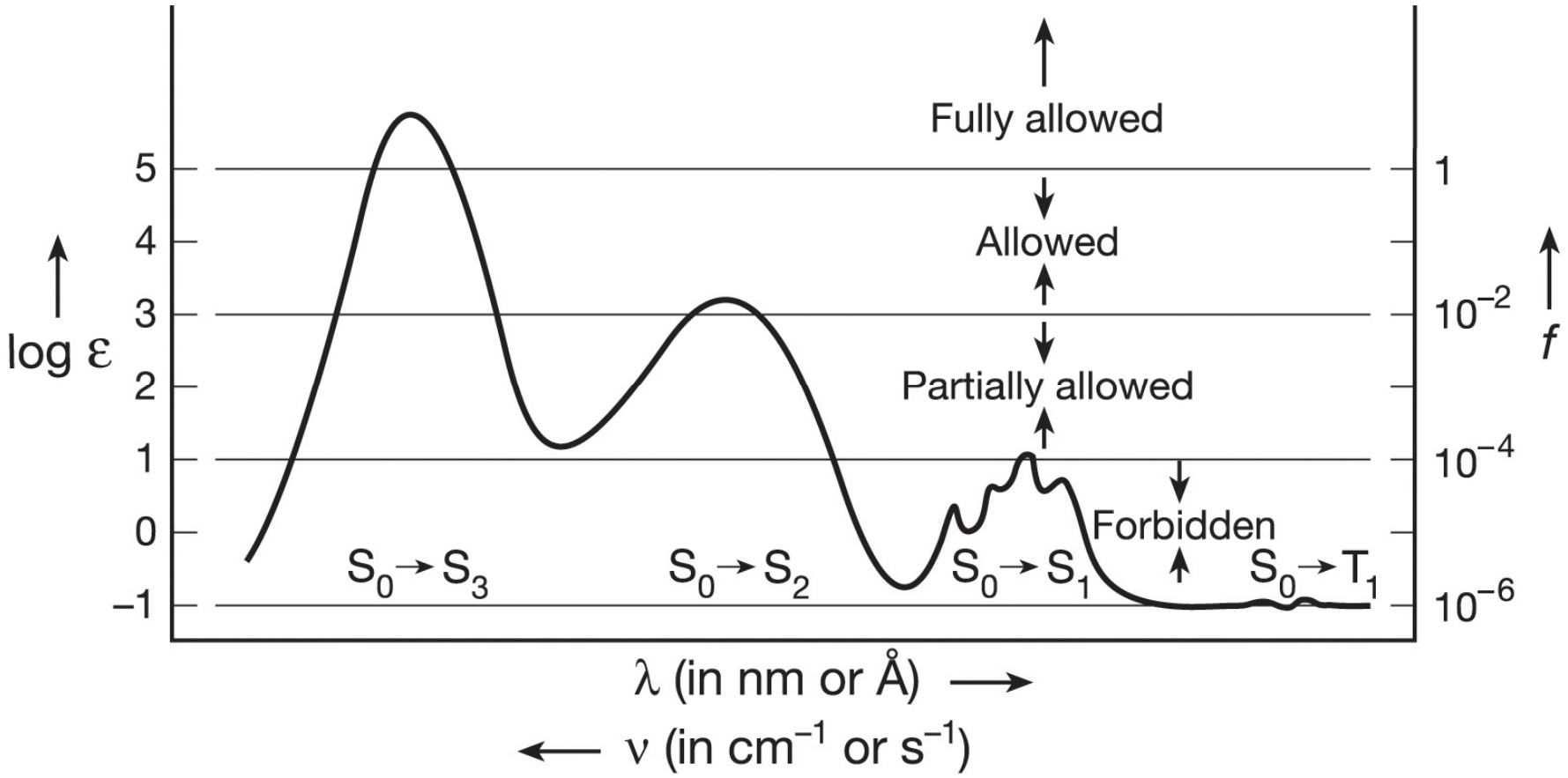
Beer-Lambert law

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

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

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

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 ($\mathbf{S}$)

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

- 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

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

- 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.

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

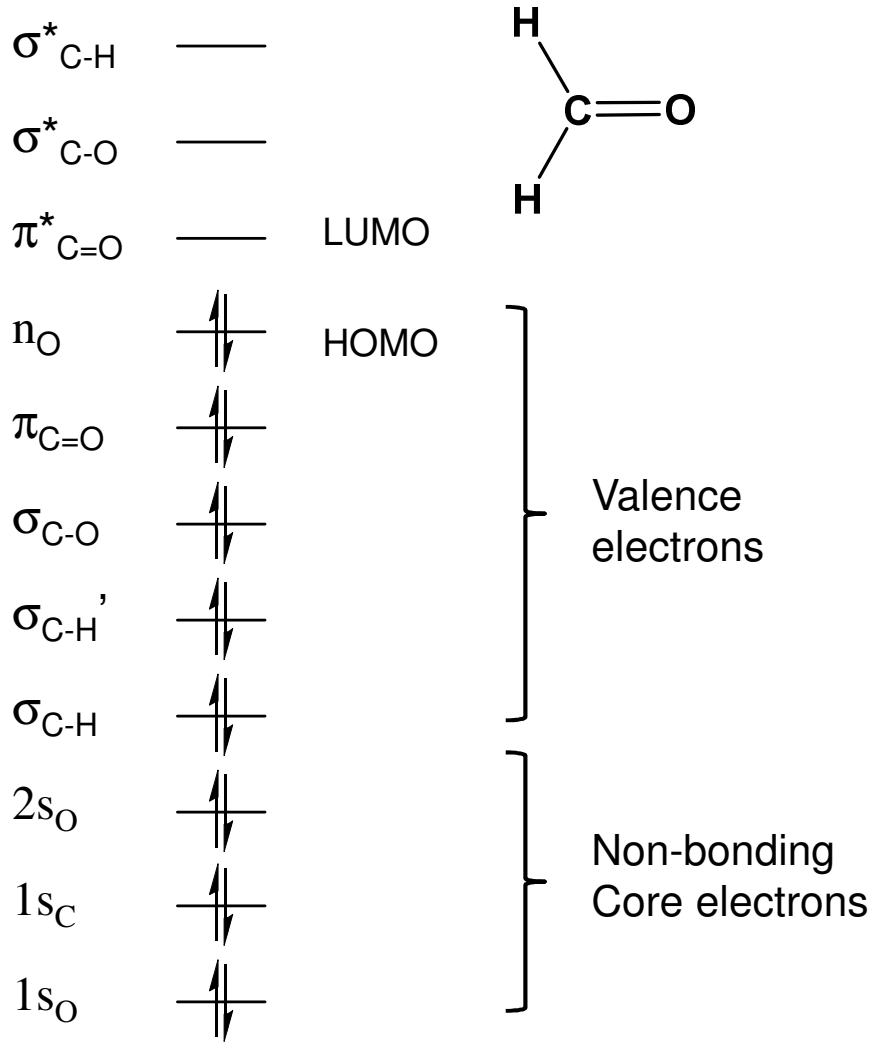
$$P_{av} = \langle\, (\phi_1 \phi_2 \ldots \phi_n)\, \chi\, \mathrm{S}\, |P|\, (\phi_1 \phi_2 \ldots \phi_n)\, \chi\, \mathrm{S}\, \rangle$$

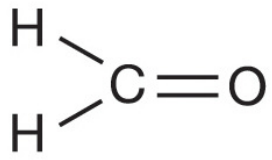
- In the ***zero-order approximation*** Ψ_0 is calculated as a product of one-electron molecular orbital wavefunctions ϕ_n for a one-electron molecule.

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

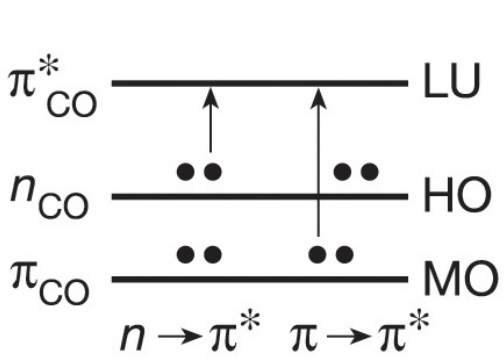
Atomic orbitals, Molecular orbitals, electronic states and configurations, e.g. formaldehyde

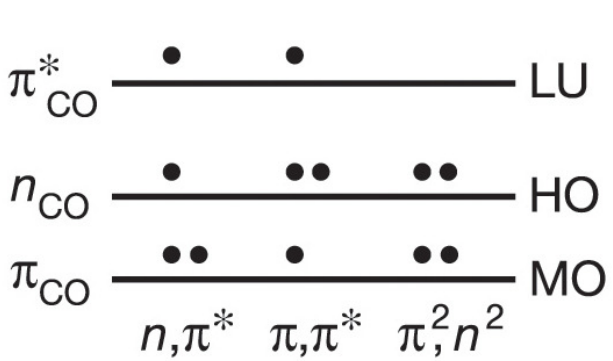
- To visualize $\Psi_{electronic}$ we must approximate the structure of Ψ_0^2 as a configuration of overlapping, but non-interacting, one-electron occupied orbitals ϕ_n
- $H_2C=O$ has a total of 16 electrons. Using a classical approach for MO energies, # of electrons, Pauli and Aufbau principle we can 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. $\Psi_0(S_0)$

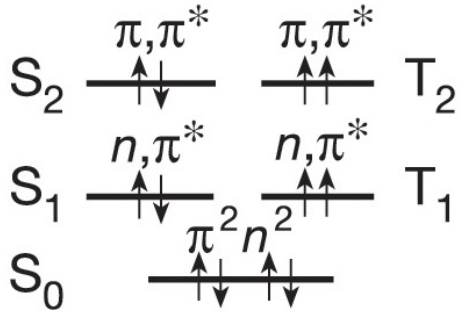


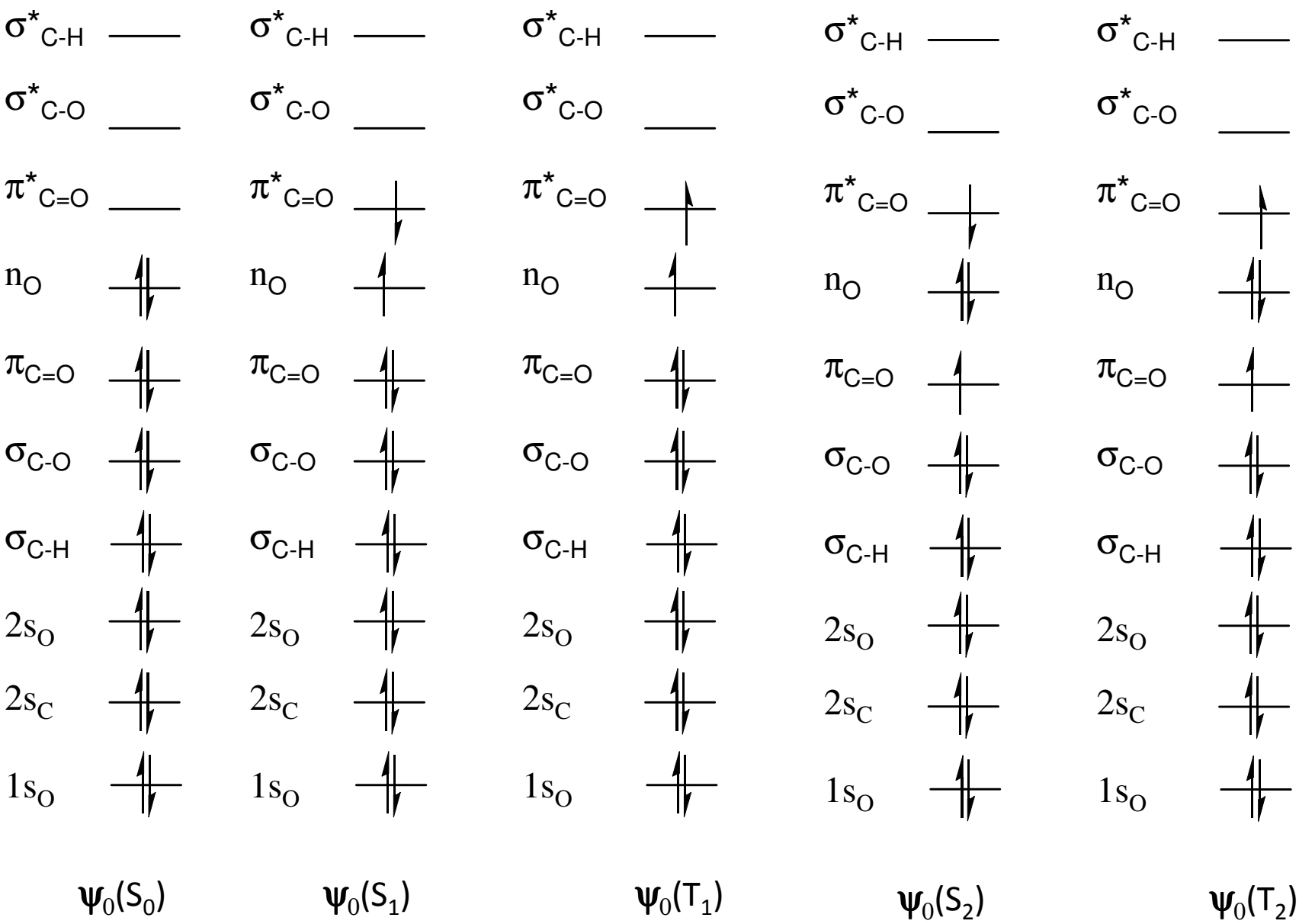


Formaldehyde








σ*C-H
σ*C-O
π*C=O
nO
πC=O
σC-O
σC-H
2sO
2sC
1sO
ψ0(S0)
ψ0(S1)
ψ0(T1)
ψ0(S2)
ψ0(T2)

energy

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.

$$T_n < S_n$$ *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

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

- 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:

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

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

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

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 $J(\mathrm{n}, \pi^*)$ and $J(\pi, \pi^*)$

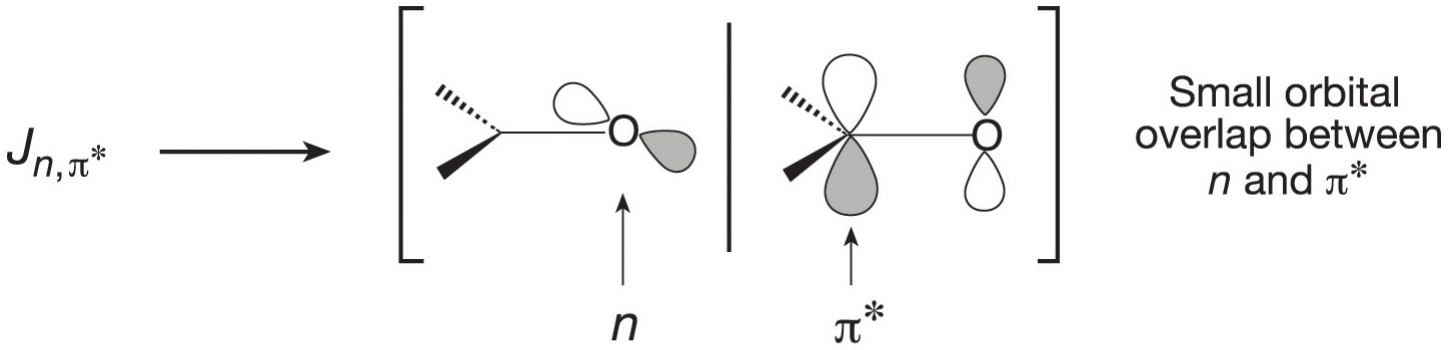
$$J(n,\pi^*) = \left\langle n(1),\pi^*(2)\left|\frac{e^2}{r_{12}}\right|n(2),\pi^*(1)\right\rangle$$

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

- 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).

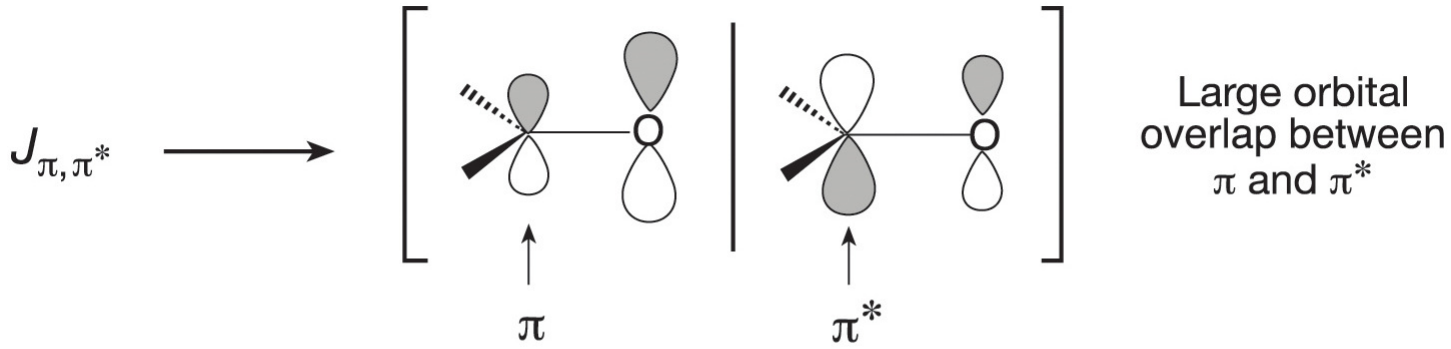
- If both wavefunctions are identical their normalized orbital overlap integral is unity, e.g. $\langle \pi \mid \pi \rangle = 1$

- 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 $\Delta E_{ST} = 0$

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

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

- This is contradictory to our rule:

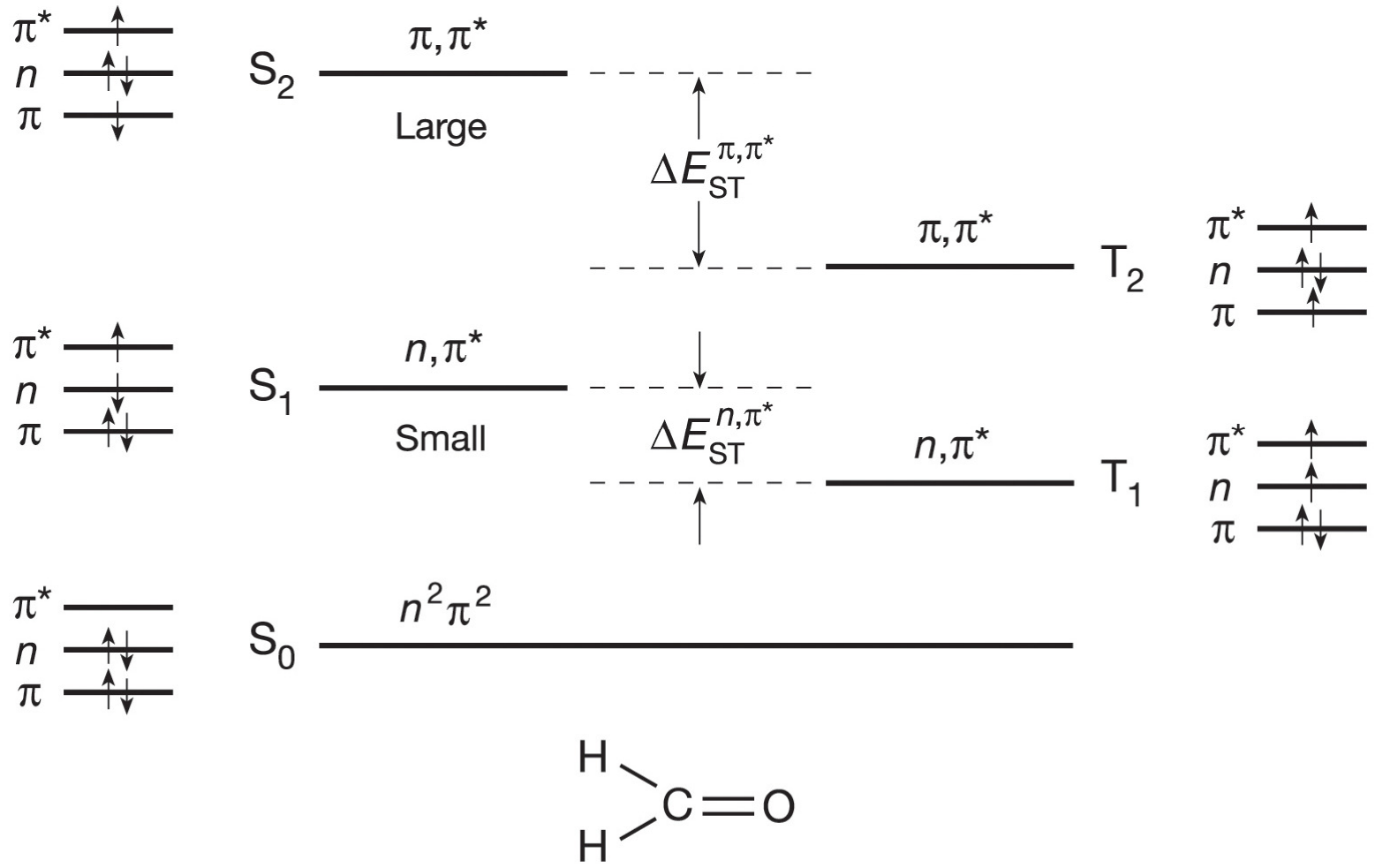
  $\mathbf{T_n < S_n}$ *always for the same electronic configuration !!!*

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

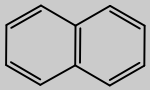
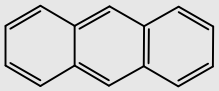
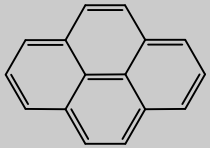
- We have effectively just derived a *selection rule* for singlet triplet energies of (n, π^*) excited states

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

- We can effectively conclude that $\Delta E_{ST}\,(\mathrm{n}, \pi^*) < \Delta E_{ST}\,(\pi, \pi^*)$ 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 (~ 10^{15} – 10^{16} s^{-1})
- spin-orbit coupling between initial and final electronic states
- the square of vibrational overlap, i.e. the *Frank-Condon factor* $\langle \chi_1 | \chi_0 \rangle^2$

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

Vibrational coupling

Spin-orbit coupling

Vibrational overlap Franck-Condon factors

The classical harmonic oscillator model for vibrational wavefunctions

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

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

- 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

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

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

- 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.

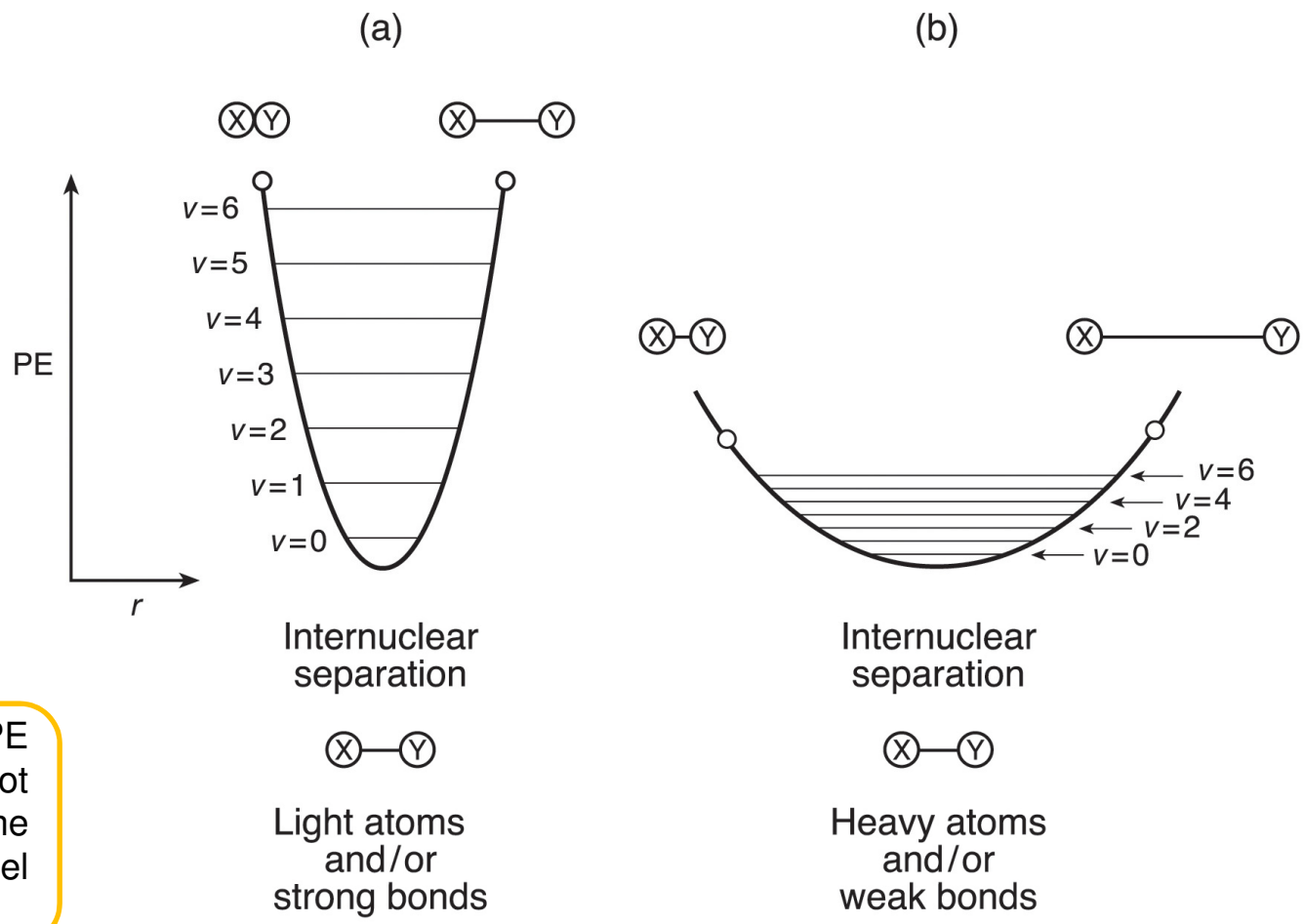
- The frequency of oscillation ν (τ^{-1}), with one period occurring in time (τ) is related to the reduced mass (μ) of the displaced atoms

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

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

- 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

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



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

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

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

- **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.**

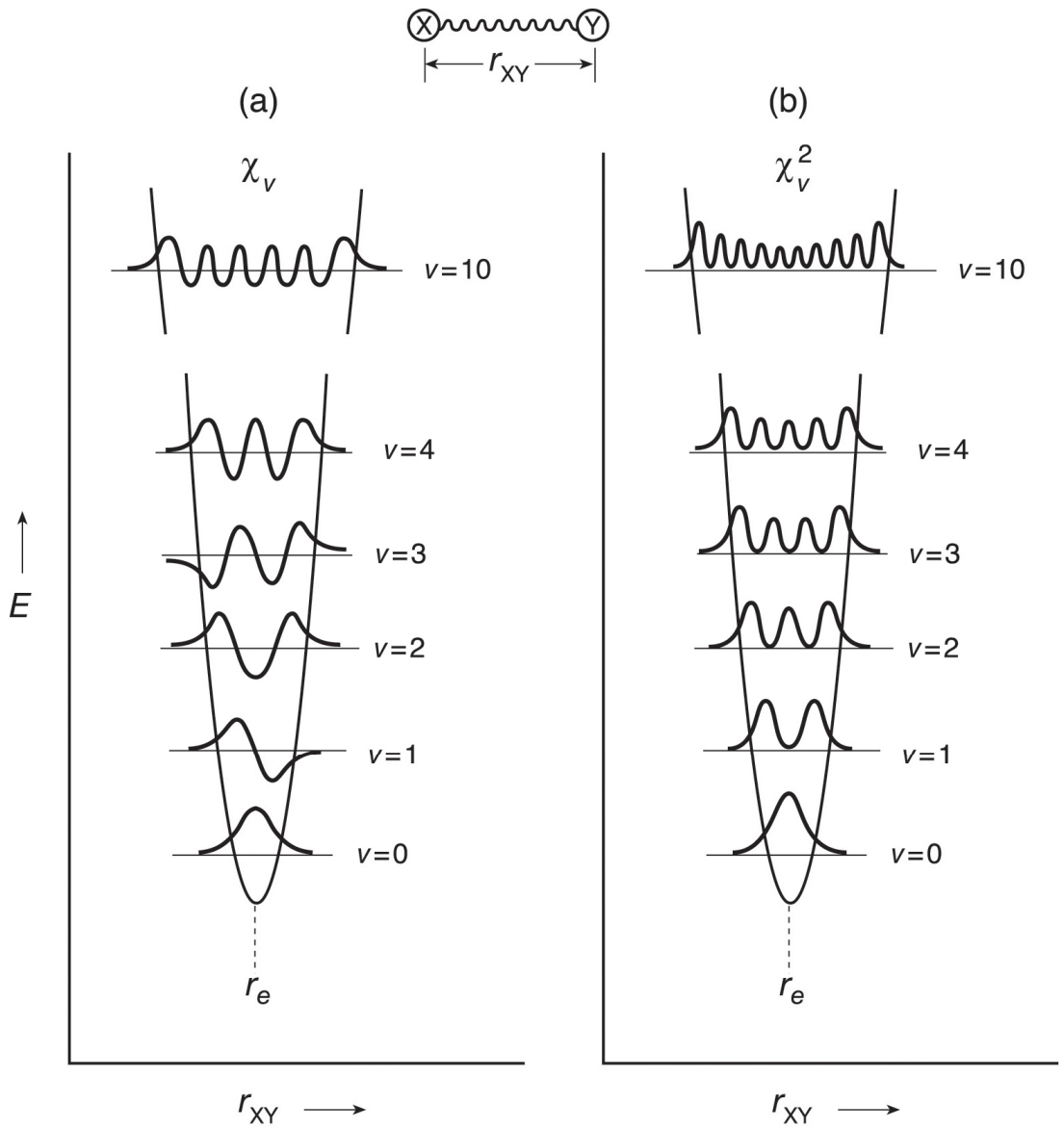
$$P_{av} = \langle \Psi_0 \, (\chi_1 \chi_2 \ldots \chi_n) S \, | P | \Psi_0 \, (\chi_1 \chi_2 \ldots \chi_n) S \, \rangle$$

- Visualization of $\boldsymbol{\chi}$ 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* v (0, 1, 2, 3,…)

$$PE_v = h\nu\ (v + 0.5)$$

- PE_v is now quantized with levels separated by units $h\nu$
- $PE_{v=0}$ 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} .

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

- 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

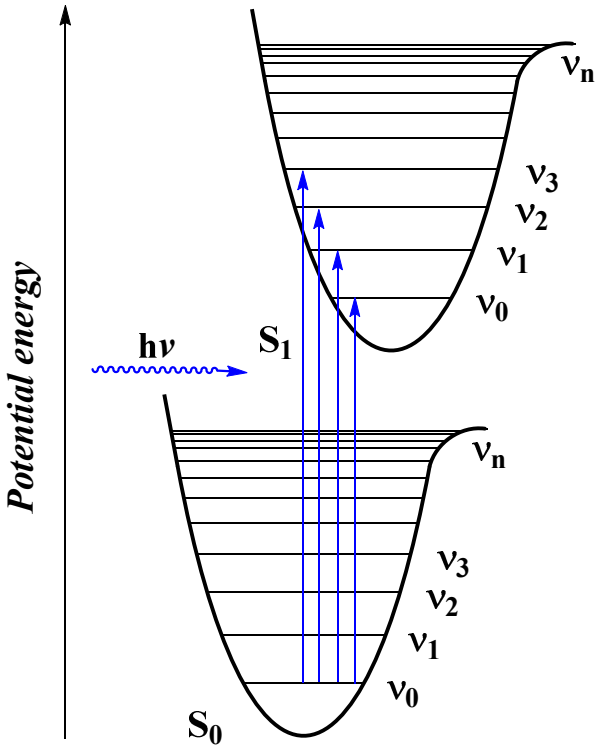
$$P(S_1 \rightarrow S_0) \sim \langle \Psi(S_1) | P(S_1 \rightarrow S_0) | \Psi(S_0) \rangle^2$$

- 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.



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

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})

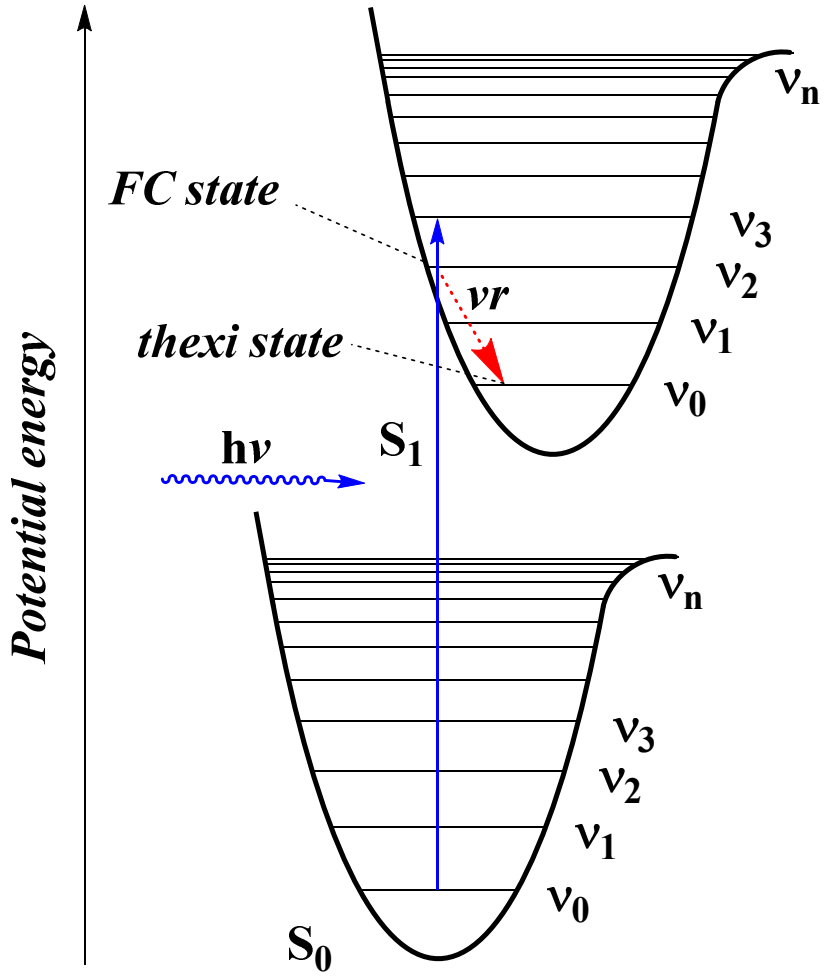
T = absolute temperature (K)

- 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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