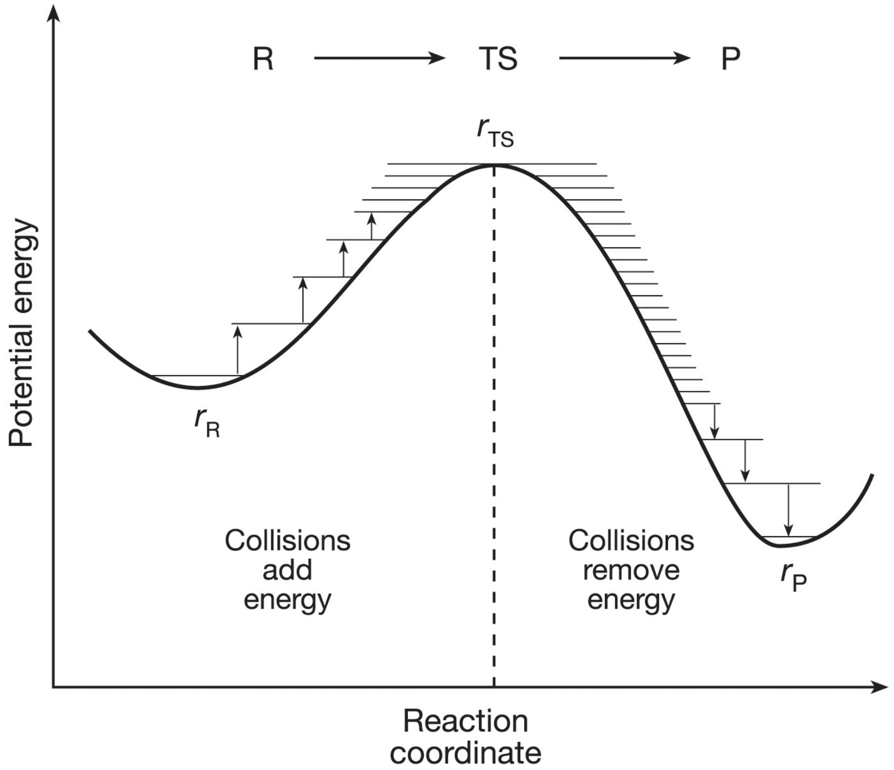
What is the difference between thermochemistry and photochemistry?

- Mode of activation
  - Activated by collisions (thermo)
  - Activated by light (photo)
- Selectivity in activation
  - Entire molecule gets activated
  - Only the chromophore that absorbs the light gets activated
- Energy distribution
  - Energy used for vibrational/rotational transition
  - Energy used for electronic transition mainly

Visualization of Thermal Reactions

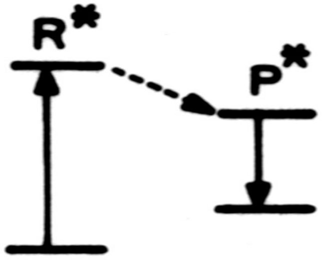


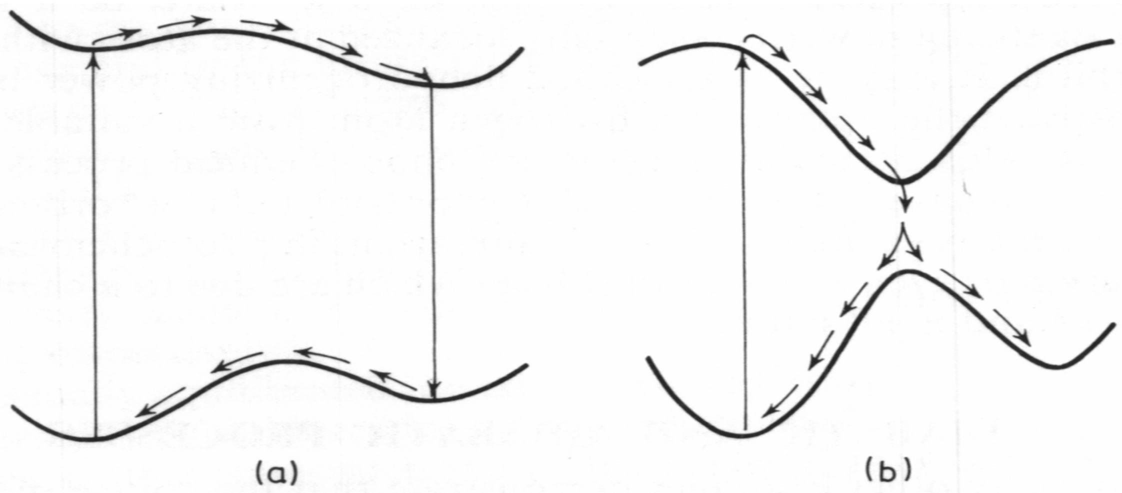
- Transition state connects a single reactant to a single product (intermediate) and it is a saddle point along the reaction course.
- Collisions are a reservoir of continuous energy (~ 0.6 kcal/mol per impact).
- Collisions can add or remove energy from a system.
- Concerned with a single surface.

Visualization of Photochemical Reactions

We need to deal with two surfaces (ground and excited state.

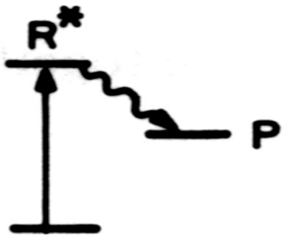
Adiabatic





Pathways of photochemical reactions: (a) adiabatic, (b) diabatic.

Diabatic



The Basic Laws of Photochemistry

Grotthuss-Draper law

The First Law of Photochemistry: light must be absorbed for photochemistry to occur.

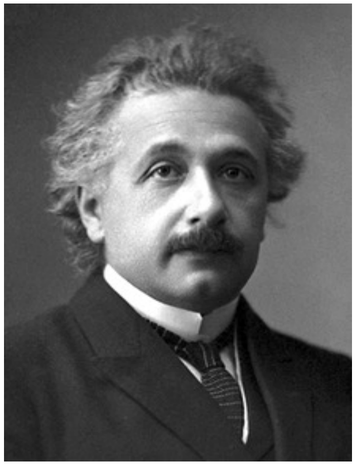
Grotthus

Drapper

Stark-Einstein law

The Second Law of Photochemistry: for each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction.

Stark

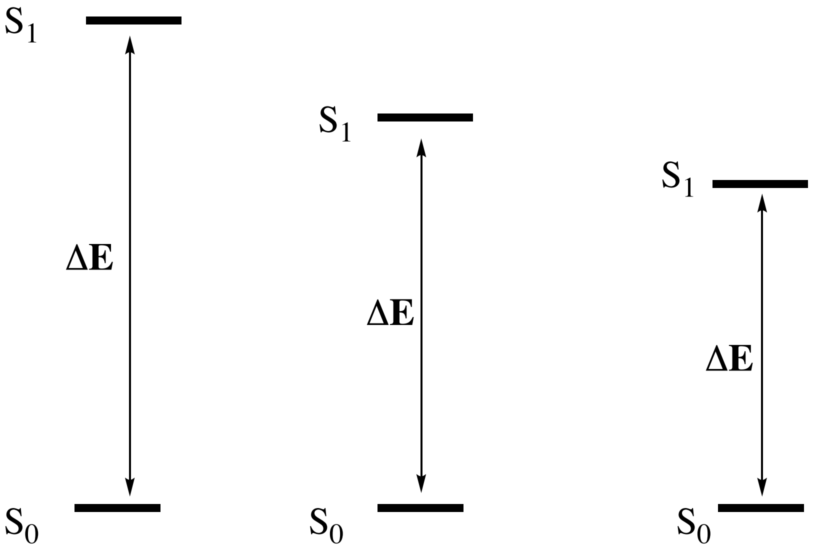


Einstein

Third law of photochemistry

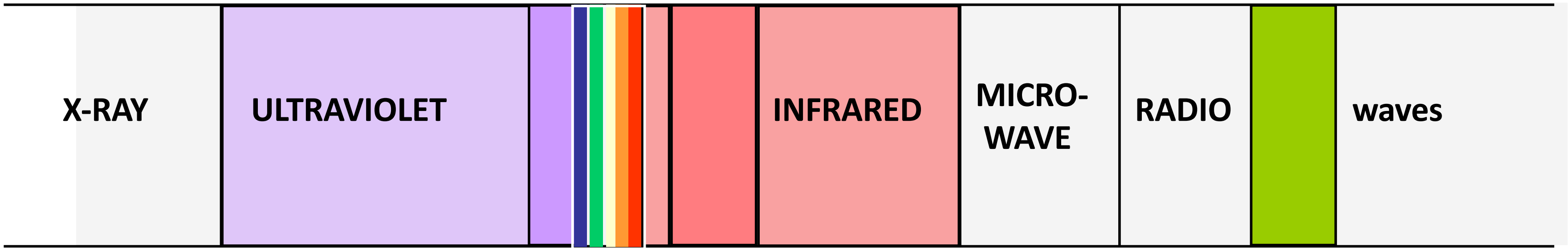
Probability of light absorption is related to the energy gap and wavelength of light

The *energy conservation rule* : There must be an exact matching of the energy difference that corresponds to the energy required for the transition (ΔE) between orbitals and the energy of the photon (hν); that is, ΔE must exactly equal hν (Eq. 4.8).



$$\mathbf{\Delta E\ (kcal\ mol^{-1}) = [2.86\ x\ 10^{4}\ kcal\ mol^{-1}\ nm]/\lambda\ nm}$$

The Range of Electromagnetic Radiation (Light)



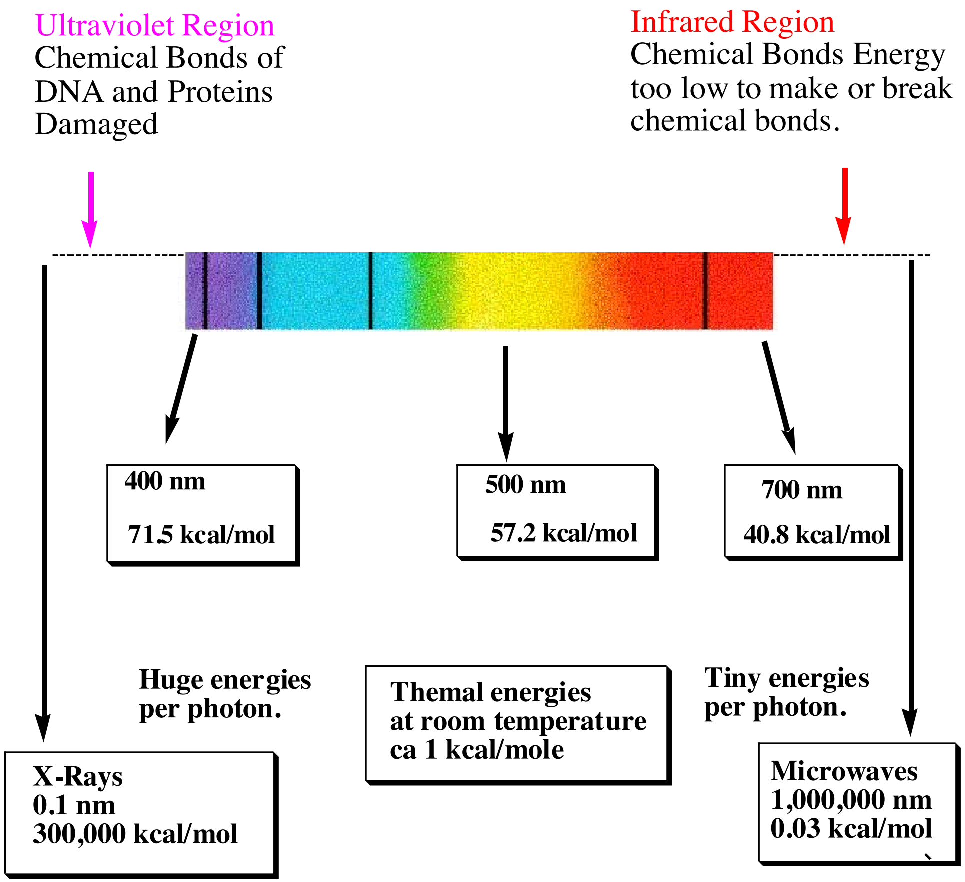
REGION	ENERGY TRANSITIONS
X-ray	Ionization
UV/Visible	Electronic ←
Infrared	Vibrational
Microwave	Rotational
Radio Frequency (NMR)	Nuclear and Electronic Spin

Light and Energy Scales

$$E\ (\text{kcal mol}^{-1}) = [2.86 \text{ x } 10^{4} \text{ kcal mol}^{-1} \text{ nm}]/\lambda \text{ nm}$$

$$E\ (\text{kcal mol}^{-1} \text{ nm}) = 2.86 \text{ x} 10^{4}/700 \text{ nm} = 40.8 \text{ kcal mol}^{-1}$$

$$E\ (\text{kcal mol}^{-1} \text{ nm}) = 2.86 \text{ x } 10^{4}/200 \text{ nm} = 143 \text{ kcal mol}^{-1}$$



Ultraviolet Region
Chemical Bonds of
DNA and Proteins
Damaged

Infrared Region
Chemical Bonds Energy
too low to make or break
chemical bonds.

400 nm
71.5 kcal/mol

500 nm
57.2 kcal/mol

700 nm
40.8 kcal/mol

Huge energies
per photon.

Themal energies
at room temperature
ca 1 kcal/mole

Tiny energies
per photon.

X-Rays
0.1 nm
300,000 kcal/mol

Microwaves
1,000,000 nm
0.03 kcal/mol

Electronic transitions are quantized
Atomic orbitals replace oscillators

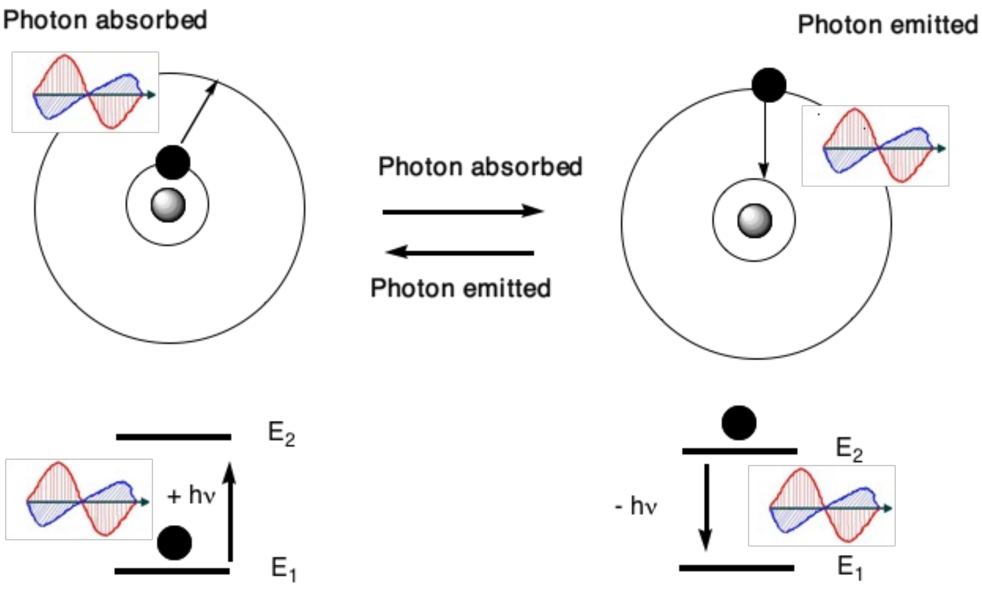
Niels Bohr
Nobel Prize 1922

The basis of all photochemistry and spectroscopy!

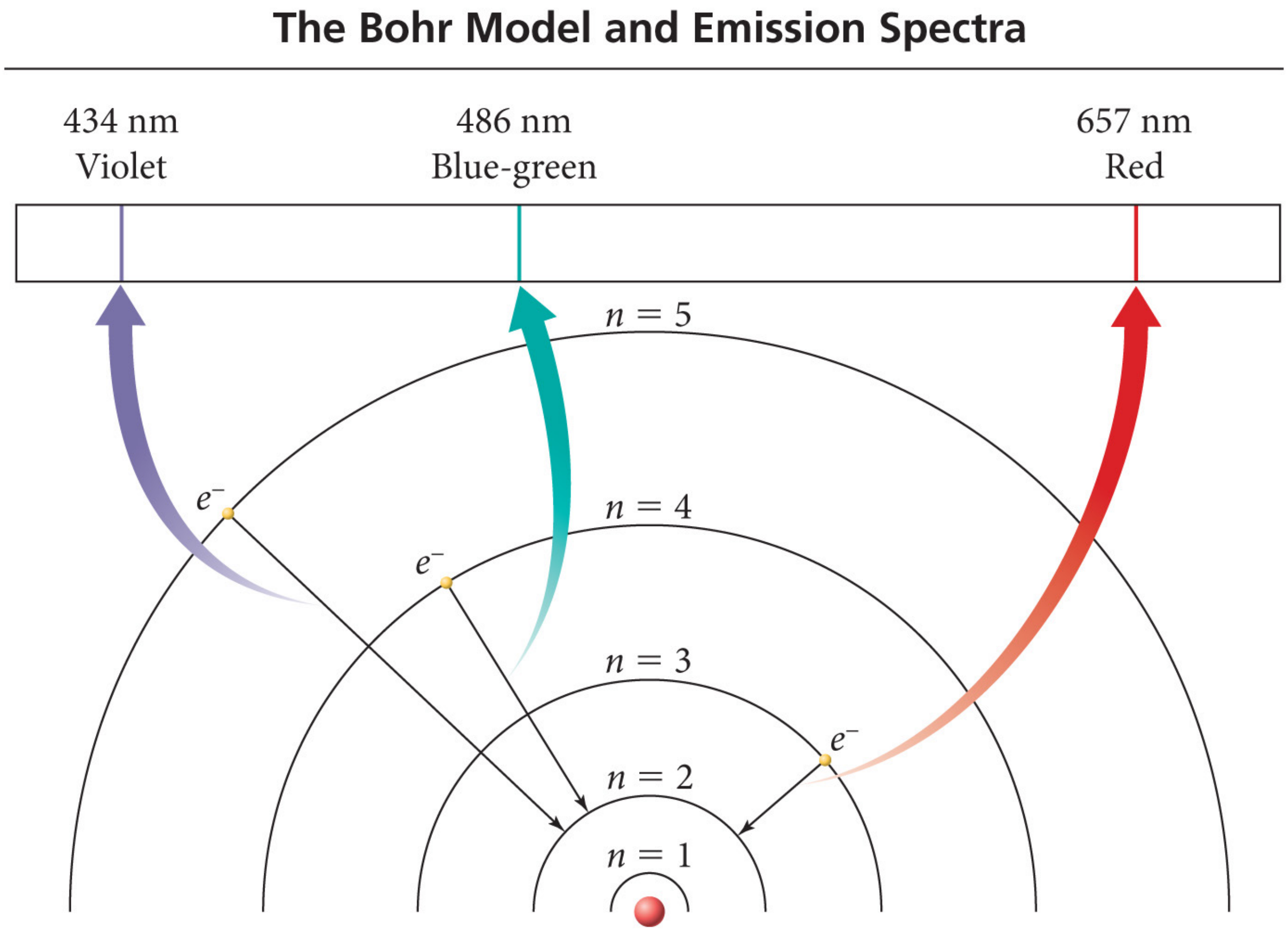
Orbitals, Absorption, Emission

Light is emitted when an electron jumps from a higher orbit to a lower orbit and is absorbed when it jumps from a lower to higher orbit.

The energy and frequency of light emitted or absorbed is given by the difference between the two orbit energies,
e.g., $E_{(photon)} = E_2 - E_1$ (Energy difference)



Bohr Model of H Atoms



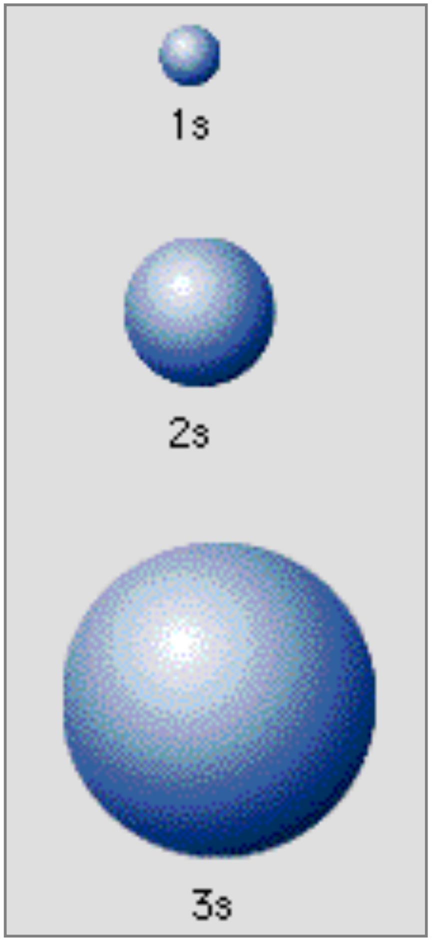
The Four Quantum Numbers Define an Electron in an Atom

- Principal quantum number (*n*) - describes the SIZE of the orbital or ENERGY LEVEL of the atom.
- Angular quantum number (*l*) or sublevels - describes the SHAPE of the orbital.
- Magnetic quantum number (*m*) - describes an orbital's ORIENTATION in space.
- Spin quantum number (*s*) - describes the SPIN or direction (clockwise or counter-clockwise) in which an electron spins.

1. Principal Quantum Number (*n*)

Energy level

Size of the orbital



The energy levels corresponding to *n* = 1, 2, 3, … are called shells and each can hold $2n^2$ electrons.

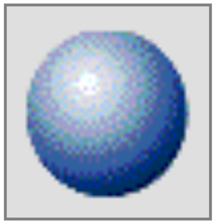
The shells are labeled K, L, M, … for *n* = 1, 2, 3, ….

2. Angular Momentum Quantum # (l)

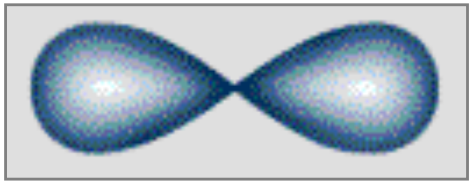
Energy sublevel

Shape of the orbital

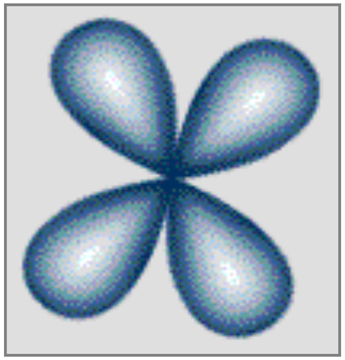
- **determines the *shape of the orbital***
- **they are numbered but are also given letters referring to the orbital type**
  - **l=0 refers to the s-orbitals**
  - **l=1 refers to the p-orbitals**
  - **l=2 refers to the d-orbitals**
  - **l=3 refers to the f-orbitals**



s



p

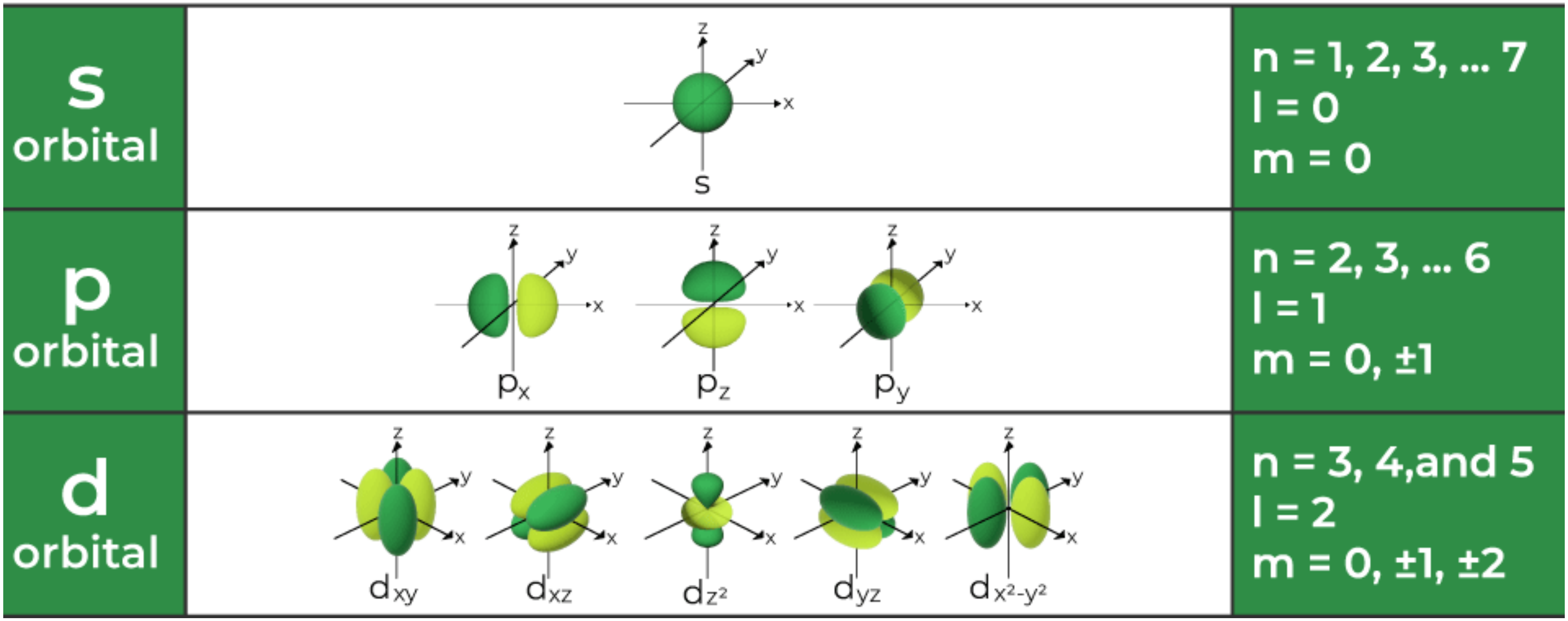


d

3. Magnetic Quantum Number (m_l)

Orientation of orbital

Specifies the number and shape of orbitals within each sublevel



s orbital	s	n = 1, 2, 3, ... 7 l = 0 m = 0
p orbital	p_x p_z p_y	n = 2, 3, ... 6 l = 1 m = 0, ±1
d orbital	d_{xy} d_{xz} d_{z^2} d_{yz} $d_{x^2-y^2}$	n = 3, 4,and 5 l = 2 m = 0, ±1, ±2

4. Spin Quantum Number (m_s)

Electron spin ⇒ +½ or -½

An orbital can hold 2 electrons that spin in opposite directions.

Visualization of Spin Chemistry

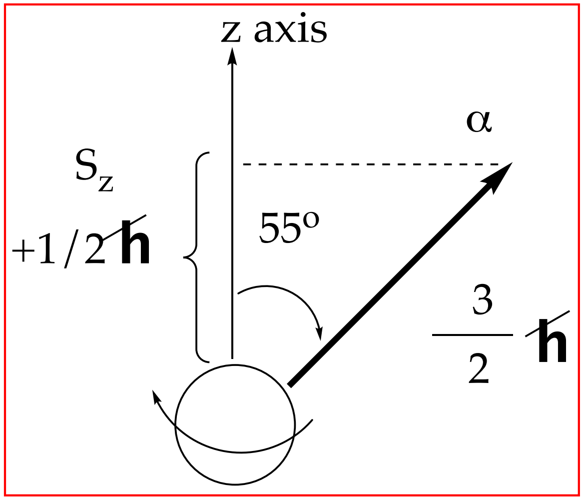
- Quantum mechanics requires mathematics for a quantitative treatment
- Much of the mathematics of quantum mechanics can be visualized in terms of pictures that capture the qualitative aspects of the phenomena under consideration
- Visualizations are incomplete, but it is important to note "correct" mathematical representations fail for complex systems as molecules

Spin angular momentum

- Electron possesses a fixed and characteristic spin angular momentum of ½ ħ

ħ : Planck's constant/2π

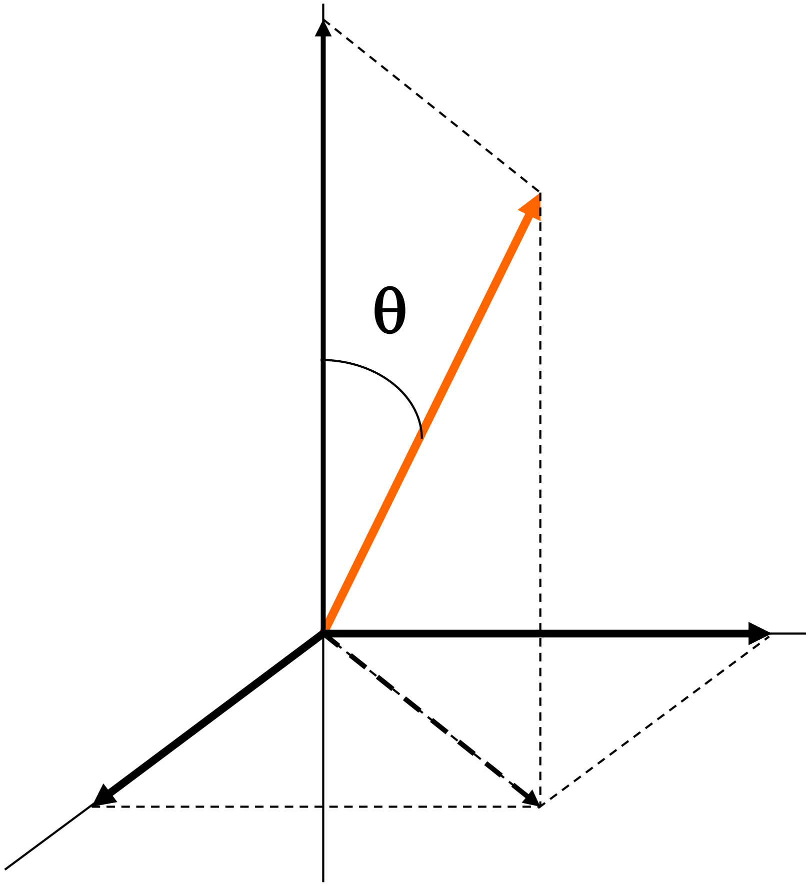
ħ = h/2π = 1.0545717 × 10−34 J·s eV·s



This value ½ ħ is independent of whether it is free or associated with a nucleus, regardless the orbital that it occupies, e.g., s, p, d, nπ*, ππ*; always the same.

If the electron spin were a classical quantity, the magnitude and direction of the vector representing the spin could assume any length and any orientation.

Angular momenta and vectors



- Angular momenta are **vector quantities** since they are determined by their **magnitude** and **direction**.
- A vector quantity is graphically represented by an arrow.
- For angular momenta:
  - the **magnitude** of the momentum is represented by the length of the arrow
  - The **direction** of the momentum is represented by the direction of the arrow (tip)
  - A vector can always be thought as the sum of three vectors oriented along each of the three cartesian axes x, y and z.

Quantum rules of electron spin angular momentum

- S, the **spin quantum number**, related to the length of the spin vector for an electron can assume only value ½

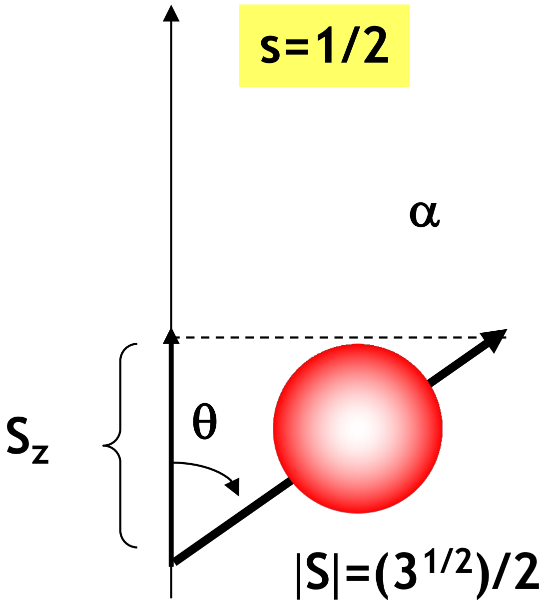
examples

S=0	1	singlet
S=1/2	2	doublet
S=1	3	triplet

- M_s (**spin multiplicity**) related to the orientation of the spin vector

Spin multiplicity= 2S+1

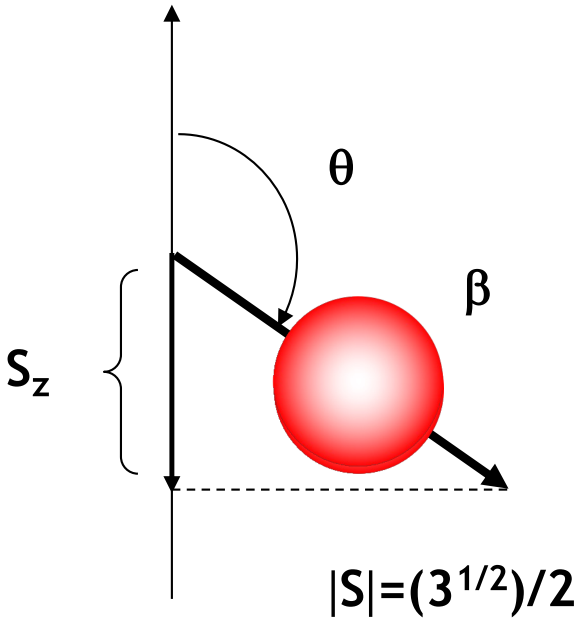
Spin multiplicity= 2S+1 = 2



In particular for

$S=1/2 \rightarrow |S|=(3^{1/2})/2$

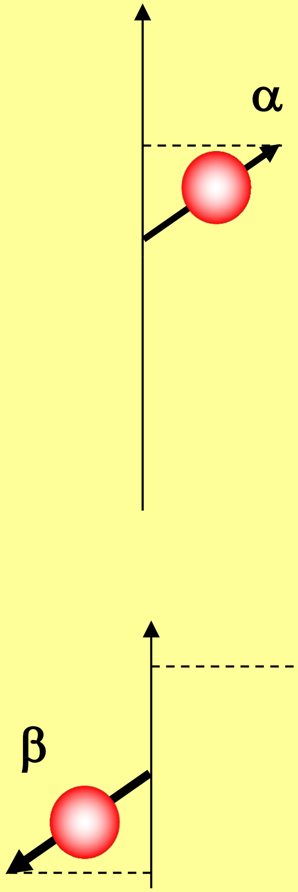
$\theta=55^{o}$ for $M_s= 1/2$



$\theta=125^{o}$ for $M_s=-1/2$

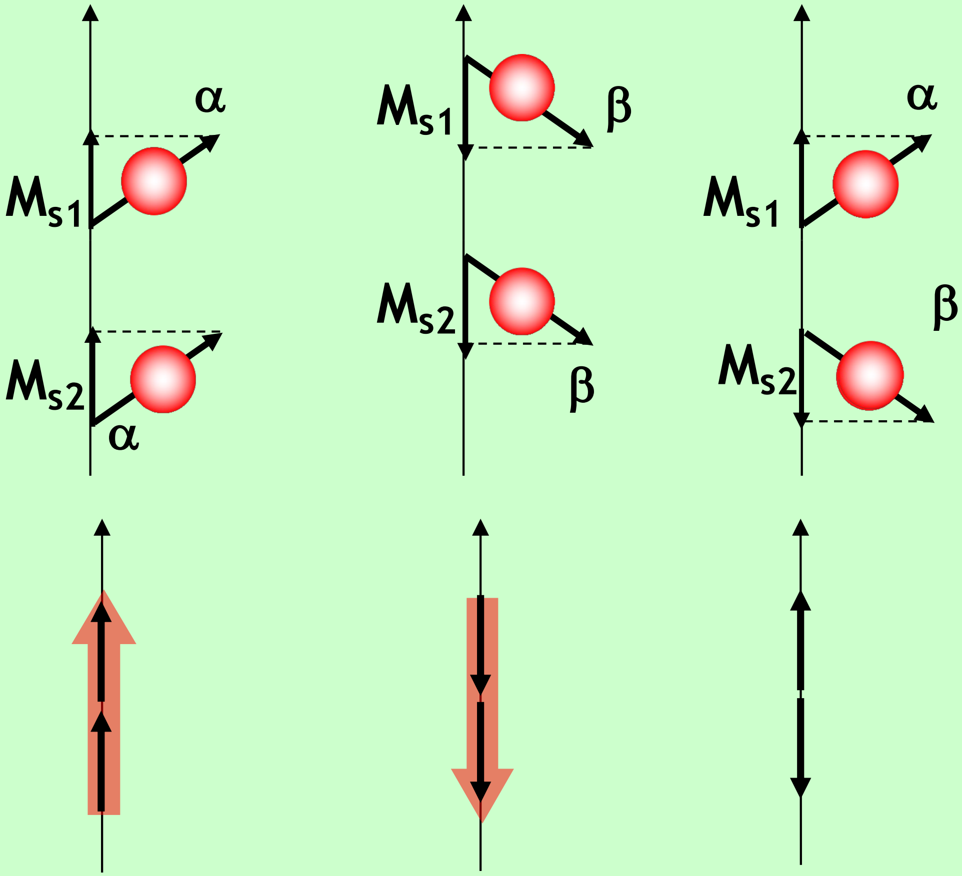
Two spins of ½: S = 0
Spin multiplicity = 2S+1 = 1

Two spins of ½: S = 1
Spin multiplicity= 2S+1 = 3



$M_S=0$

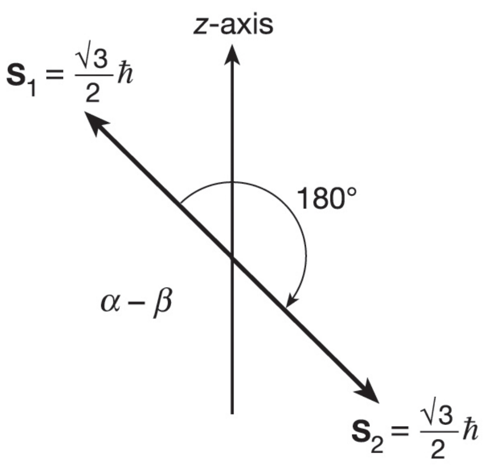
$\alpha\beta-\beta\alpha$



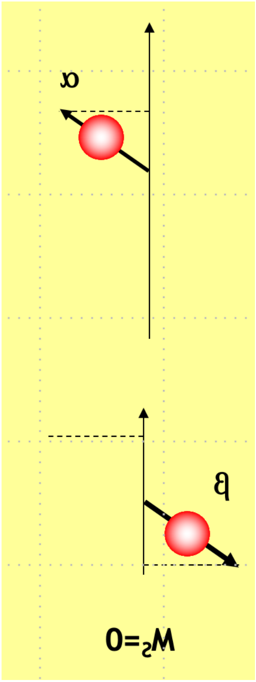
$M_S=1$ $M_S=-1$ $M_S=0$

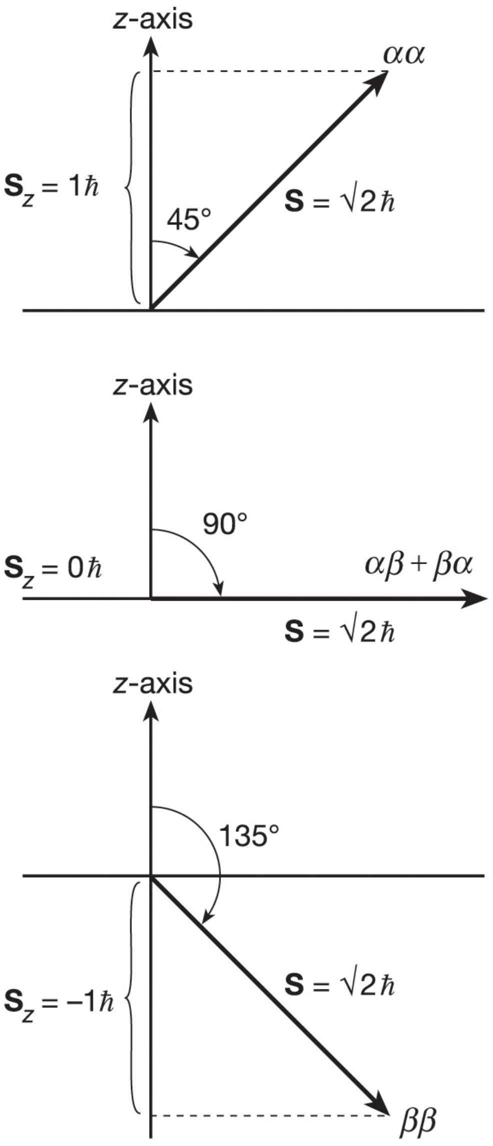
$\alpha\alpha$ $\beta\beta$ $\alpha\beta+\beta\alpha$

2D Vector representations for two interacting electrons

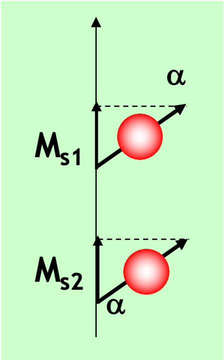


(a)

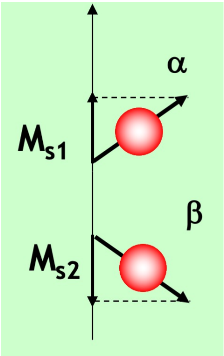




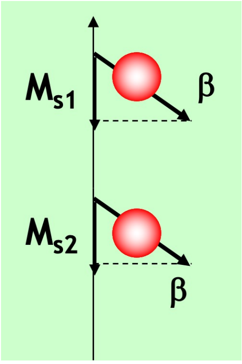
$M_S = +1$



$M_S = 0$



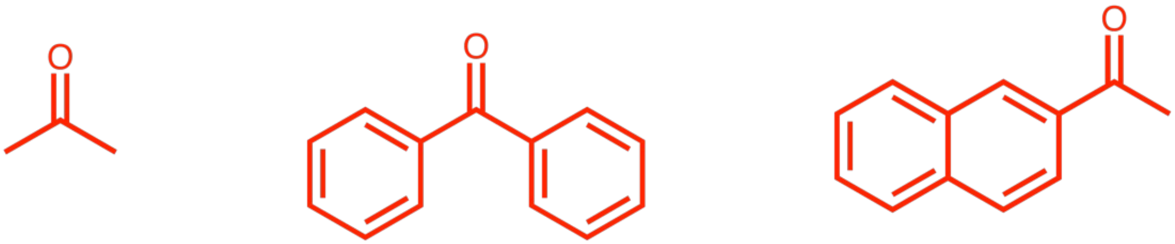
$M_S = -1$



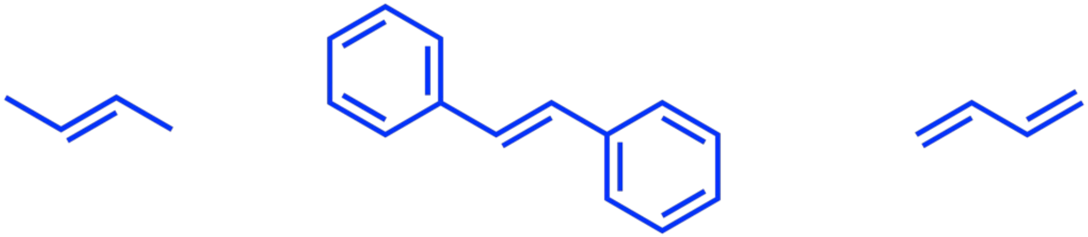
(c)

Examples of Common Organic Chromophores

Carbonyls



Olefins



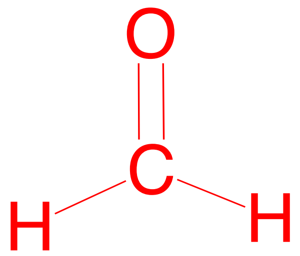
Enones

Aromatics

Viewing electrons in atoms and molecules

Atoms: Electrons are present in atomic orbitals (Bohr)

Molecules: Electrons are present in molecular orbitals (Mulliken)



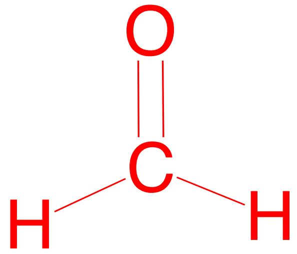
Inner orbitals

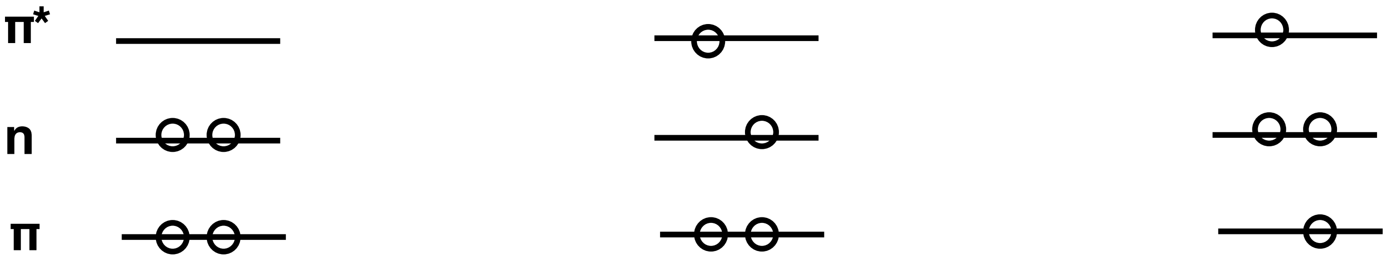
Bonding orbitals

Frontier orbitals

$$\Psi_0(H_2C{=}O) = \overline{(1s_O)^2(1s_C)^2(2s_O)^2}\underline{(\sigma_{CH})^2(\sigma'_{CH})^2(\sigma_{CO})^2}\overline{\underline{(\pi_{CO})^2}(n_O)^2\,(n_o)^2}$$

Types of transitions in formaldehyde





Ground state

n,π*

π,π*

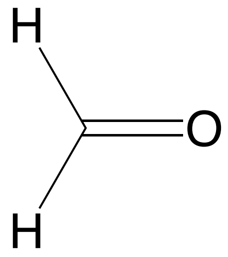
Excited states

---

standard abbreviations

Orbital diagram

Common Chromophores
Carbonyl Compounds



$n \longrightarrow \pi^*$

290 nm

$\varepsilon = 10$

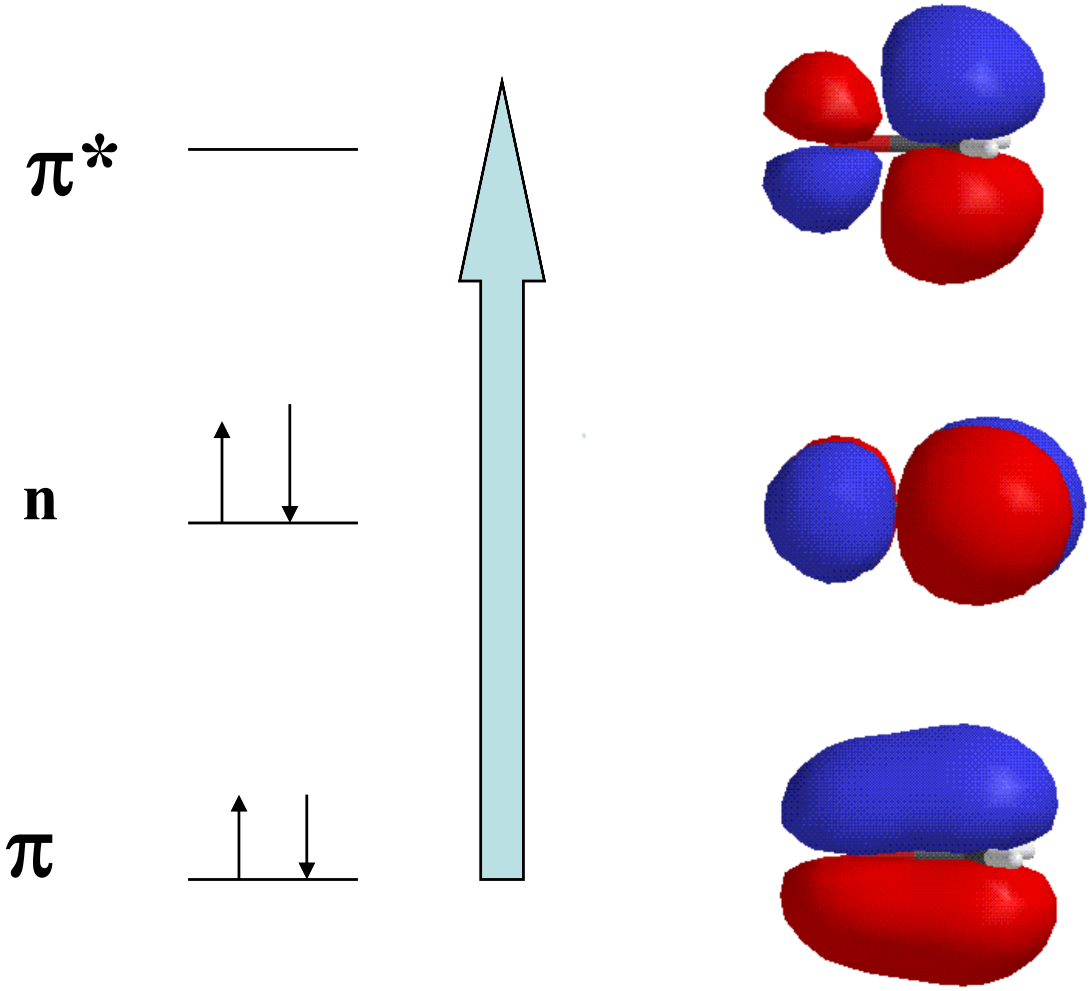
forbidden

$\pi \longrightarrow \pi^*$

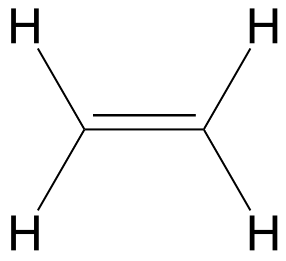
170 nm

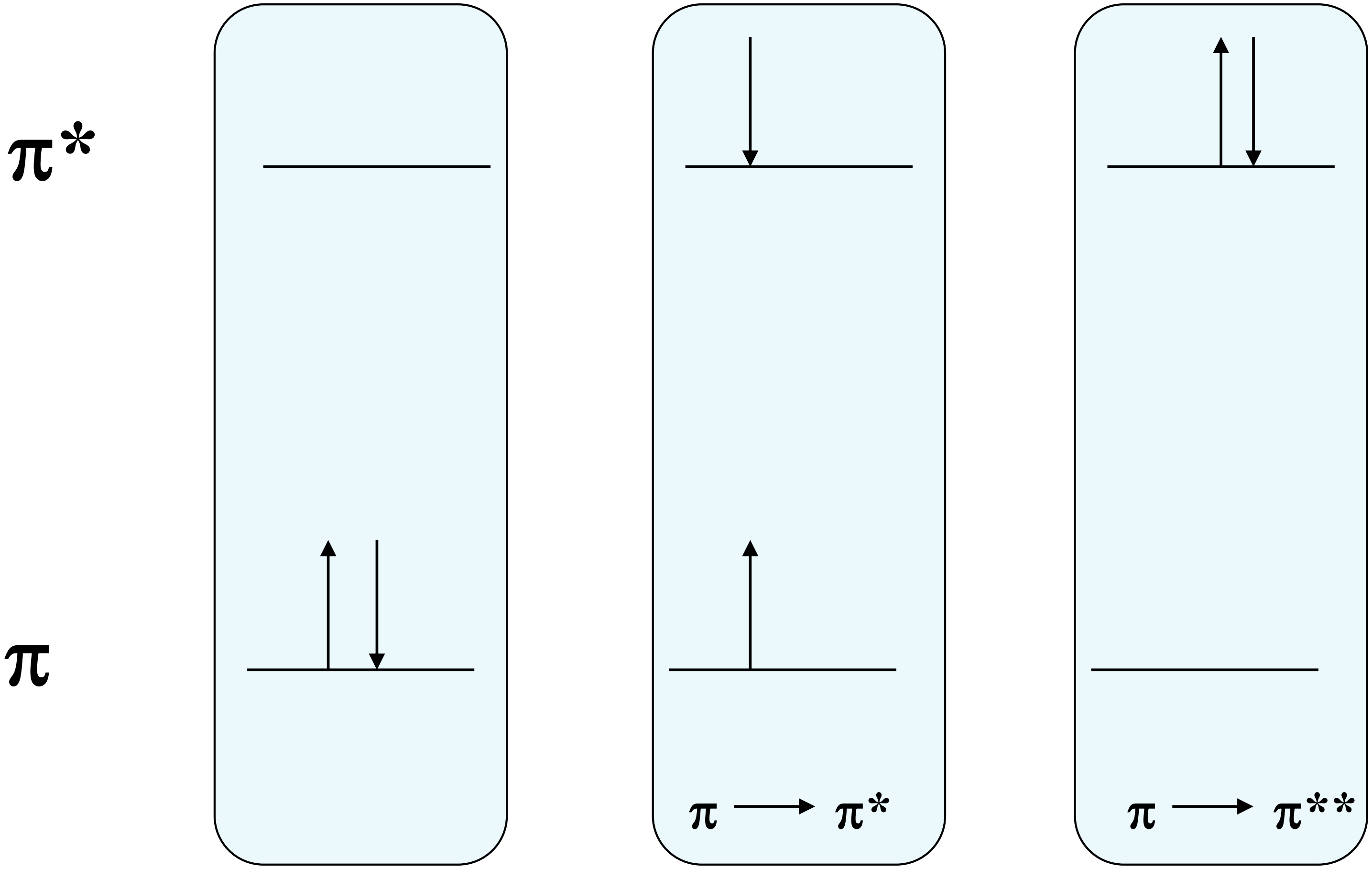
$\varepsilon = 100$

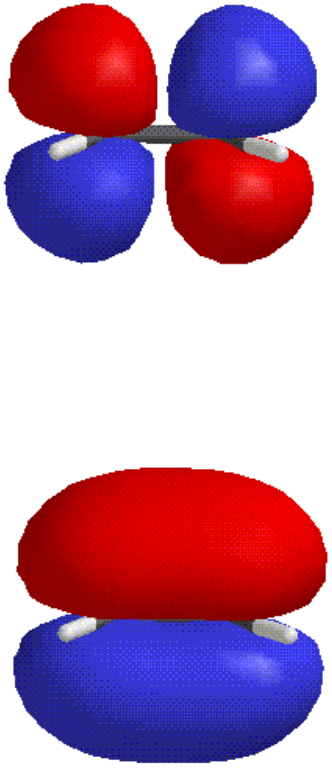
allowed



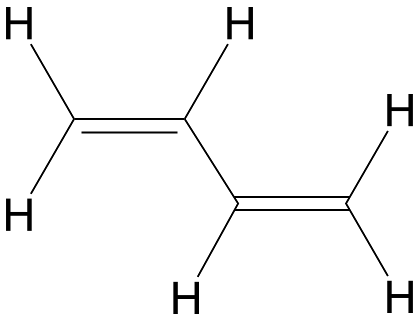
Common Chromophores: Olefins
Ethylene

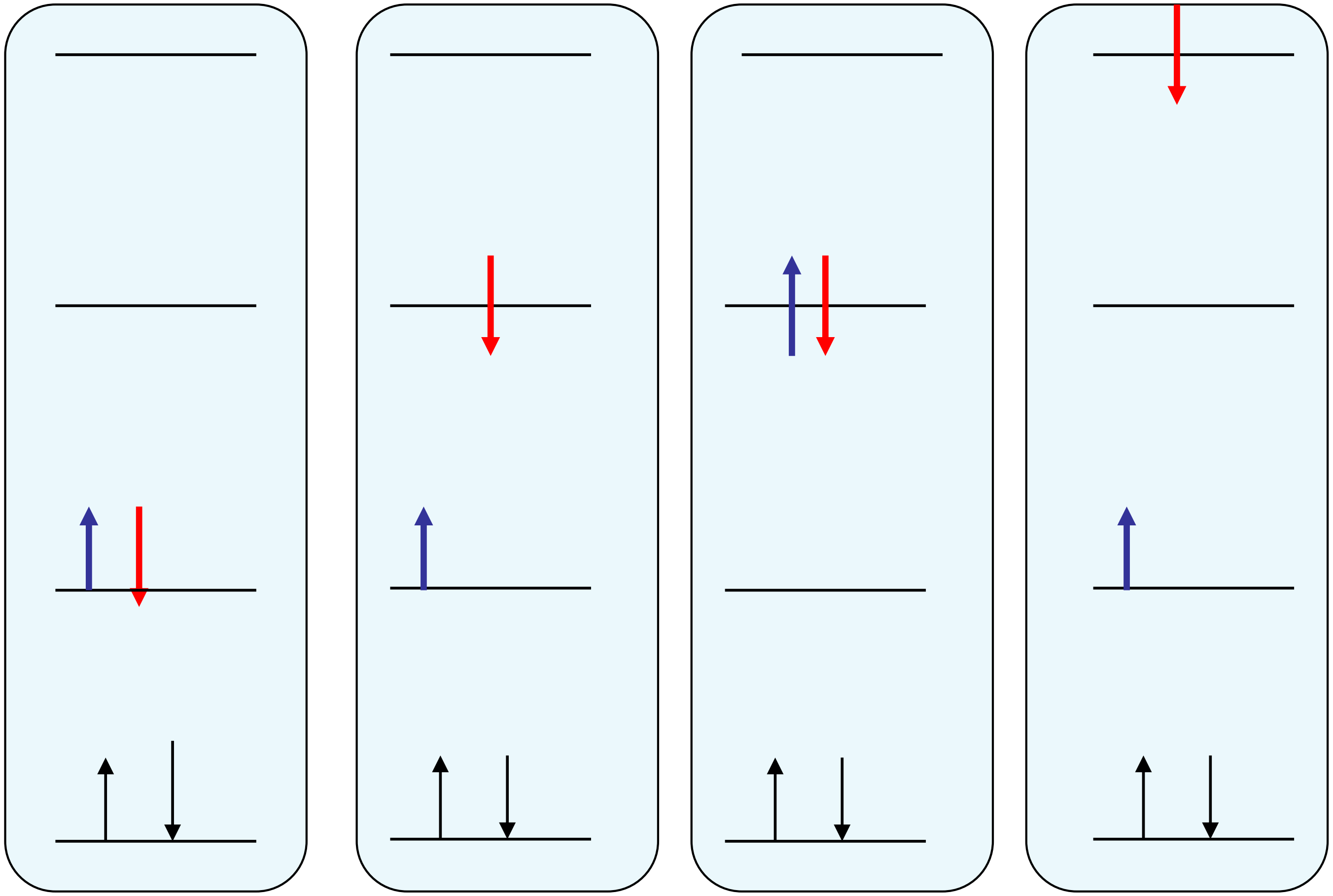


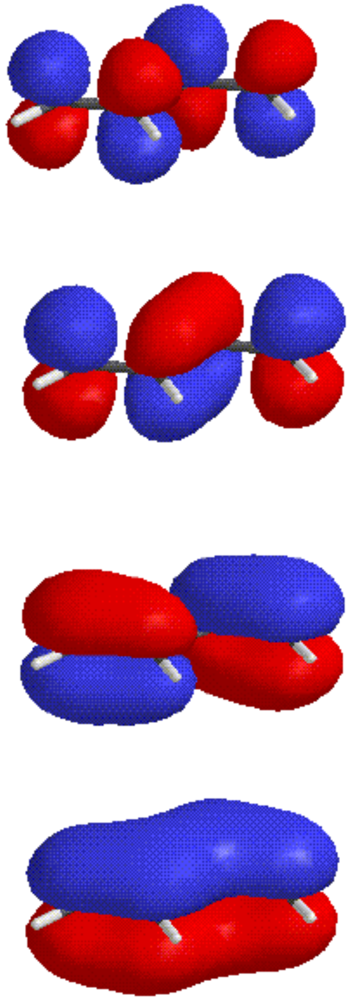




Common Chromophores: Olefins
1,3-Butadiene





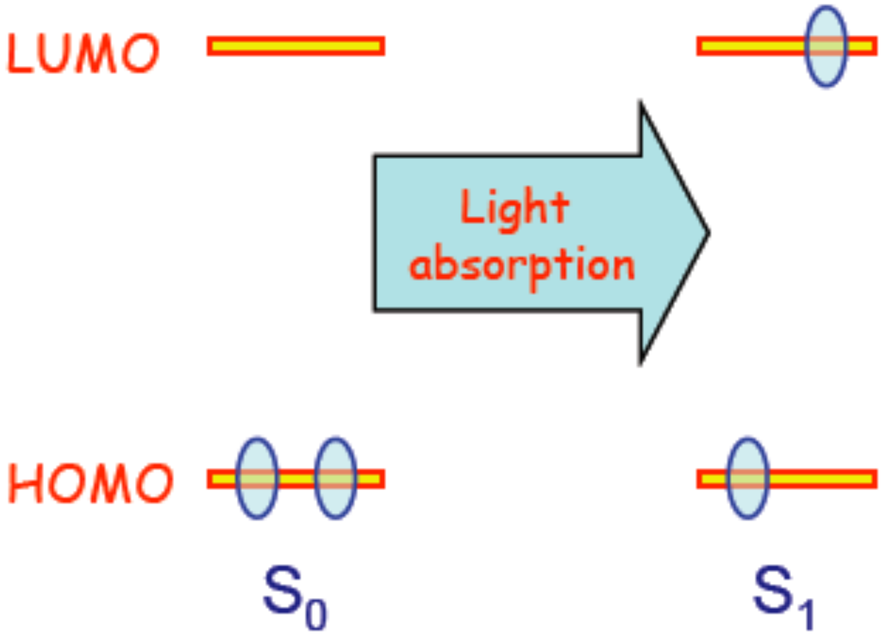


π → π*

π → π**

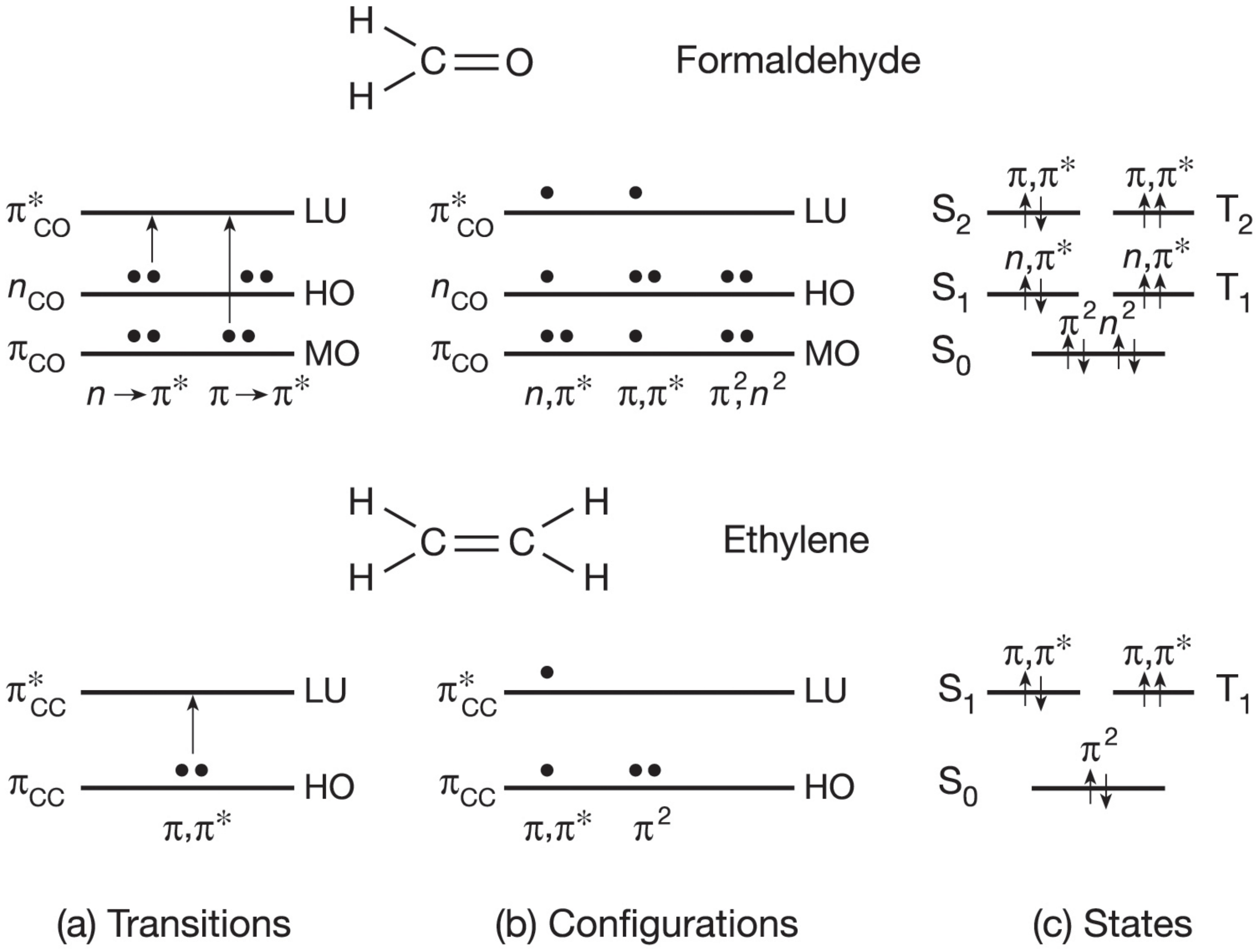
π → π*

Light absorption and electron movement



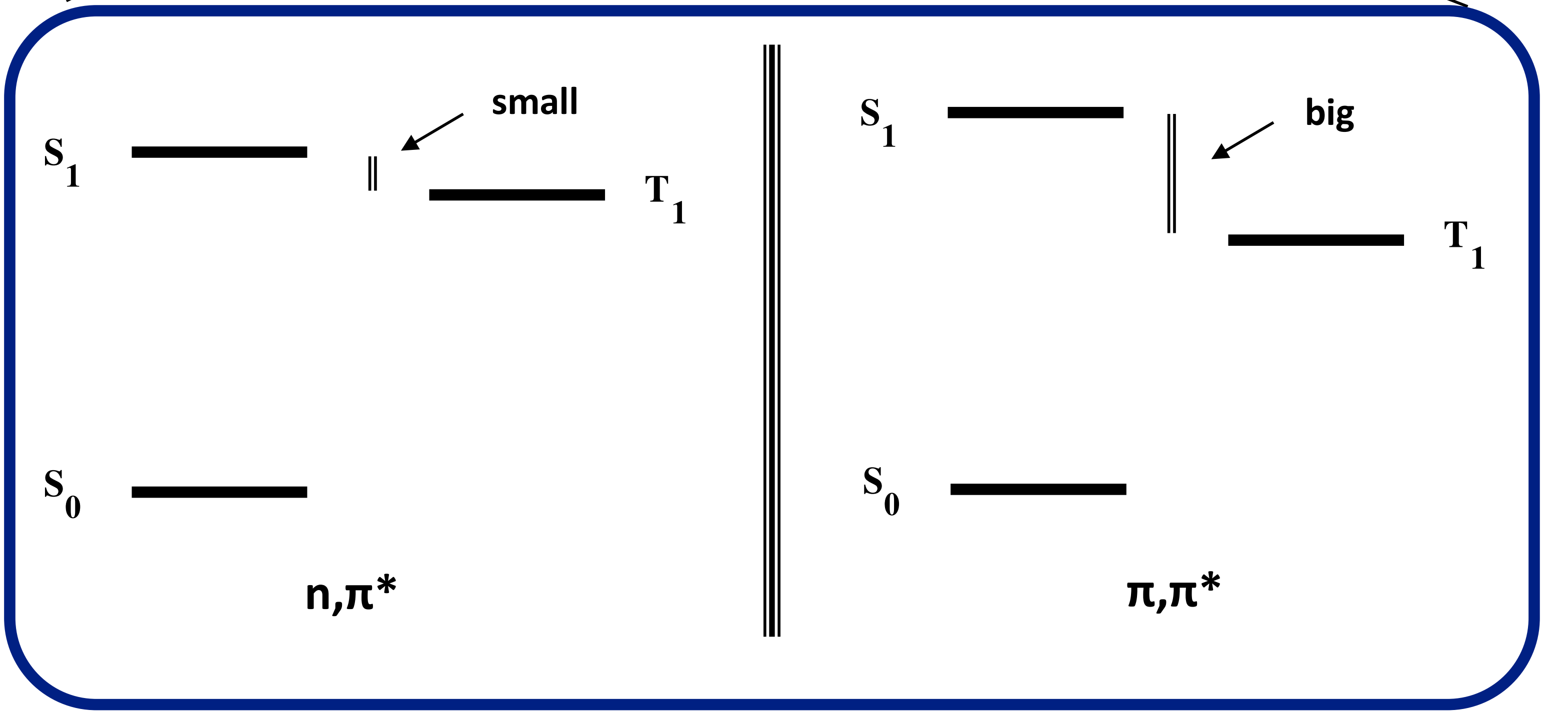
State diagram

Electronic and Spin Configuration of States



S_1-T_1 energy gap

Ground state reactants → Excited state reactants → Reaction Intermediates → Ground state products

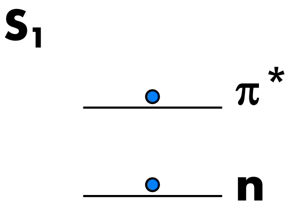


Singlet-Triplet separation in molecules and diradical intermediates and Intersystem crossing

Role of exchange integral (J)

Why triplets are lower in energy than singlets?

What controls the singlet-triplet energy gap?



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

$E_T = E_0(n,\pi^*)$

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

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

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

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

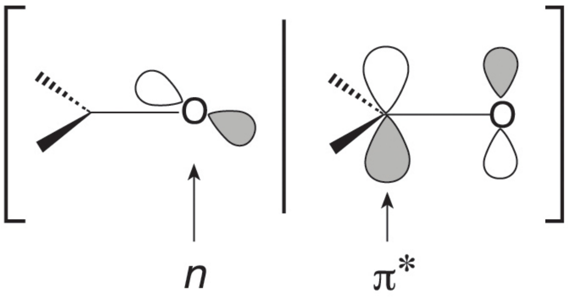
$$\Delta E_{ST} = E_S - E_T = E_0(n,\pi^*) + K(n,\pi^*) + J(n,\pi^*) - [E_0(n,\pi^*) + K(n,\pi^*) - J(n,\pi^*)]$$

$$\Delta E_{ST} = E_S - E_T = 2J(n,\pi^*)$$

$$J(n,\pi^*) \sim e^2/r_{12} < n(1)\pi^*(2)|n(2)\pi^*(1)$$

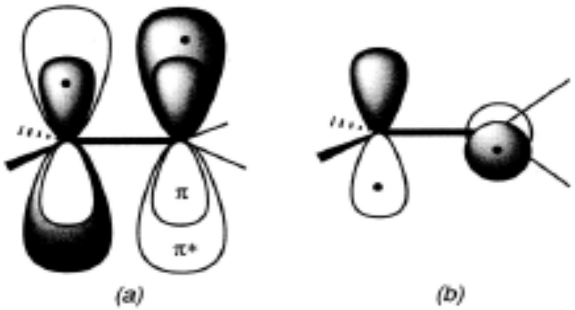
overlap integral controls the gap

$J_{n,\pi^*} \longrightarrow$

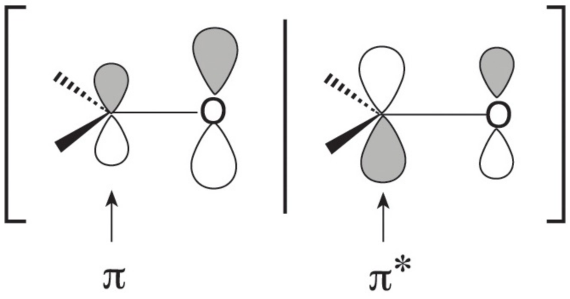


Small orbital overlap between *n* and π*

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



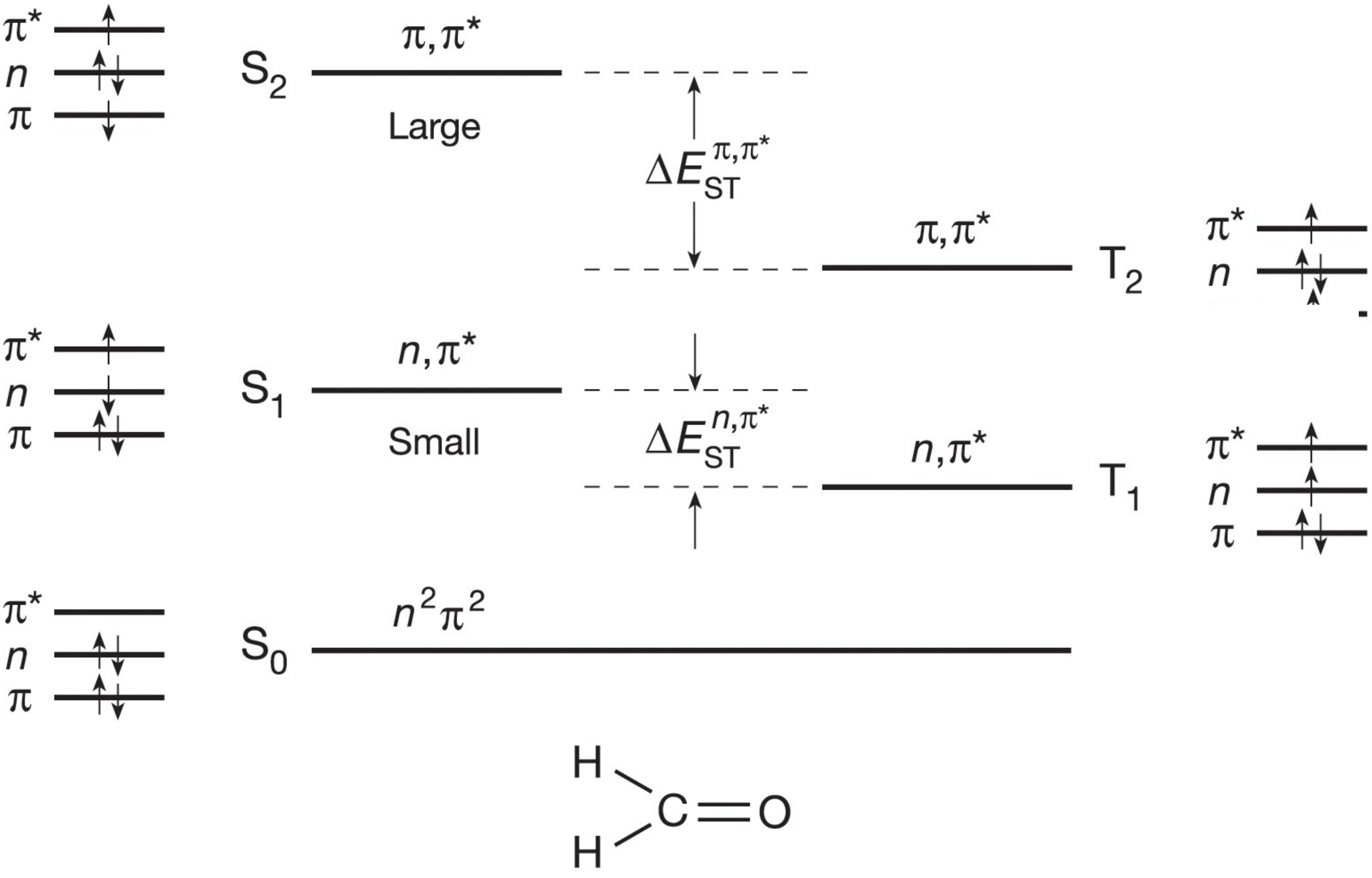
$J_{\pi,\pi^*} \longrightarrow$



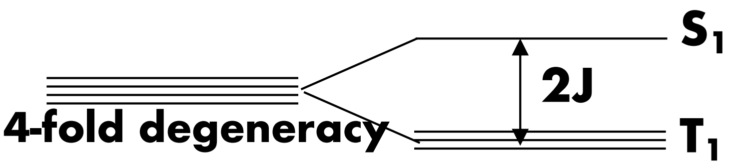
Large orbital overlap between π and π*

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

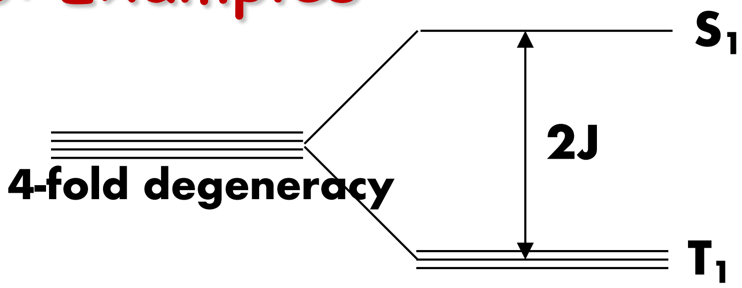
Energies of singlet and triplet states



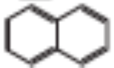
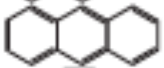
S_1-T_1 energy gap: Examples



Splitting for
n,π* states

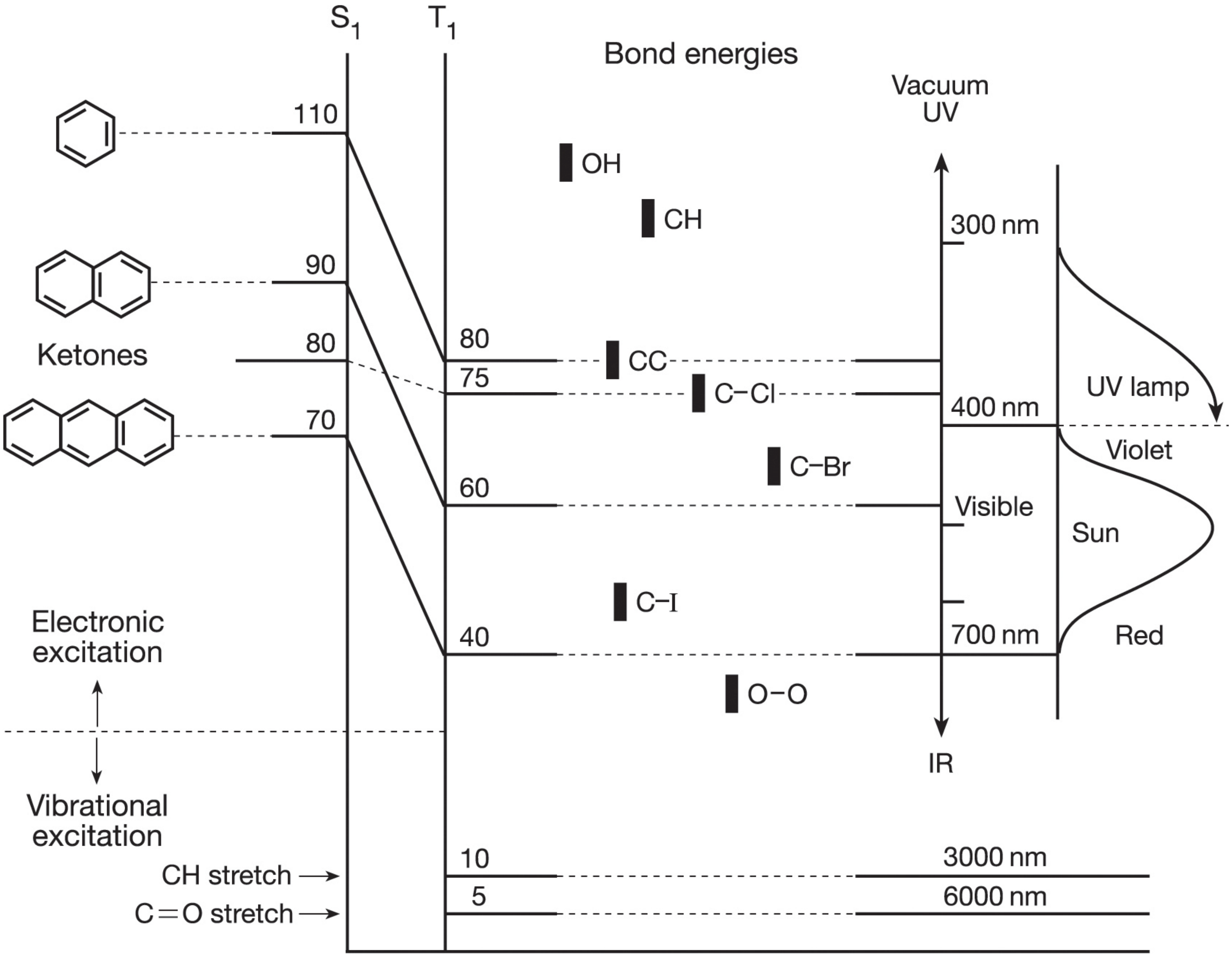


Splitting for
π,π* states

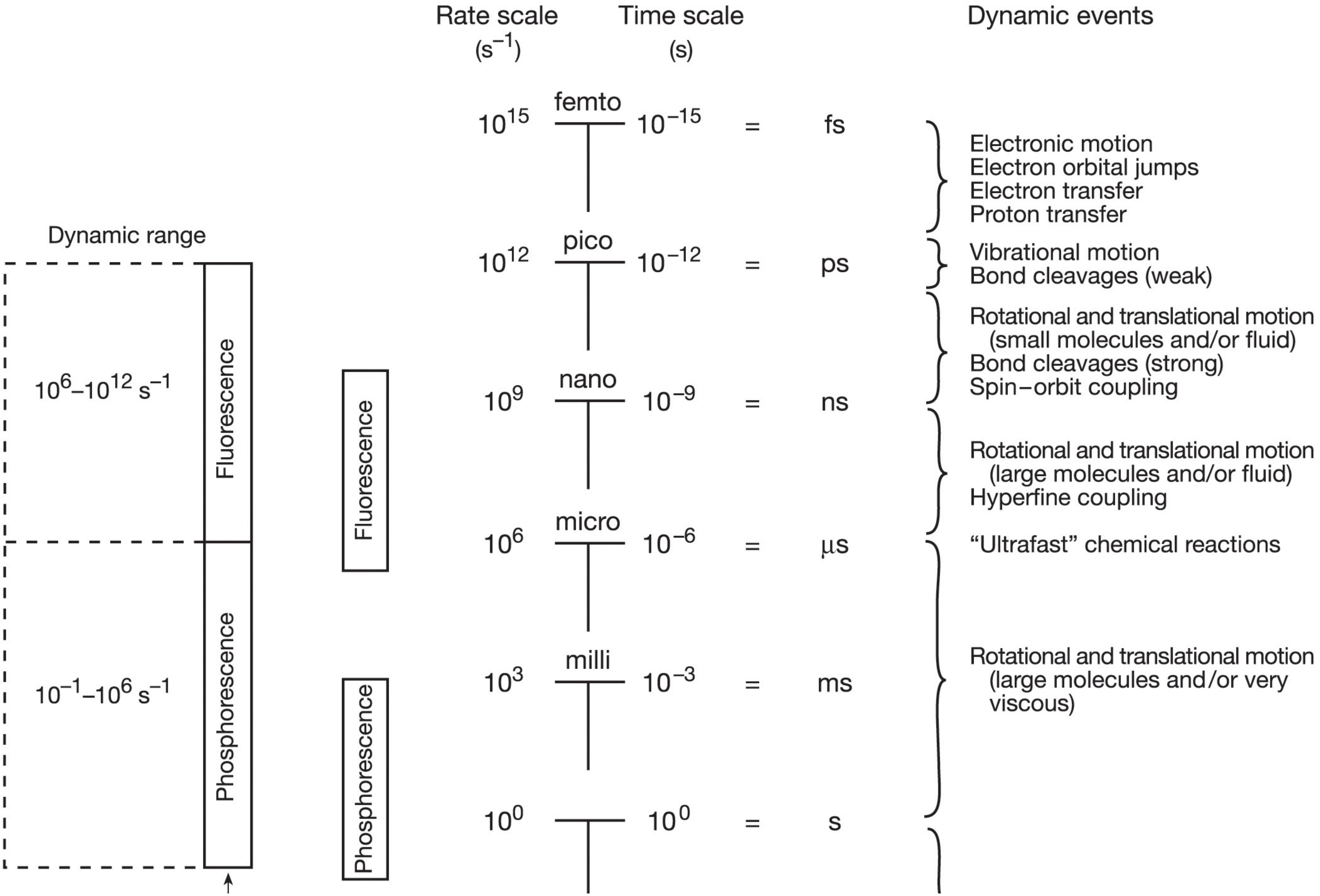
Molecule	Configuration of S_1 and T_1	ΔE_{ST} (kcal mol^{-1})
$CH_2{=}CH_2$	π,π^*	~ 70
$CH_2{=}CH{-}CH{=}CH_2$	π,π^*	~ 60
$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$	π,π^*	~ 48
	π,π^*	25[a] (52)[b]
	π,π^*	31[a] (38)[b]
	π,π^*	~ 34
	π,π^*	30
$CH_2{=}O$	n,π^*	10
$(CH_3)_2C{=}O$	n,π^*	7
$(C_6H_5)_2C{=}O$	n,π^*	5

a. ΔE_{ST} between states of different orbital symmetry.
b. ΔE_{ST} between states of the same orbital symmetry.

Excitation energy, bond energy and radiation wavelength



Time scales



Rate scale (s^{-1})		Time scale (s)		
10^{15}	femto	10^{-15}	=	fs
10^{12}	pico	10^{-12}	=	ps
10^{9}	nano	10^{-9}	=	ns
10^{6}	micro	10^{-6}	=	µs
10^{3}	milli	10^{-3}	=	ms
10^{0}		10^{0}	=	s

Dynamic events

- Electronic motion
- Electron orbital jumps
- Electron transfer
- Proton transfer

- Vibrational motion
- Bond cleavages (weak)

- Rotational and translational motion (small molecules and/or fluid)
- Bond cleavages (strong)
- Spin–orbit coupling

- Rotational and translational motion (large molecules and/or fluid)
- Hyperfine coupling

- “Ultrafast” chemical reactions

- Rotational and translational motion (large molecules and/or very viscous)

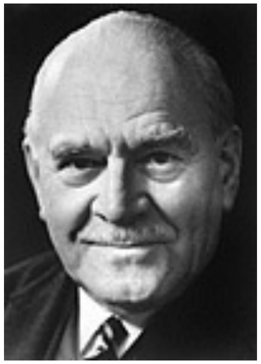
Dynamic range

10^6–10^{12} s^{-1} Fluorescence

10^{-1}–10^6 s^{-1} Phosphorescence

Nobels in Photochemistry

Development of Flash Photolysis and Femtosecond Chemistry

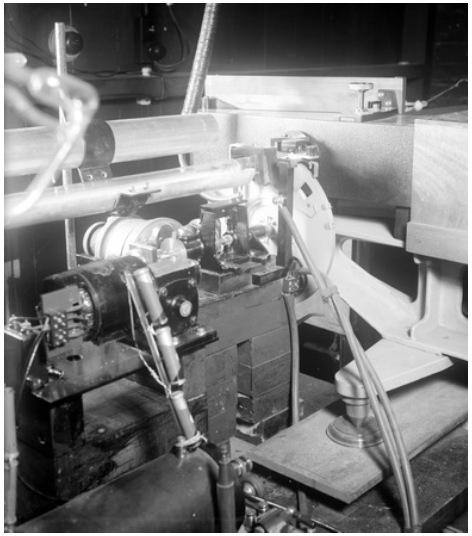


Norrish

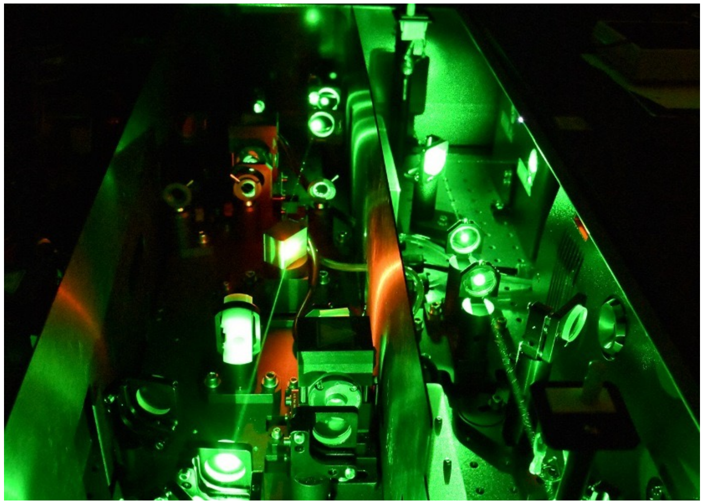
Porter

Zewail

The Nobel Prize in Chemistry 1967



The Nobel Prize in Chemistry 1999

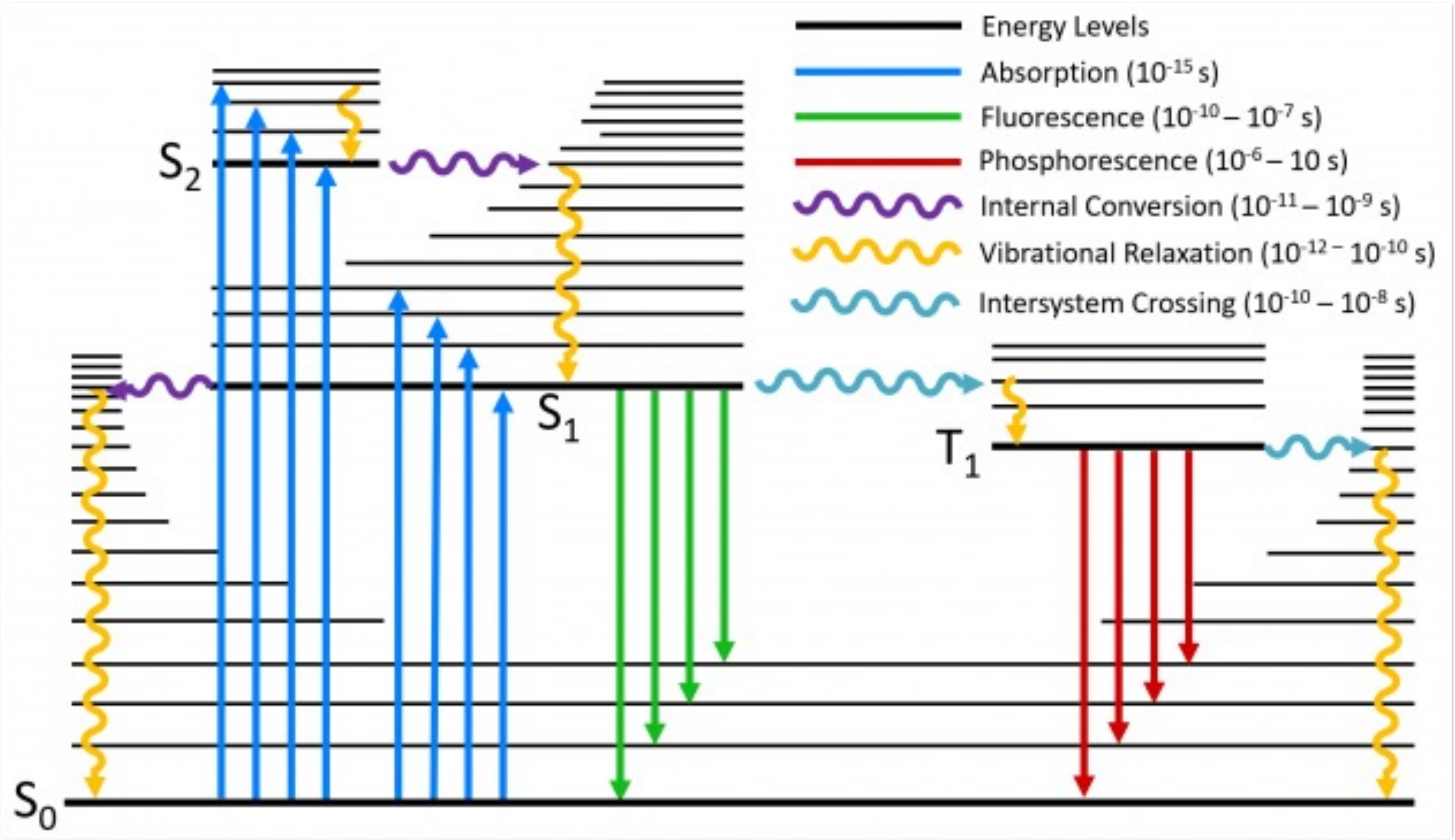


Perrin-Jablonski Diagram

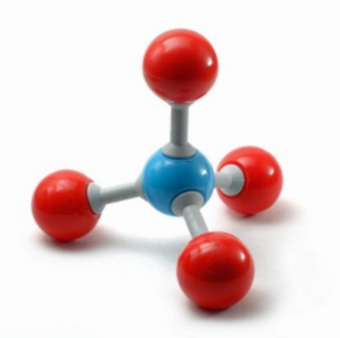
A. Jablonski
(1898-1980)

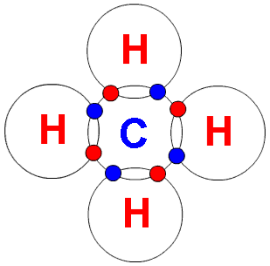
F. Perrin
(1901-1992)

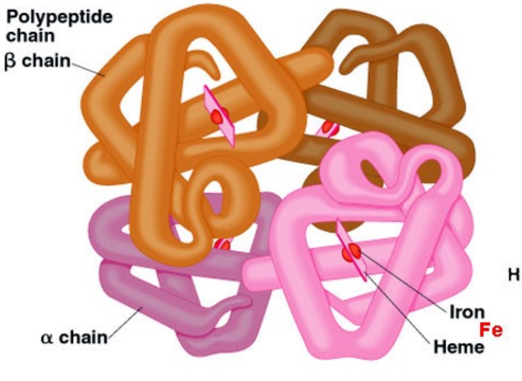
J. Perrin 1870-1942
Nobel Prize, 1926



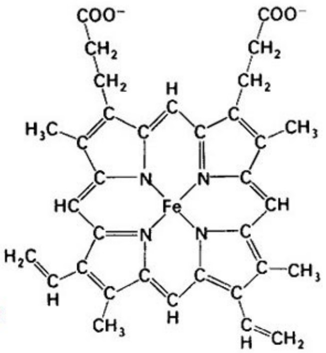
Molecule, a collection of atoms is defined by Ψ







Hemoglobin



Heme
(Fe-protoporphyrin IX)

Nobel Prize in Physics (1933)

$$H\Psi = E\Psi$$

Operator

Eigenvalue

Schrödinger equation

What is Ψ ?

Ψ defines a molecule in terms of nuclei and electrons

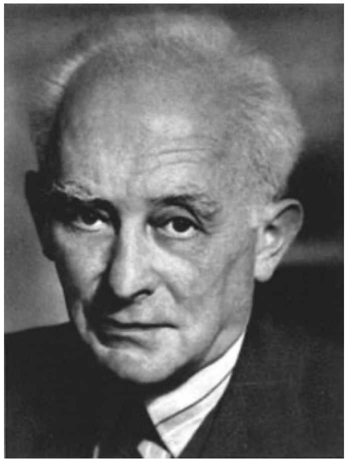
Ψ is made of three parts

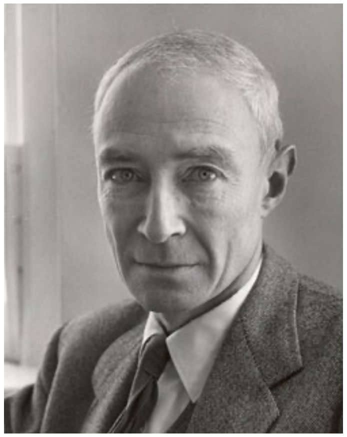
$$\Psi = \underset{\textbf{Electronic}}{\Psi_o} \quad \underset{\textbf{Nuclear}}{\chi} \quad \underset{\textbf{Spin}}{S}$$

The three parts are interconnected. So, it is hard to define a molecule precisely in terms of Ψ

Born – Oppenheimer Approximation

Max Born
(1882-1970)
Nobel Prize, 1954





J. R. Oppenheimer
1904-1967
Director, Manhattan Project

- Electronic motion faster than nuclear motion (vibration).
- Weak magnetic-electronic interactions separate spin motion from electronic and nuclear motion.

Electronic **Nuclear** **Spin**

Time scale matter

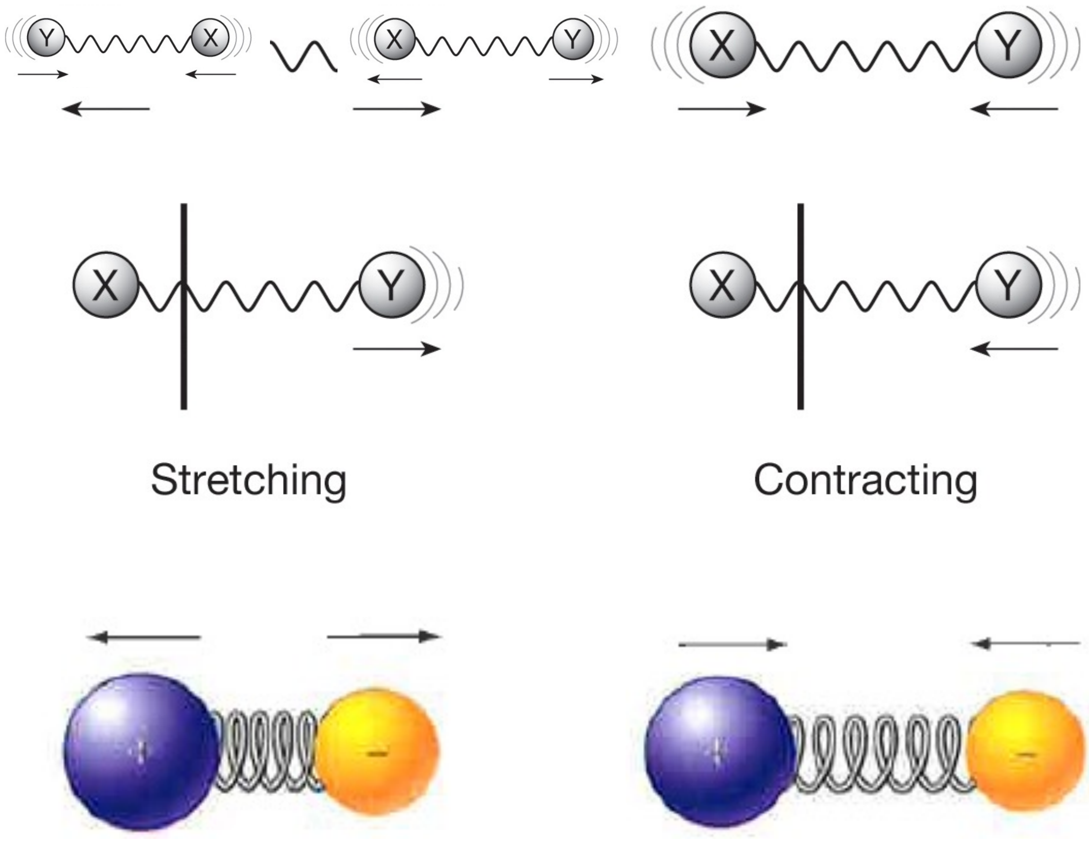
Born – Oppenheimer Approximation

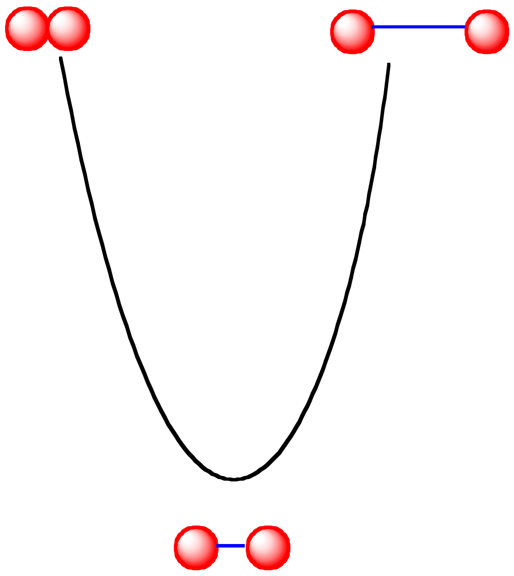
- Electronic motion and nuclear motion can be separated (Born-Oppenheimer approximation)

- To understand molecules, first focus on the location and energies of electrons

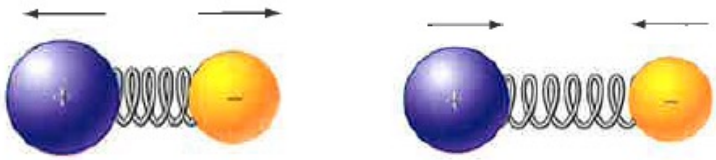
- Understand: Ψ_o(electronic) independent of χ and S

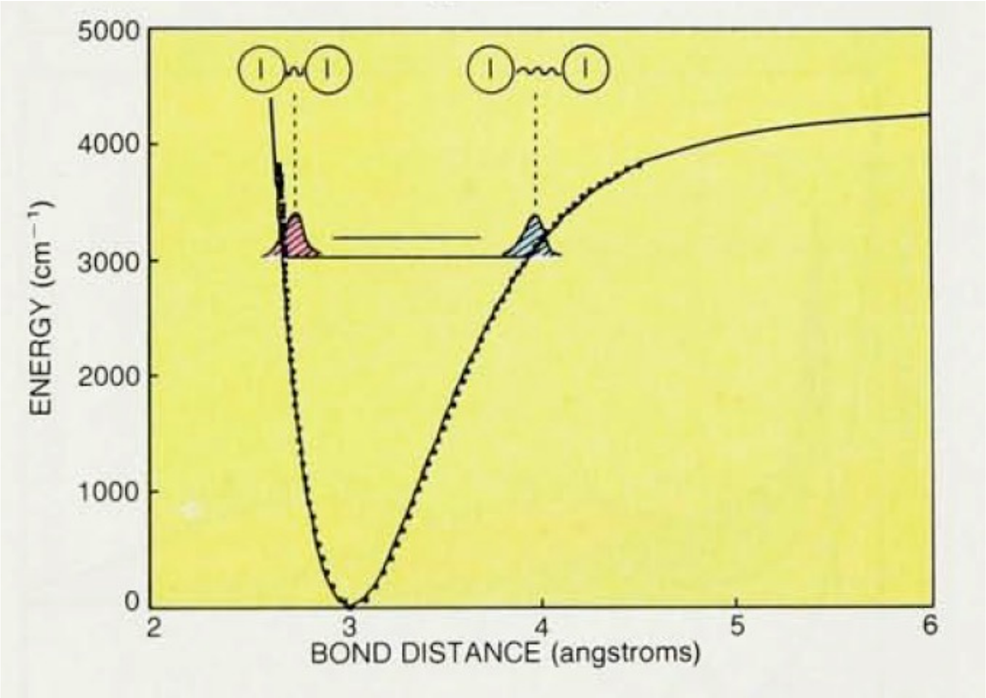
A Model for Vibrational Wavefunctions
The Classical Harmonic Oscillator

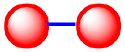




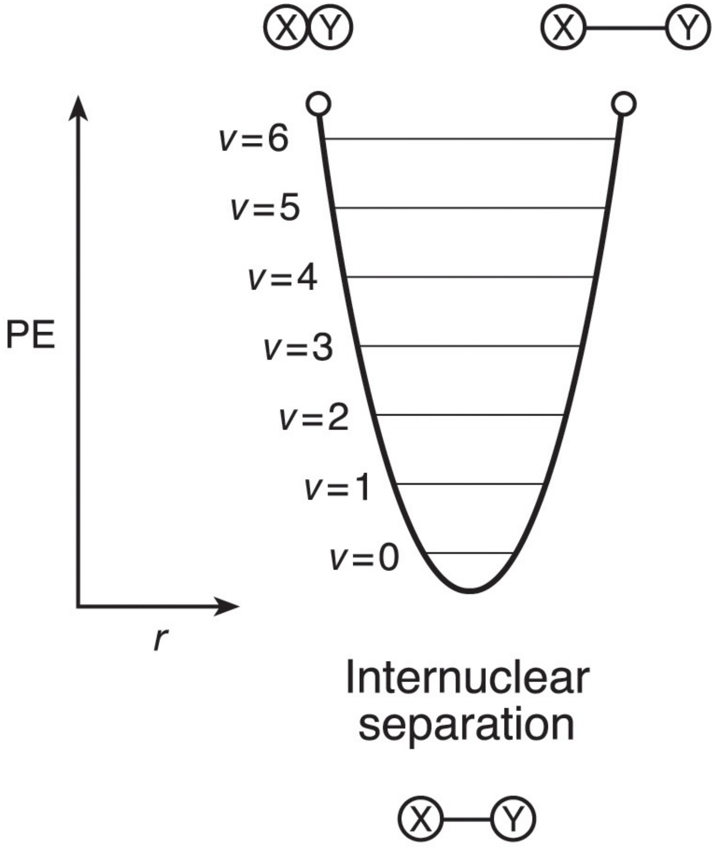
A Model for Vibrational Wavefunctions
The Classical Harmonic Oscillator







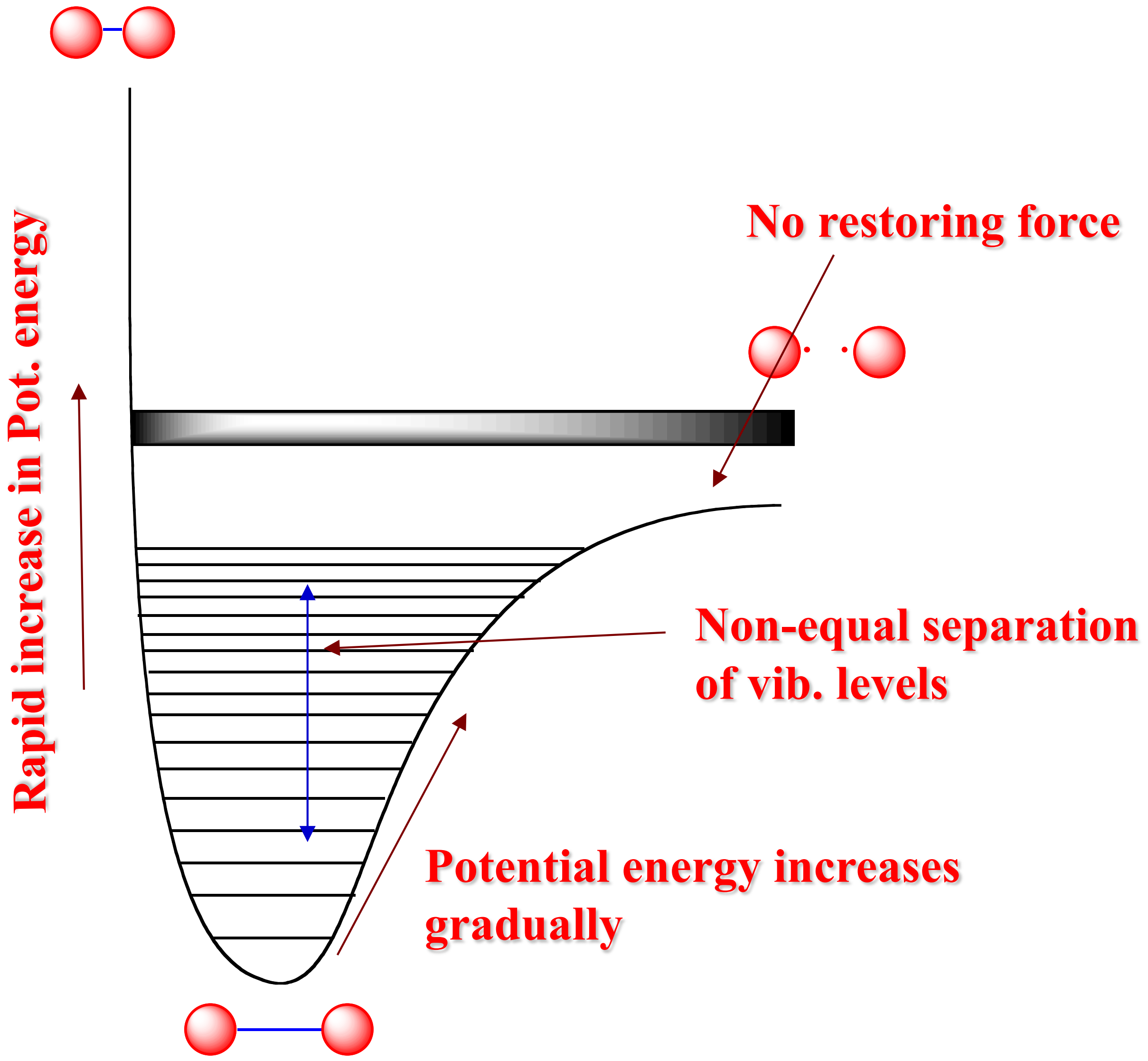
$$E_\nu = PE + KE$$



Quantized Harmonic Oscillator

$$PE_v = h\nu(v + 1/2)$$

The Anharmonic Quantum Mechanical Oscillator



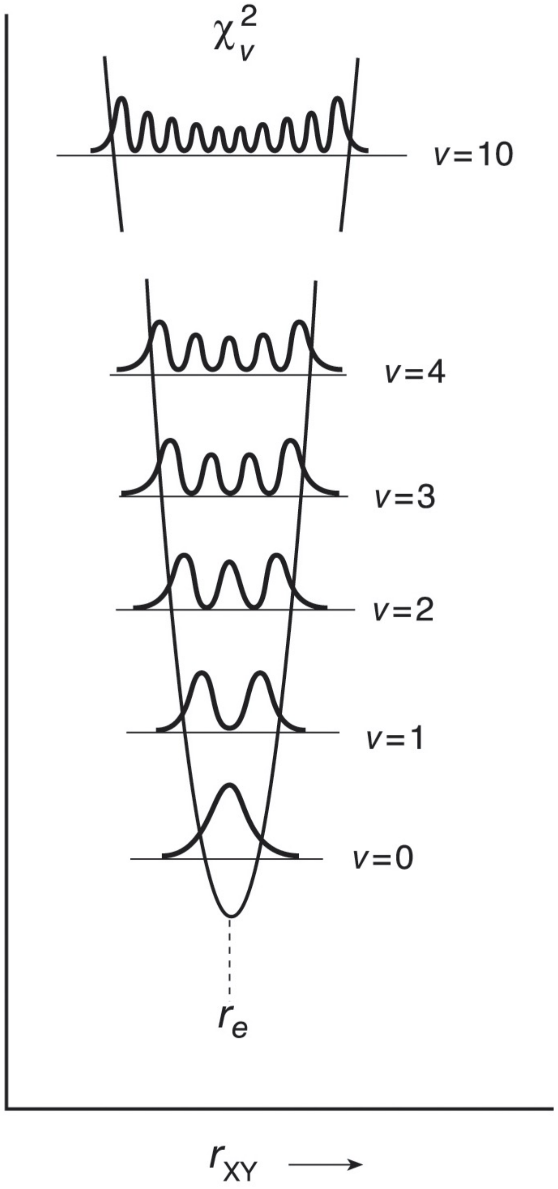
Rapid increase in Pot. energy

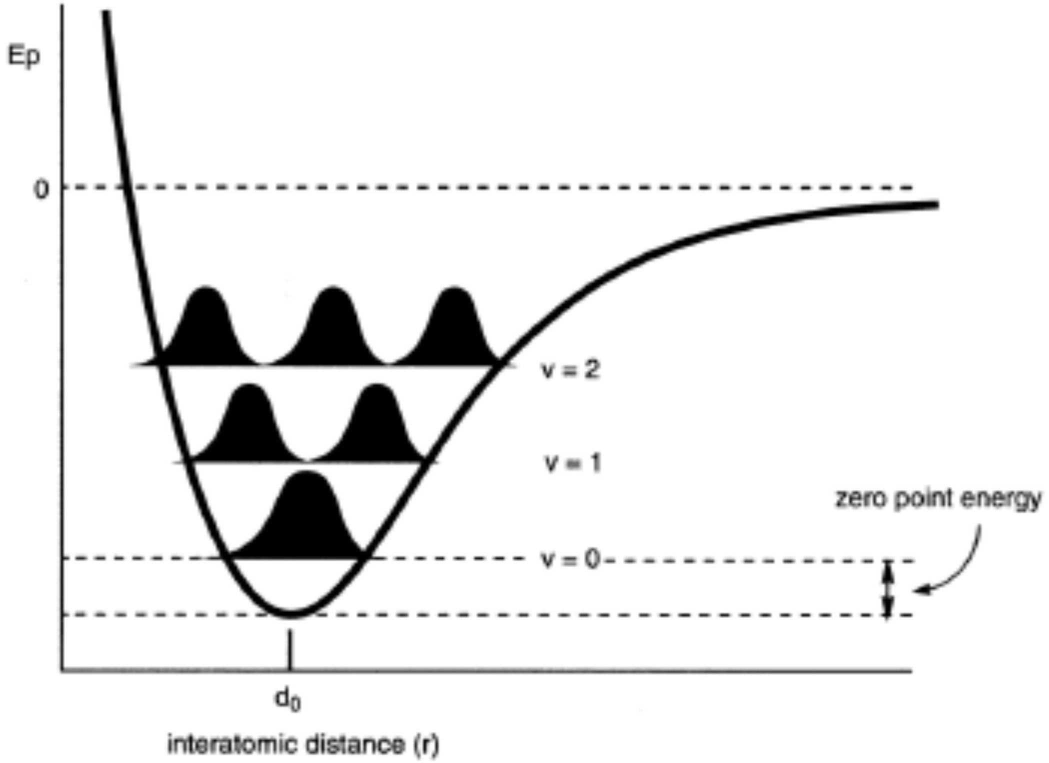
No restoring force

Non-equal separation of vib. levels

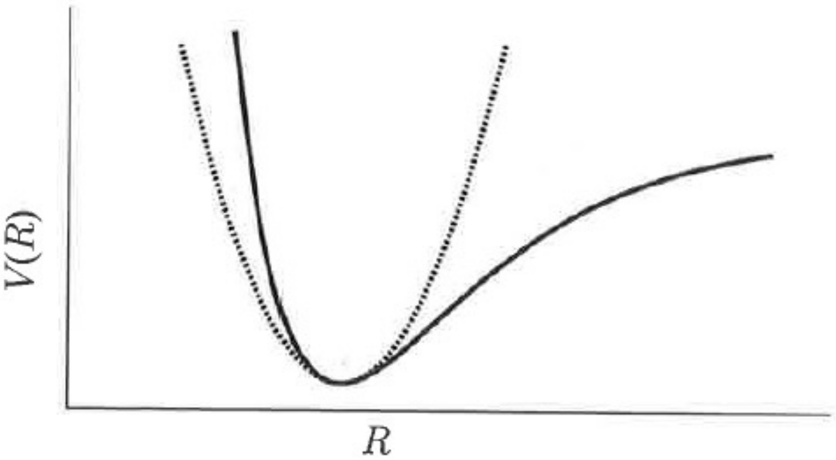
Potential energy increases gradually

Anharmonic Oscillator-Probablity Density

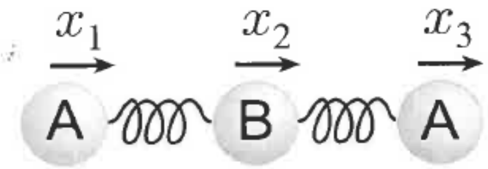


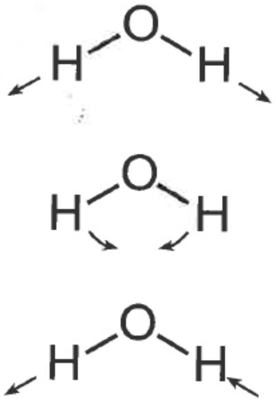


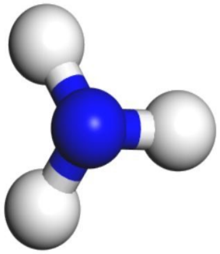
- Anharmonic
- Quantized energy level
- Probability of location of the nuclei



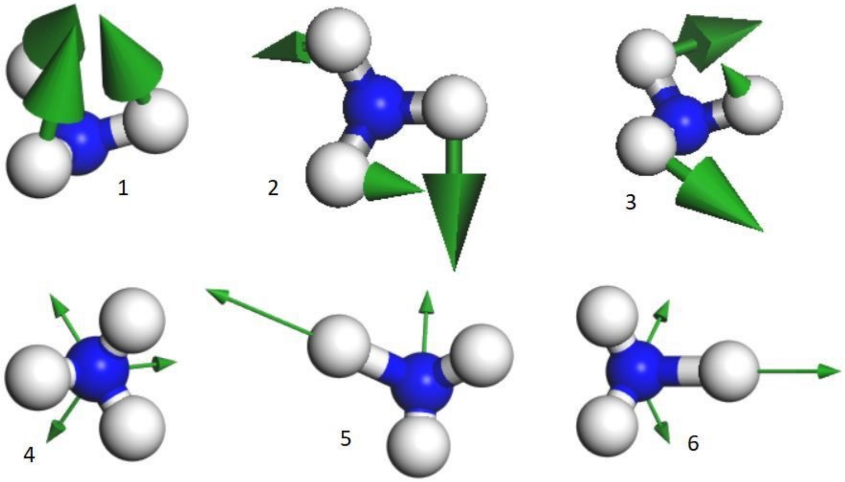
To represent molecules with more than three atoms one needs 3N–6 space



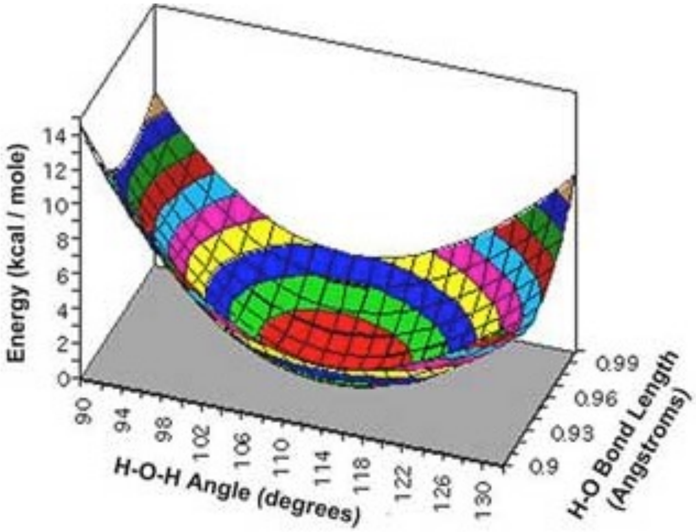




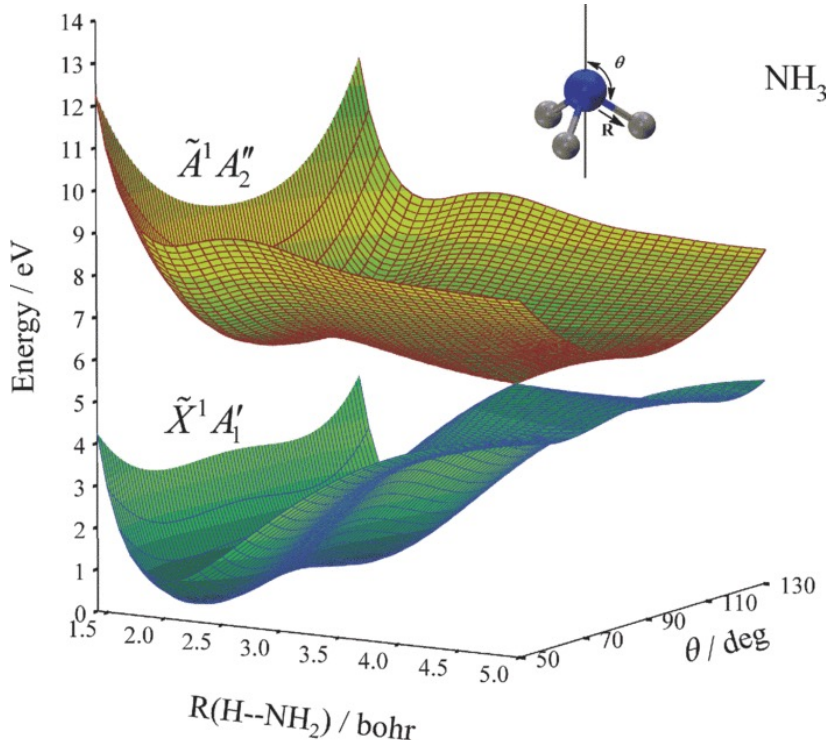
Ammonia



Representation of Polyatomic Molecules



Water



To represent molecules with more than three atoms one needs 3N–6 space

Polyatomic molecules are represented in two or three dimensional space.

What may appear to be a minimum, barrier or saddle point in one subspace may turn out to be nothing of the kind when viewed in another cross section

Energy level diagram of molecules

S_2

T_1

S_1

T_0

S_0