Molecular and Supramolecular Photochemistry

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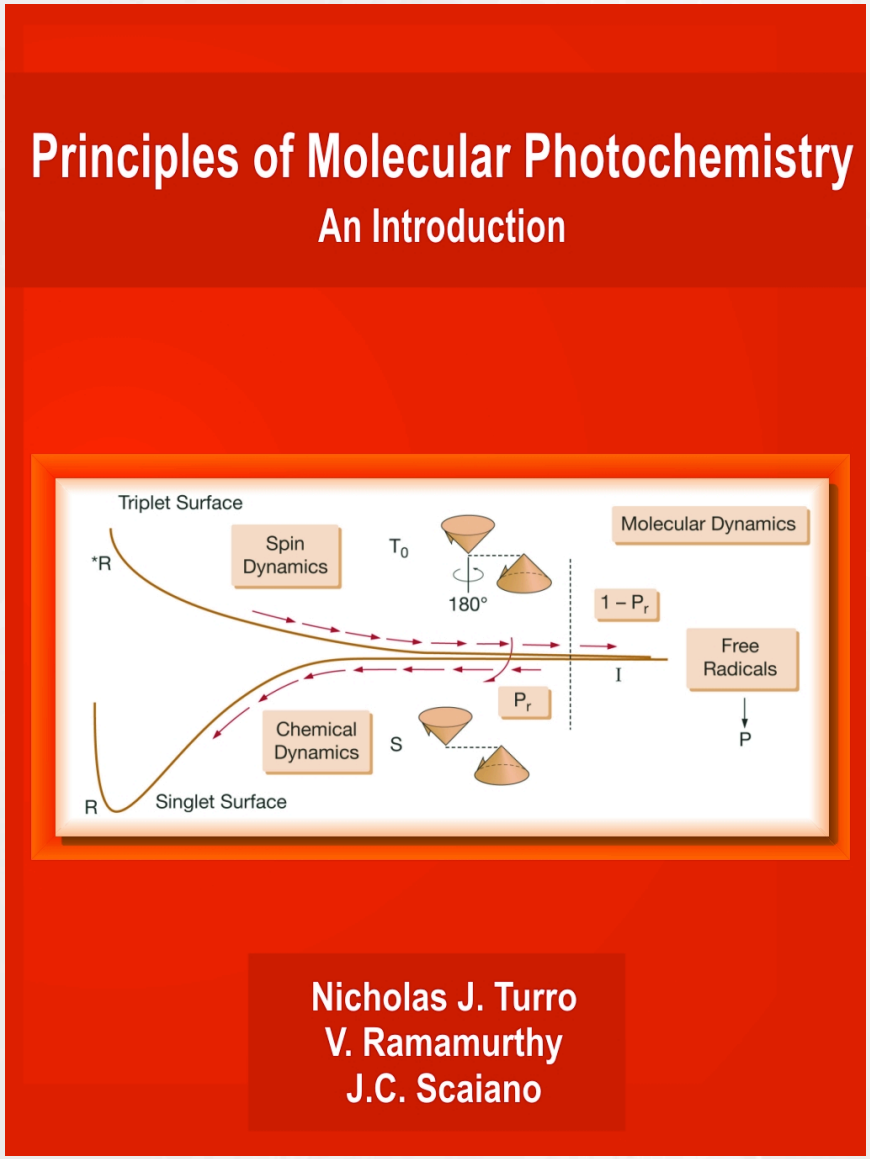

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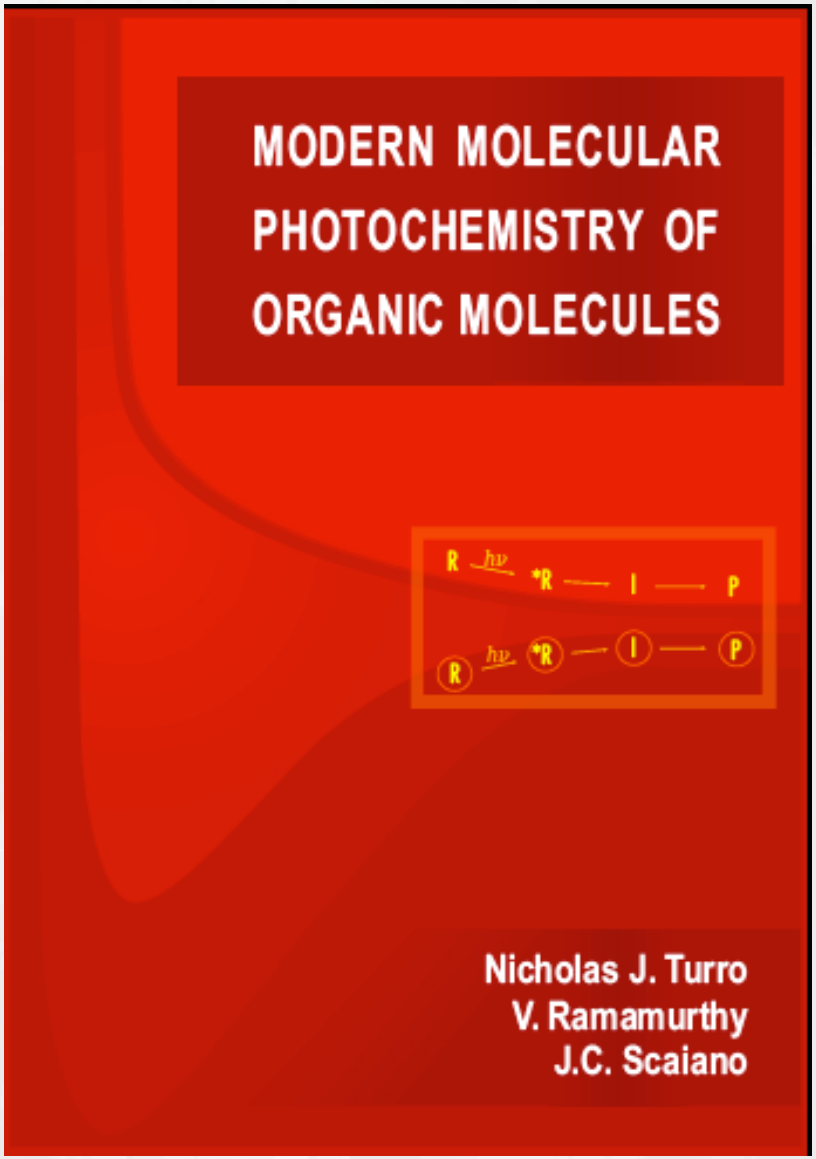

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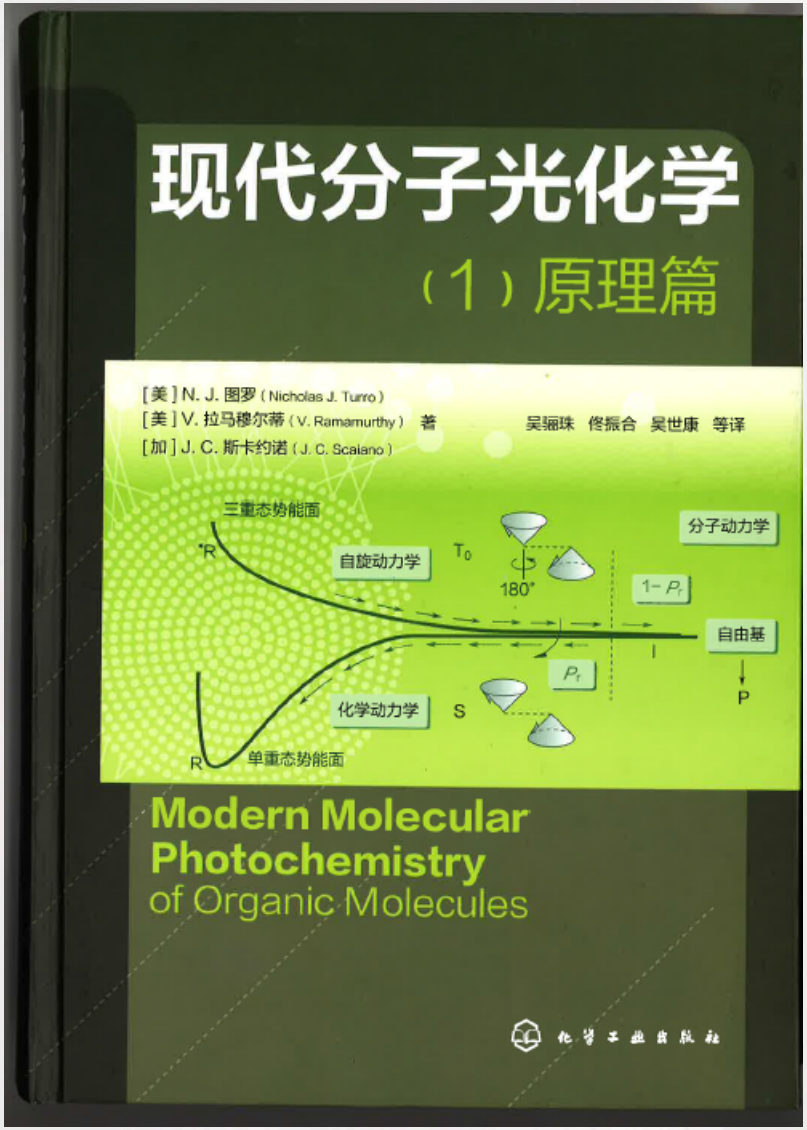
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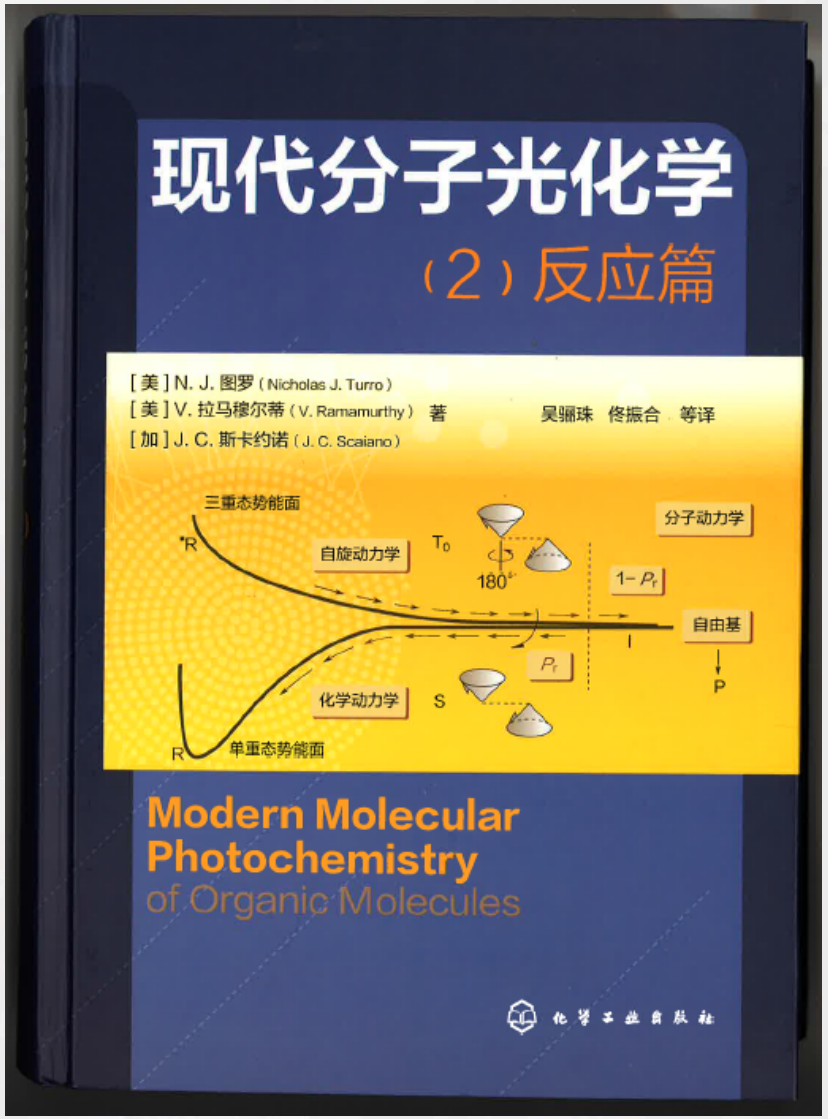
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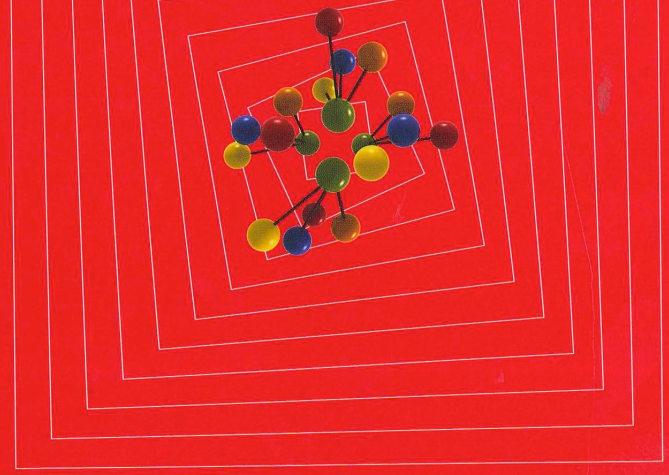
分子光化学の原理

Principles of Molecular Photochemistry : An Introduction

井上晴夫・伊藤 攻 監訳
Nicholas J. Turro, V. Ramamurthy, J. C. Scaiano



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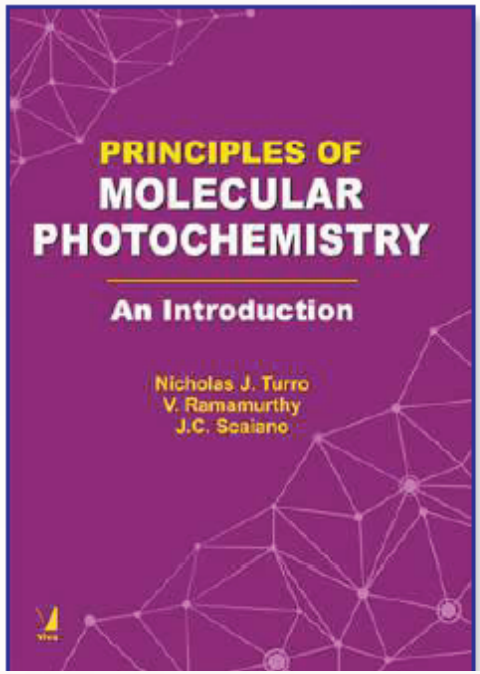

Principles of Molecular Photochemistry
An Introduction

Nicholas J. Turro, V. Ramamurthy, J C Scaiano

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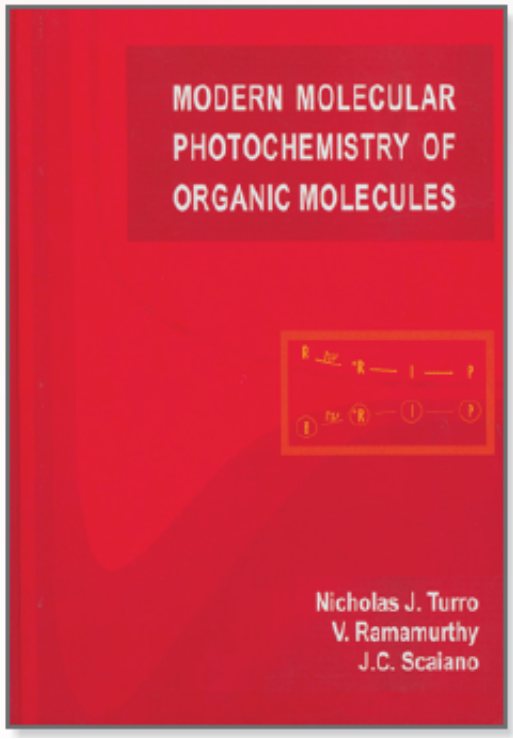

Modern Molecular Photochemistry of Organic Molecules

Nicholas J. Turro, V. Ramamurthy & J.C. Scaiano

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Photochemistry

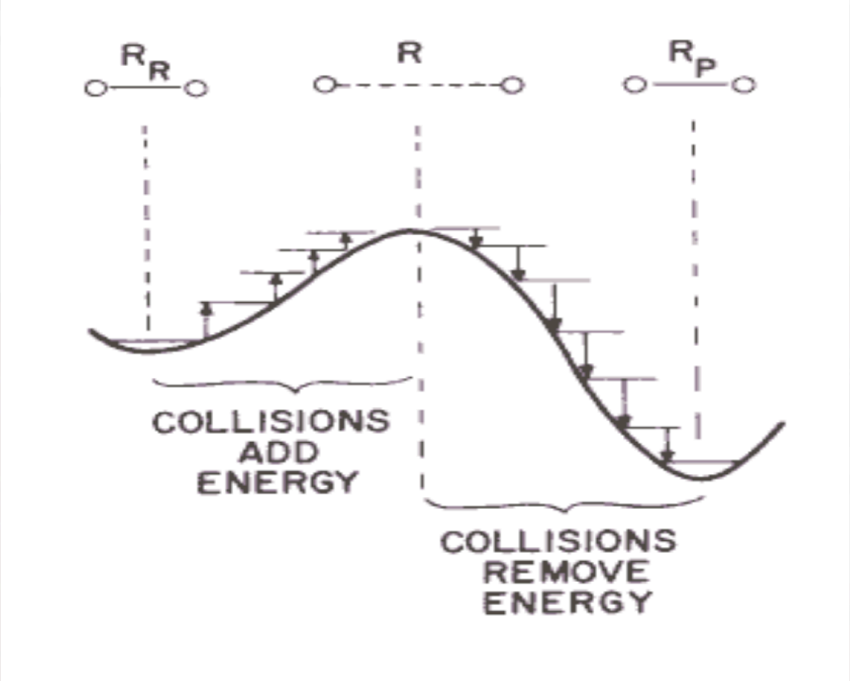
Interaction of Light with Molecules

- *Organic Photochemistry*
- *Inorganic Photochemistry*
- *Photobiology*

What is the difference between thermal Chemistry and photochemistry?

- **Mode of activation**
  - Activated by heat (Thermal)
  - Activated by light (Photo)
- **Selectivity in activation**
  - Only the chromophore that absorbs the light gets activated
- **Energy distribution**
  - Only electronic excitation (Photo)
  - Only vibrational (Thermal)

Visualization of Thermal Reactions

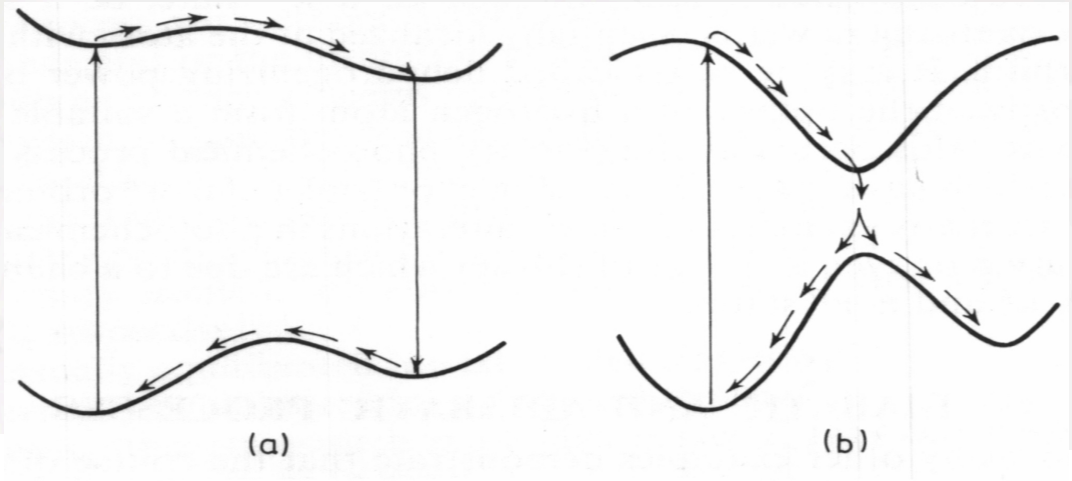


- Transition state connects a single reactant to a single product and it is a saddle point along the reaction course.
- Collisions are a reservoir of continuous energy (~ 0.6 kcal/mol per impact).
- Collisions can add or remove energy from a system.
- Concerned with a single surface.

Visualization of Photochemical Reactions

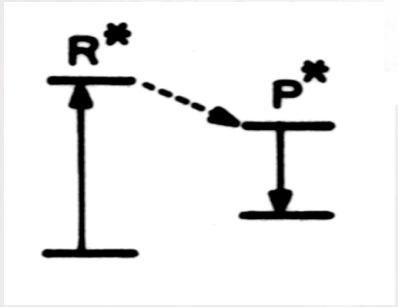
We need to deal with two surfaces.

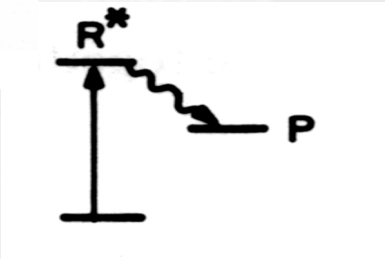
Adiabatic



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

Diabatic



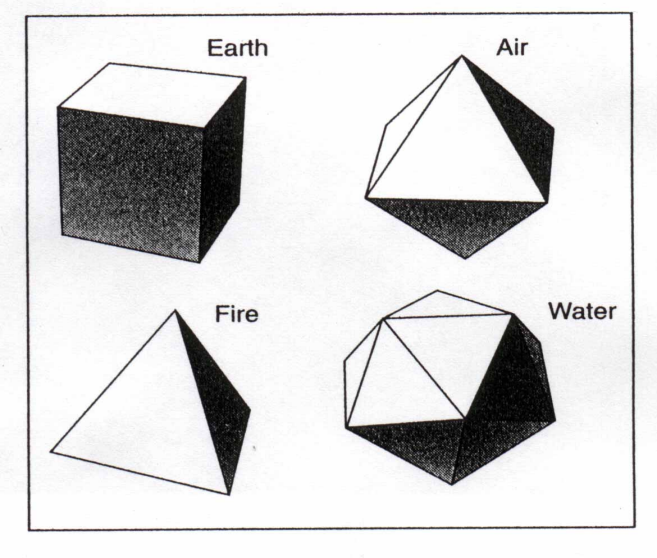


Interaction of Photon and Matter

- What is photon?
- What is matter?
- How do they interact?
- What are the consequences of interaction?

What is photon?

Light and Sight **: Emedocles (500 BC) postulated that Aphrodite made the human eye out of the four elements (fire, air, earth and water) and that she lit *the fire which beamed from the eye and making sight possible.***

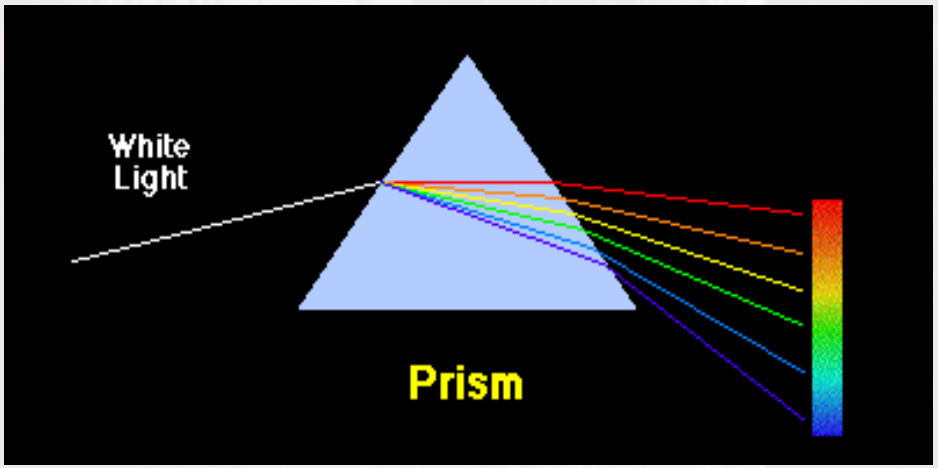


Lucretius (50 BC) The light and heat of the sun is composed of minute atoms which, when they are shoved off, lose no time in shooting right across the interspace of air in the direction imparted by the shove.

Paradigm: Light consists of tiny ***particles*** similar to atoms.

The Paradigm of 1700s: Light consists of particles (energy is propagated by particles which are highly localized in space)

Isaac Newton 1643-1727



Light consists of moving *particles* whose motion imparts them with energy.

The Prism: "Which plainly shows, that the lights of several colours are more and more refrangible one than another, in this order of their colours, red, orange, yellow, green, blue, indigo, deep violet…" Newton

Paradigm: *Light consists of particles that carry energy and can be decomposed into components.*

Is the white light being corrupted or purified?

James Clerk Maxwell
1831-1879

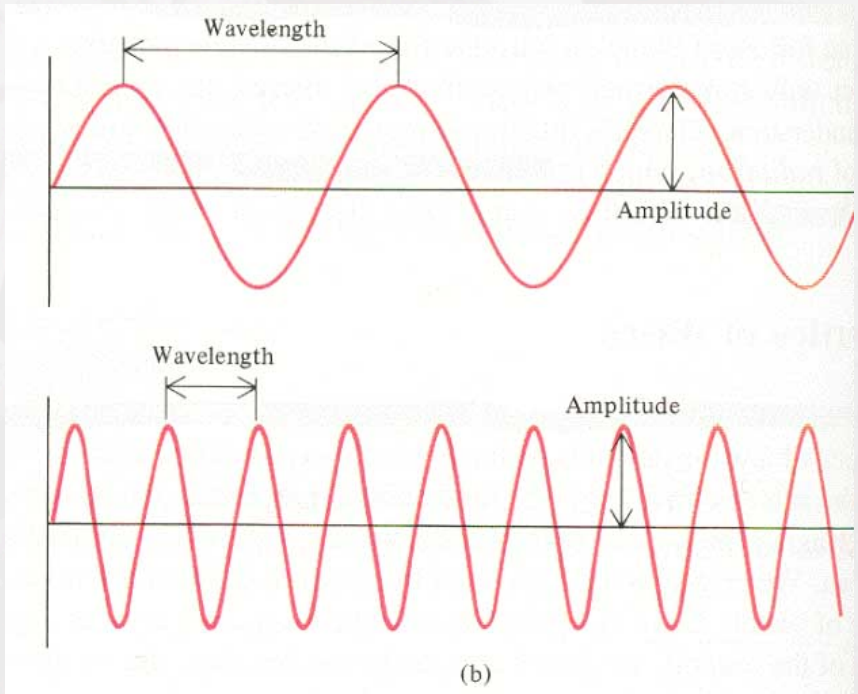
Paradigm 1800s: Light consists of waves (energy propagated by waves): Energy is spread over space like a liquid.

Maxwell's theory is called the ***classical*** theory of light.

Key equations:
$c = \lambda\nu$, λ (Gk lambda), ν(Gk nu)
c = speed of light wave wave propagation
λ = wavelength, ν = frequency

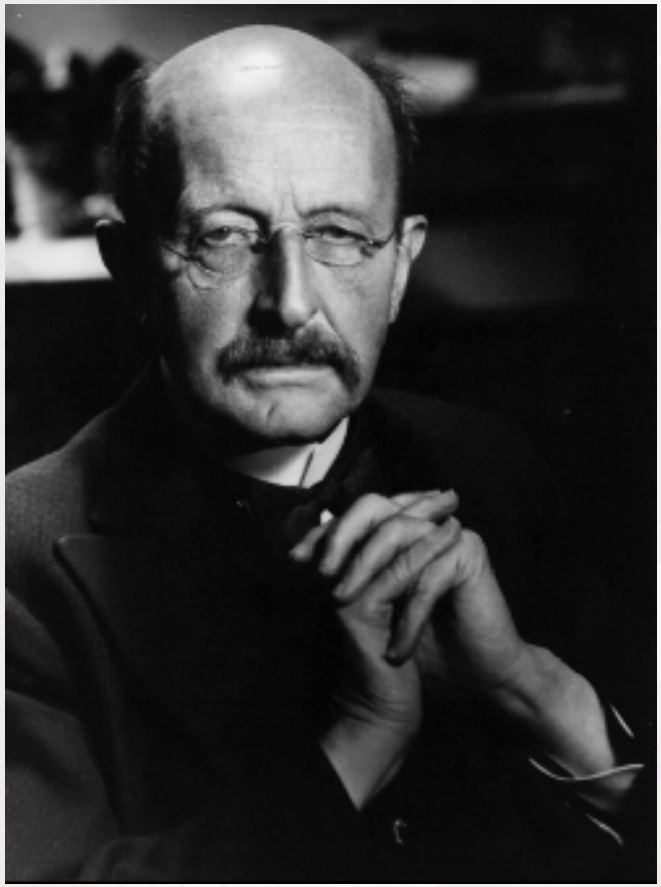
Classical: Energy carried by a light wave is proportional to the *Amplitude* of wave.

λ



Low Frequency

High Frequency



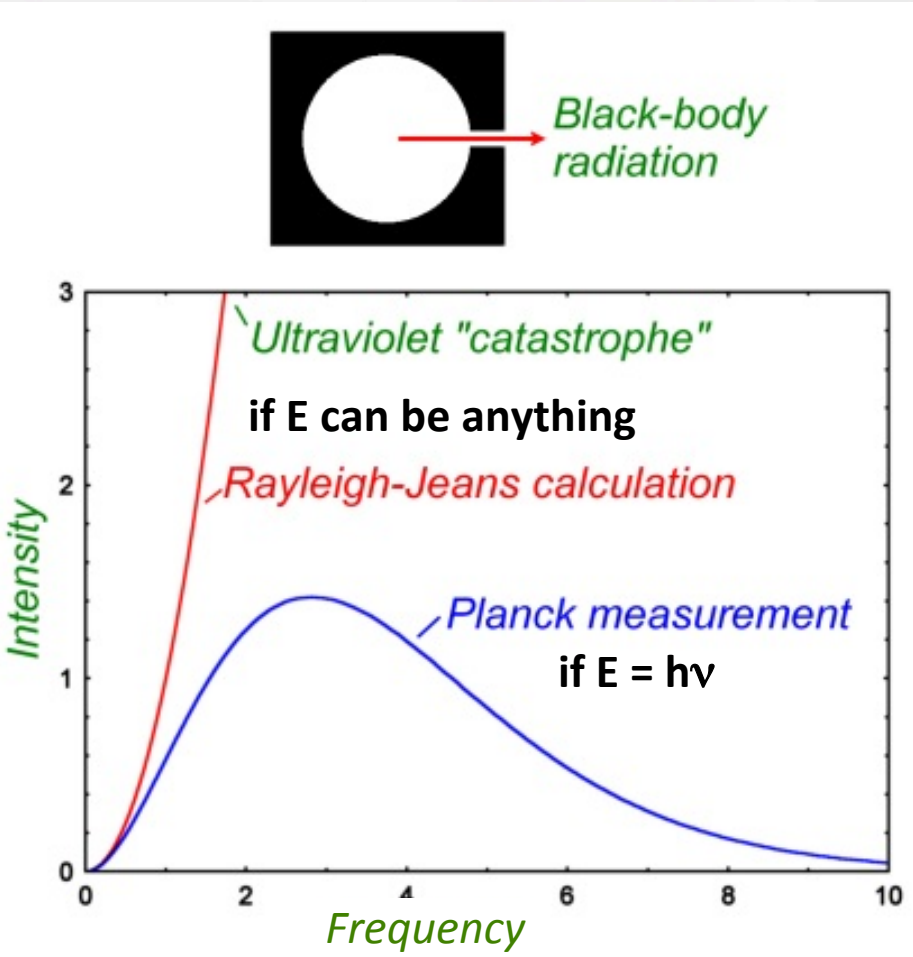
Max Planck
Nobel Prize 1918

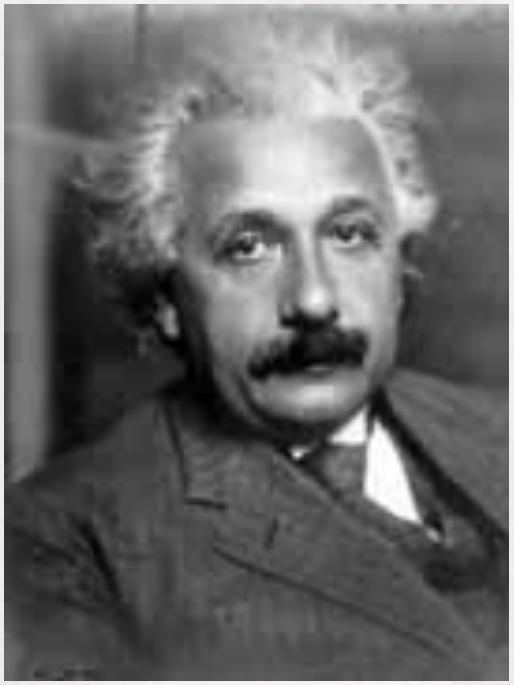
"for his explanation of the ultraviolet catastrophe", namely **E = hν**, the energy of light is bundled and comes in quanta.

1899: Classical Theory says light is beyond doubt a wave.

WAIT A MINUTE: NOT SO FAST (c)!

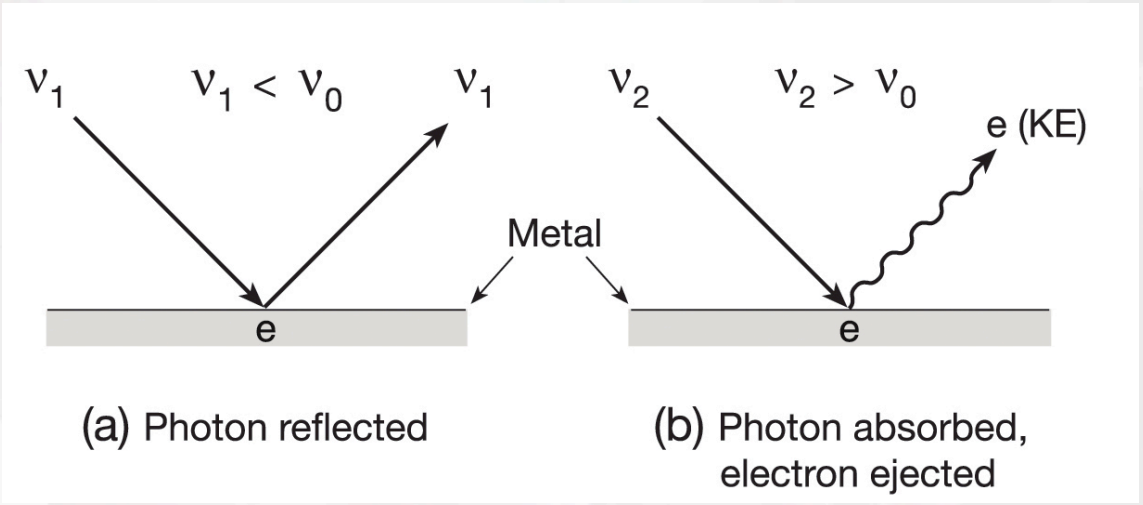
There's this *tiny* little disagreement between theory and experiment. (Which became affectionately known as the ultraviolet catastrophe!)

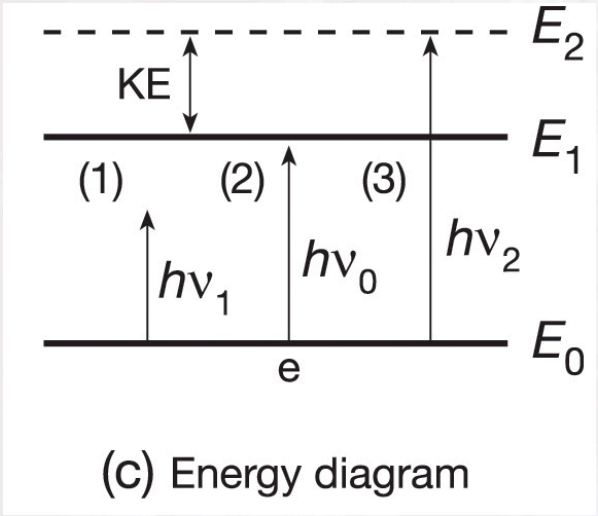




Albert Einstein
Nobel Prize 1921

"For his explanation of the photoelectric effect", namely,
$E_2 - E_1 = h\nu$, light is
quantized as photons (particles).





Niels Bohr
Nobel Prize 1922

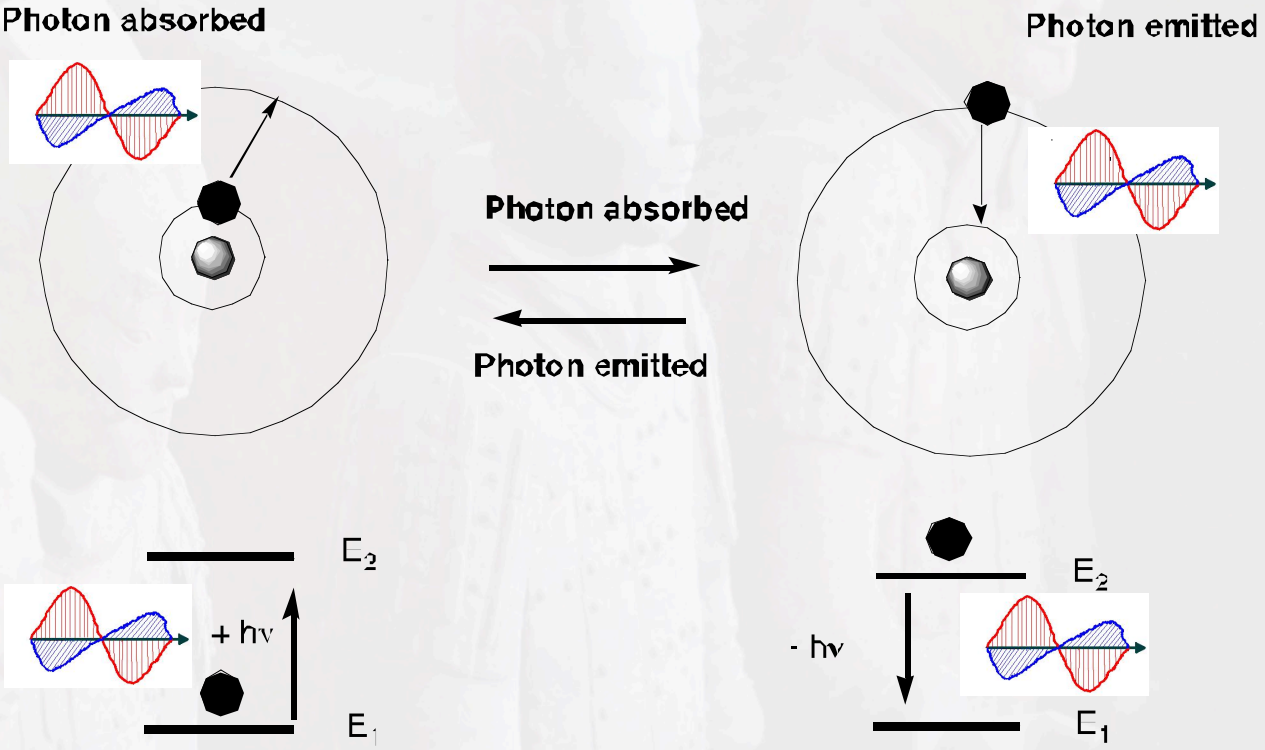
"the structure of atoms and the radiation emanating from them"

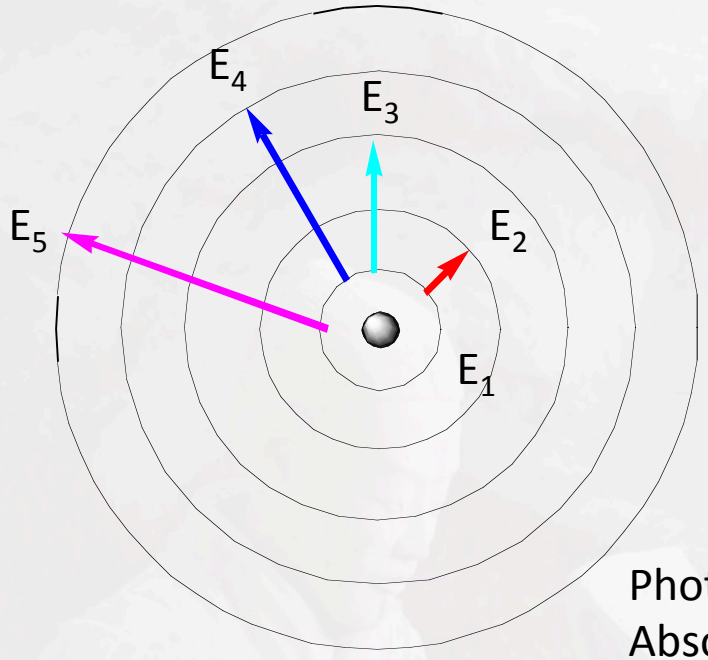
The basis of all photochemistry and spectroscopy!

Absorption Emission Atom

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.

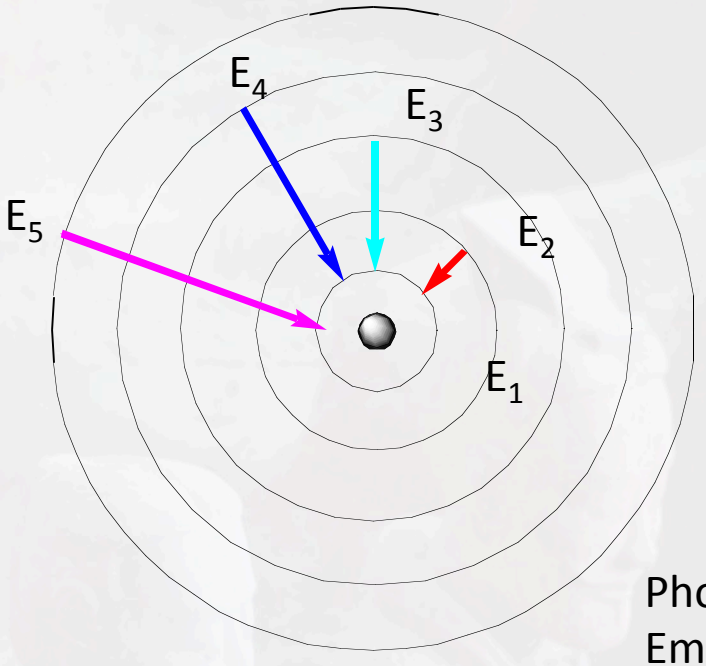
The energy and frequency of light emitted or absorbed is given by the difference between the two orbit energies, e.g., E(photon) = E_2 - E_1 (Energy difference)





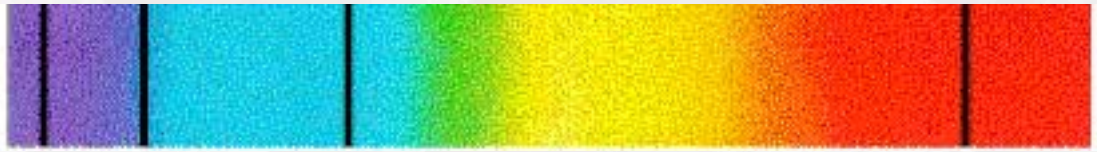
$E_2 - E_1 = h\nu$

Photon Absorbed



Photon Emitted

$E_2 - E_1$ $E_2 - E_1$ $E_2 - E_1$ $E_2 - E_1$



Bohr atom: Light absorption occurs when an electron absorbs a photon and makes a transition from a lower energy orbital to a higher energy orbital. ***Absorption spectra appear as sharp lines.***

Bohr atom: Light emission occurs when an electron makes a transition from a higher energy orbital to a lower energy orbital and a **photon is emitted.** ***Emission spectra appear as sharp lines.***

What next? If waves can mimic particles, then particles can mimic waves

Louis de Broglie
1892-1987

Nobel Prize 1929
"for his discovery of the wave nature of electrons"

Light: $E = h\nu$ (Planck)

Mass: $E = mc^2$ (Einstein)

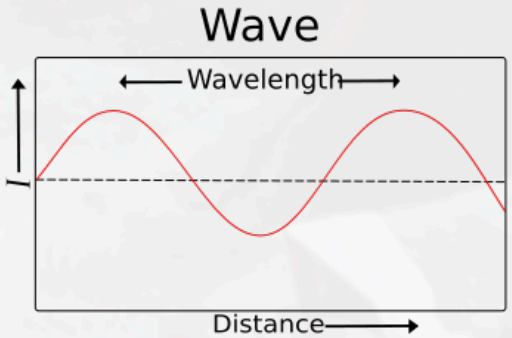
then

$h\nu = h(c/\lambda) = mc^2$ (de Broglie)

Light = Matter!

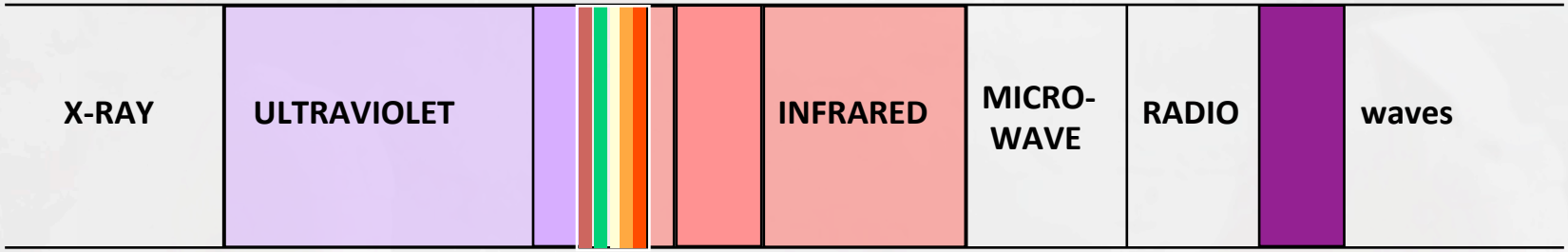
Two seemingly incompatible concepts can each represent an aspect of the truth ... They may serve in turn to represent the facts without ever entering into direct conflict. ***de Broglie, Dialectica***

Light is a particle and wave



Wavelength	λ	c/ν
Wavenumber:	υ	$1/\lambda$
Frequency:	ν	c/λ
Energy	$h\nu$	hc/λ
Einstein:	$Nh\nu$	Mole of photon
Velocity:	186,281 miles/sec; 2.9979 x 10^{10}cm/sec	
Momentum:	E/c	
Mass:	Momentum/c (no real mass)	
Charge:	0 (no charge)	

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

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.

X-Rays
0.1 nm
300,000 kcal/mol

Themal energies at room temperature ca 1 kcal/mole

Tiny energies per photon.

Microwaves
1,000,000 nm
0.03 kcal/mol

Photons, Energy, Einstein

Unit of light = photon
Einstein = mole of photons

$E = h\nu = h(c/\lambda)$ Energy of a single photon

$E = nh\nu = nh(c/\lambda)$ Energy of 'n' photons

$E = N_0 h\nu = N_0 h(c/\lambda)$ Energy of N_0 photons

(avagardo number of photons; an Einstein)

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

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

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

What is matter?

- Matter made of molecules
- Molecules made of atoms
- Atoms made of nuclei and electrons
- Electrons defined by their location (orbital), energy and spin

The first paradigms: What is matter?

Lucretius: ca 99-55 BC

All *matter* consists of tiny fundamental building blocks called ***atoms***

"All nature consists of twain of things: of *atoms* and of the void in which they're set."

"DE RERUM NATURA"
(Everything you wanted to know about the universe but were afraid to ask!)

John Dalton 1766-1844

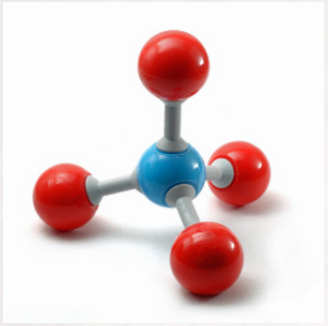
All matter is composed of small indivisible particles termed *atoms*. Atoms of a given element possess unique characteristics and weight.

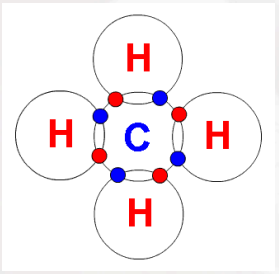
"A New System of Chemical Philosophy"

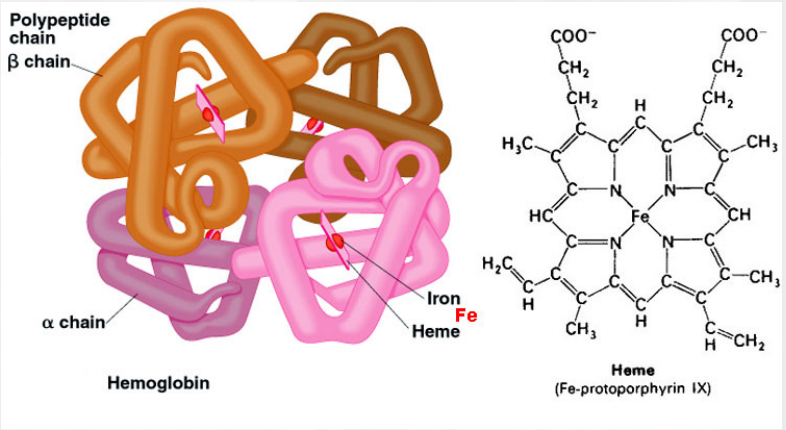
Paradigm: Matter consists of tiny particles called atoms.

A molecule is made up of atoms

Independent of the size and shape of the molecule it is defined by Ψ







$$H\Psi = E\Psi$$

Operator

Eigenvalue

A molecule made up of atoms is defined by Ψ

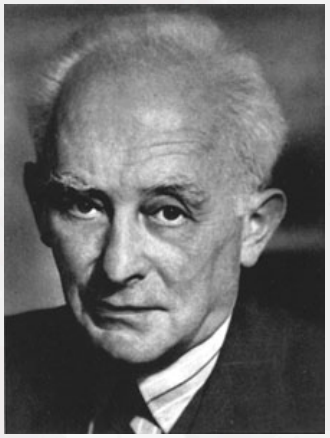
Ψ is made of three parts

The three parts are interconnected

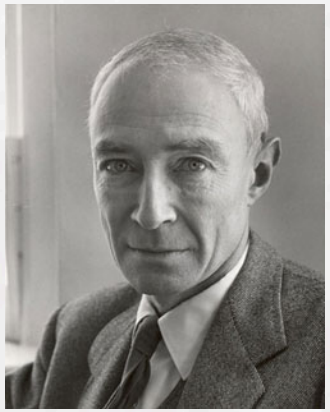
$$\Psi = \Psi_o \quad \chi \quad S$$

Electronic Nuclear Spin

Born – Oppenheimer Approximation



Born



Oppenheimer

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

$\Psi \quad - \quad \Psi_o \qquad \chi \qquad S$

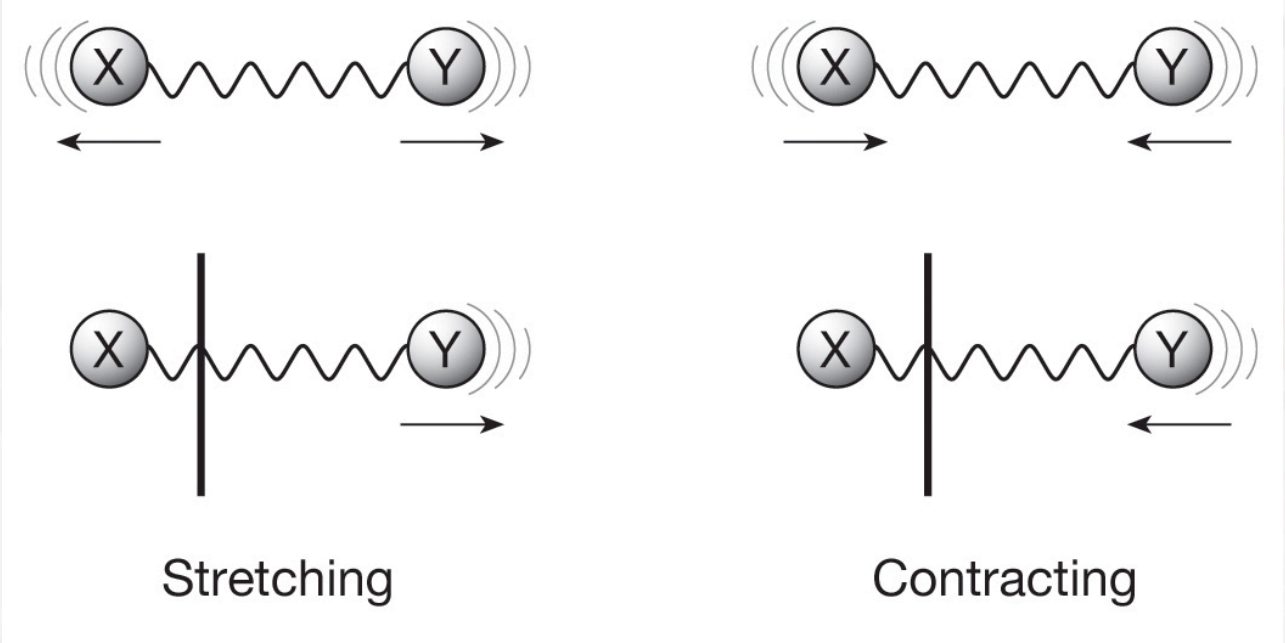
Electronic Nuclear Spin

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

- **To understand molecules it is important to focus on the location and energy of electrons**

- Understand: Ψ_o independent of χ and S

Visualization of nuclear vibrations
The Classical Harmonic Oscillator

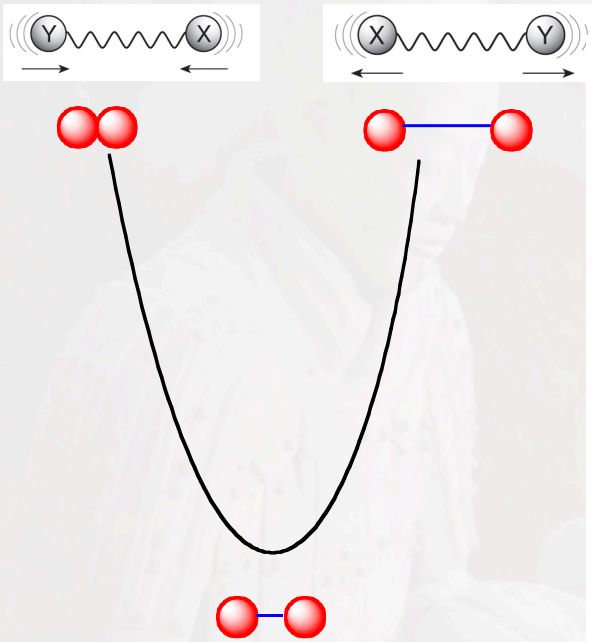


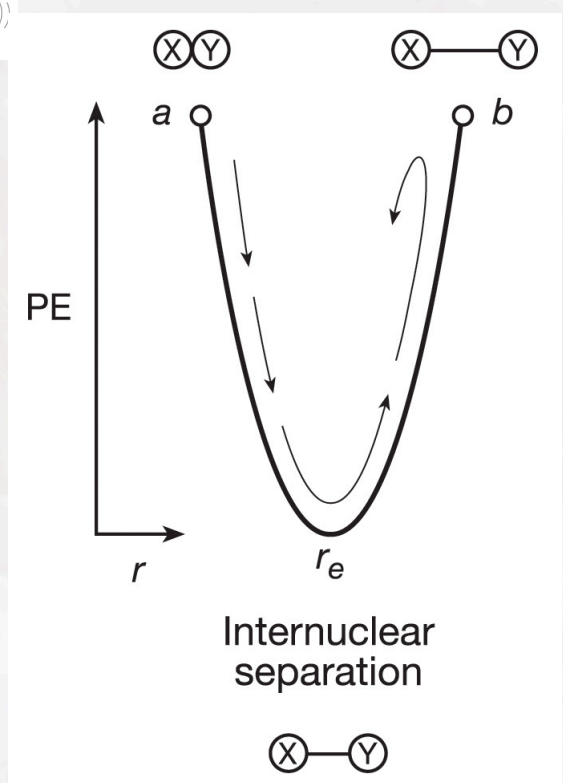
ν (frequency) $= (k/\mu)^{1/2}$

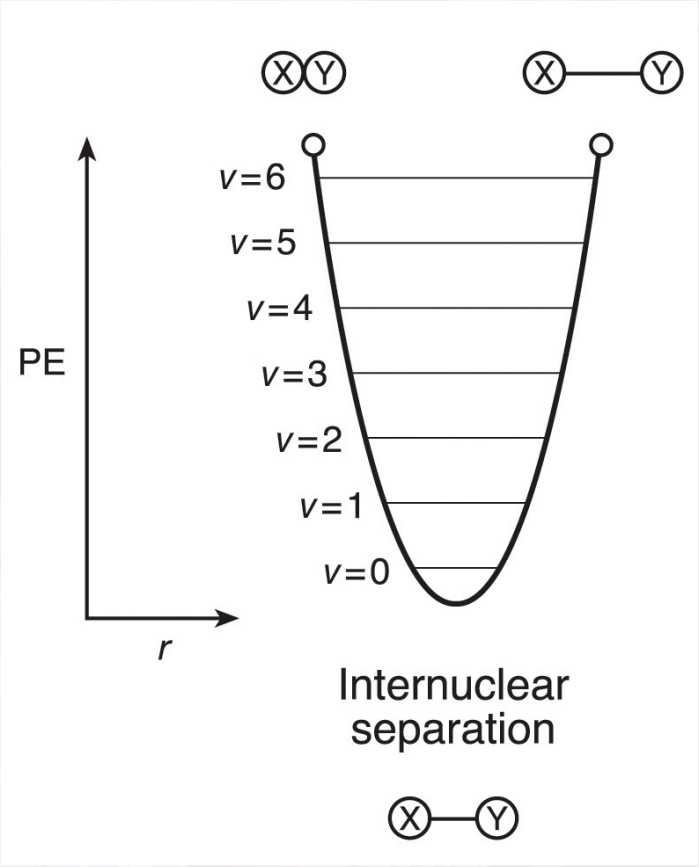
$\mu = (m_1 + m_2/m_1m_2)^{1/2}$

F = restoring force

Independent of number of atoms we think in terms of two dimensional drawings







Harmonic Oscillator

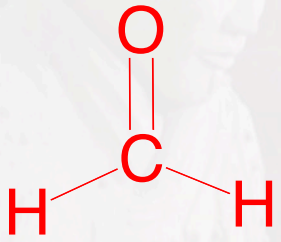
Quantized Harmonic Oscillator

Electron

- It has dual wave and particle properties, just like a photon
- Negatively charged, does not vary with energy
- Electric charge oscillates with time
- Constantly spinning on its axis (spin)
- It is a small magnet
- Coupled with protons and neutrons it holds atoms, molecules and everything in the world
- It is small, 0.00028 nm.

Viewing electrons in molecules

Electrons are present in atomic orbitals in the case of atoms and molecular orbitals in the case of molecules)



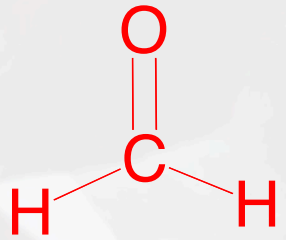
Inner orbitals

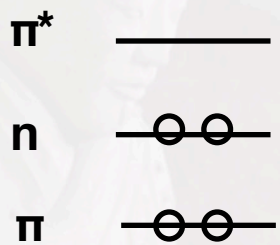
Bonding orbitals

Frontier orbitals

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

Types of transitions in formaldehyde





ground state

Visualization of Spin Chemistry

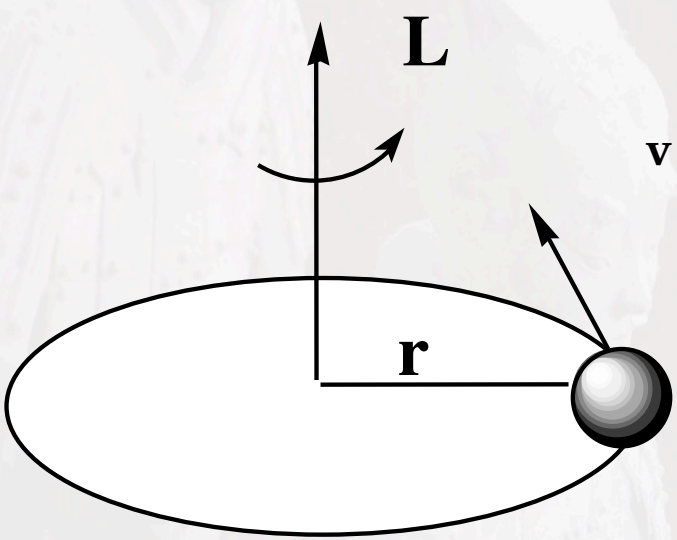
- Quantum mechanics requires mathematics for a quantitative treatment

- 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 also "correct" mathematical representations fail for complex systems as molecules

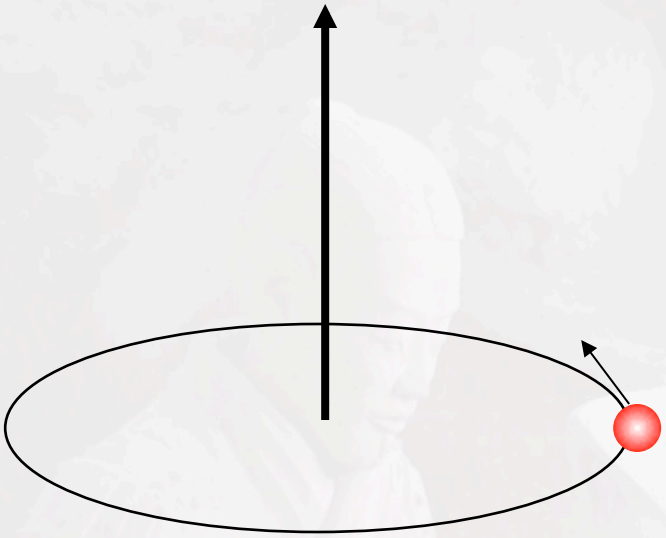
Electron spin and orbital angular momenta

orbitral angular momentum vector, **L**

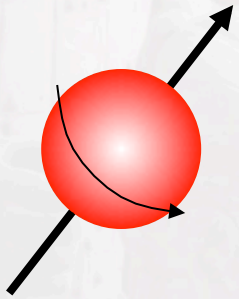


spin angular momentum vector, **S**

Spin



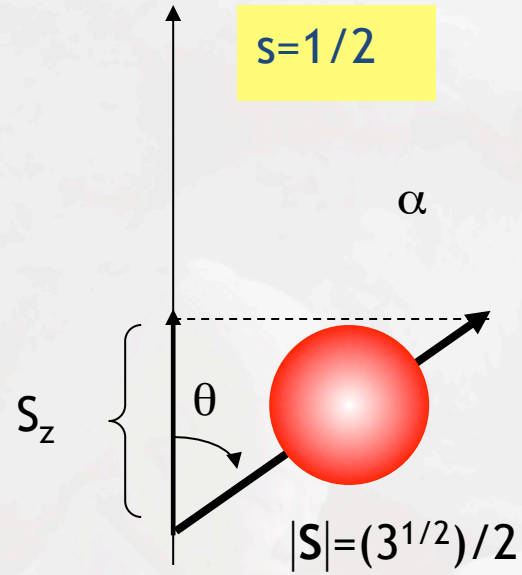
- Quantum particles possess an intrinsic angular momentum called spin which is not associated to a rotation about an axis, although we can visualize it as if it was generated by a rotation of the particle about its own axis



- Classically angular momentum is a property of a macroscopic object which is in rotation about an axis

s=1/2

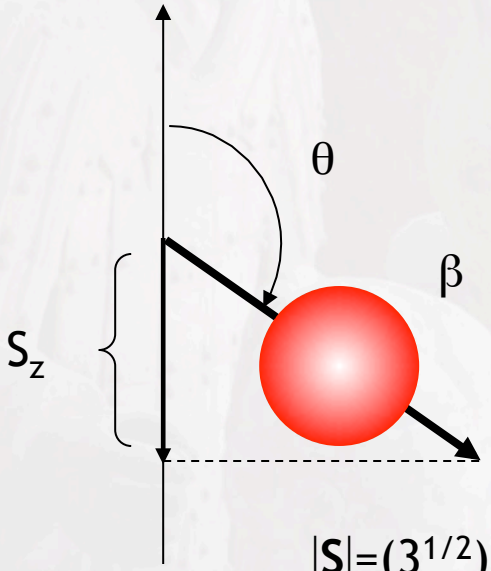
Spin multiplicity= 2S+1 = 2



In particular for

S=1/2 →|S|=(3^1/2)/2

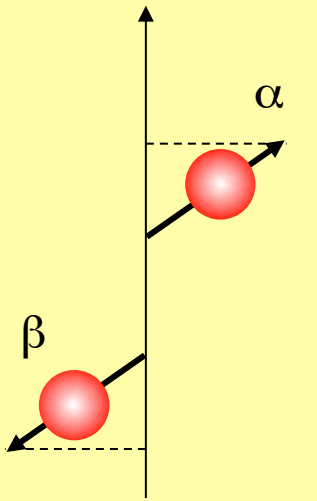
θ=55º for M_s= 1/2

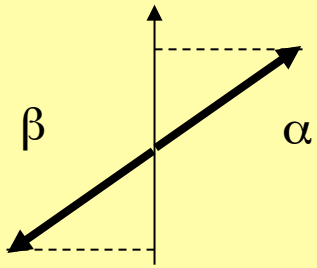


θ=125º for M_s=-1/2

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

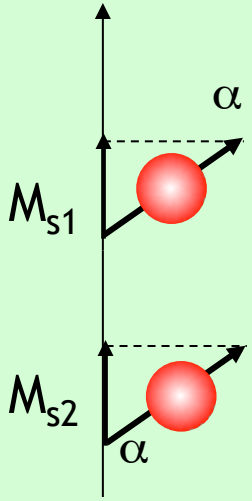
Two spins of ½: S = 1
Spin multiplicity= 2S+1 = 3

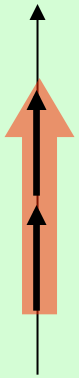




$M_S=0$

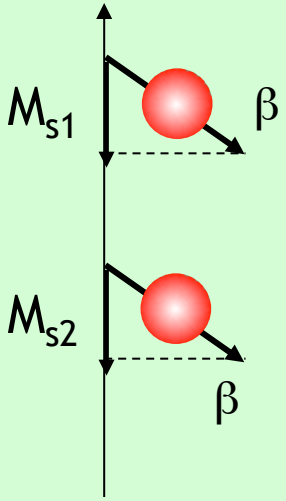
$\alpha\beta-\beta\alpha$





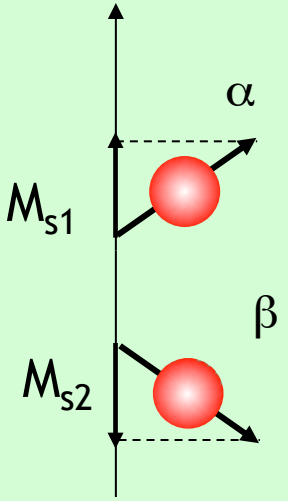
$M_S=1$

$\alpha\alpha$



$M_S=-1$

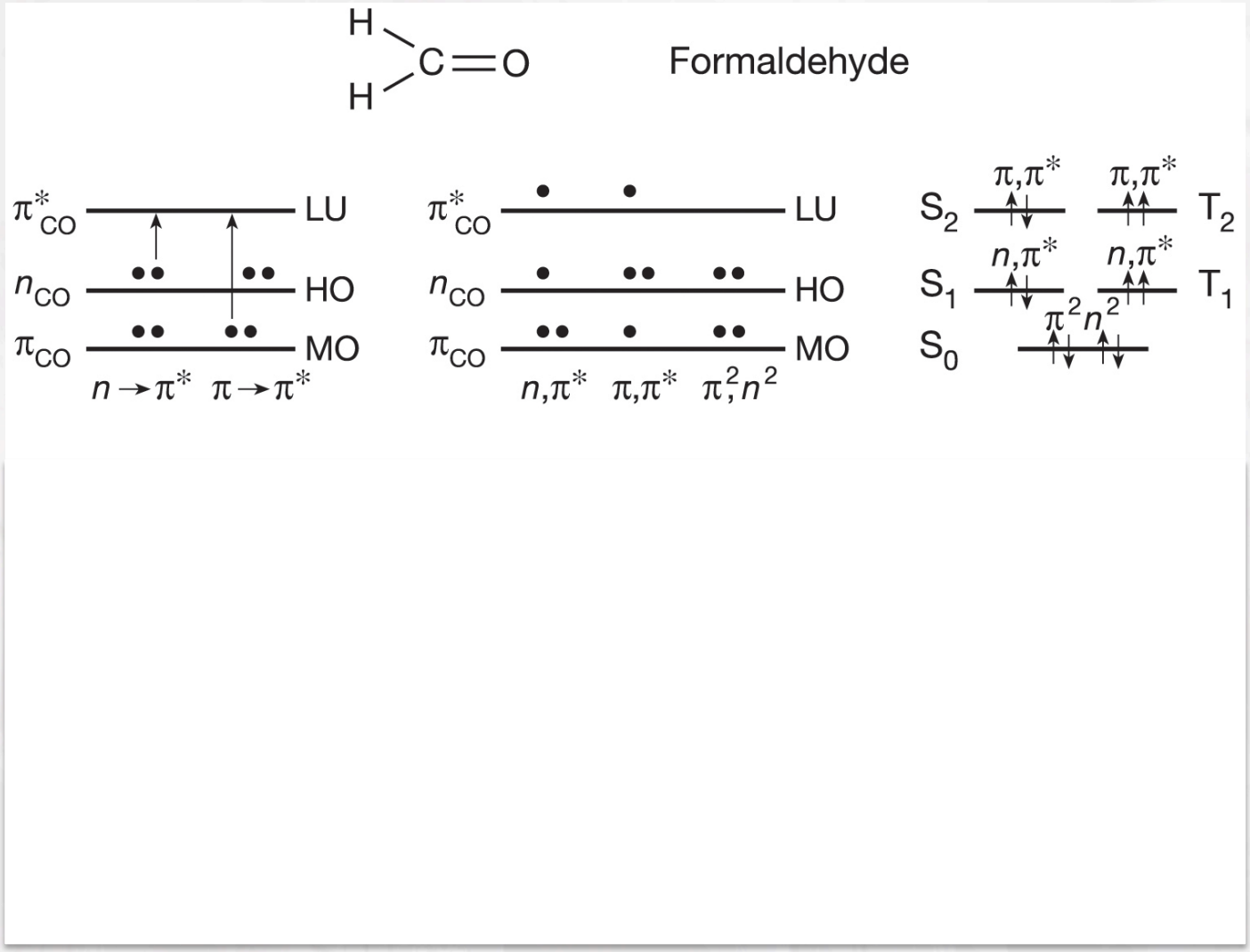
$\beta\beta$



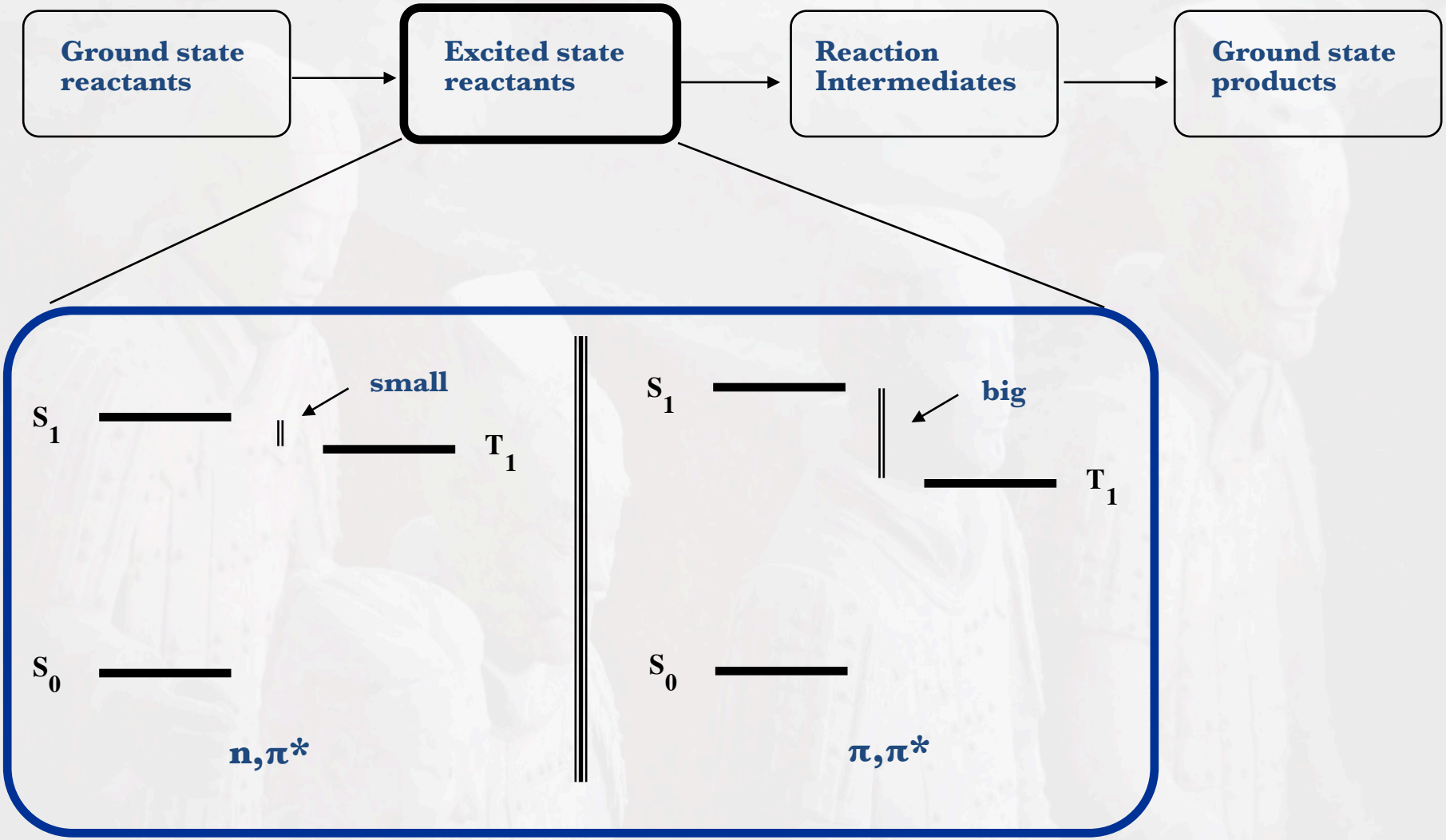
$M_S=0$

$\alpha\beta+\beta\alpha$

Electronic and Spin Configuration of States



S_1-T_1 energy gap



Why triplets are lower in energy than singlets?

What controls the singlet-triplet energy gap?

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

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

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

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

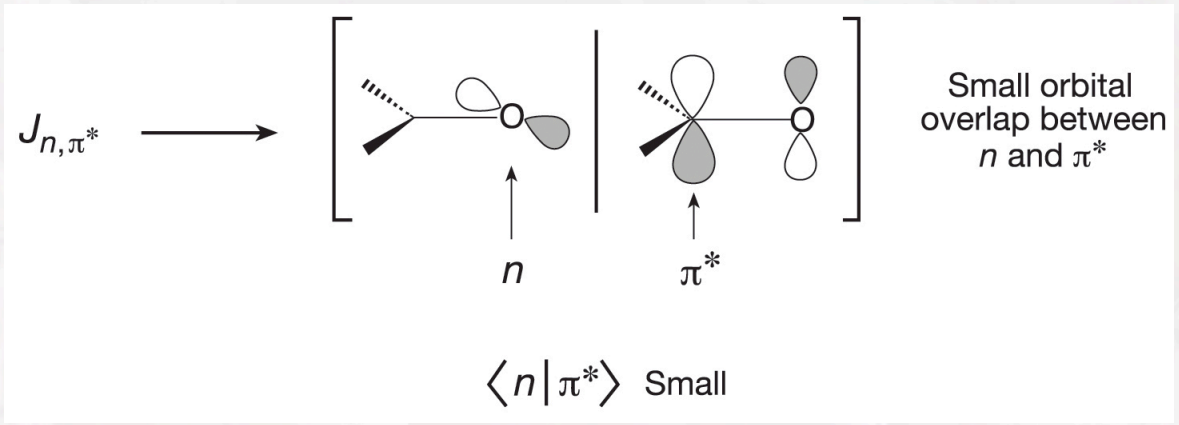
$$J(n,\pi^*) = \langle n\phi(1)\pi^*(2)|e^2/r_{12}|\, n\phi(2)\pi^*(1)\rangle$$

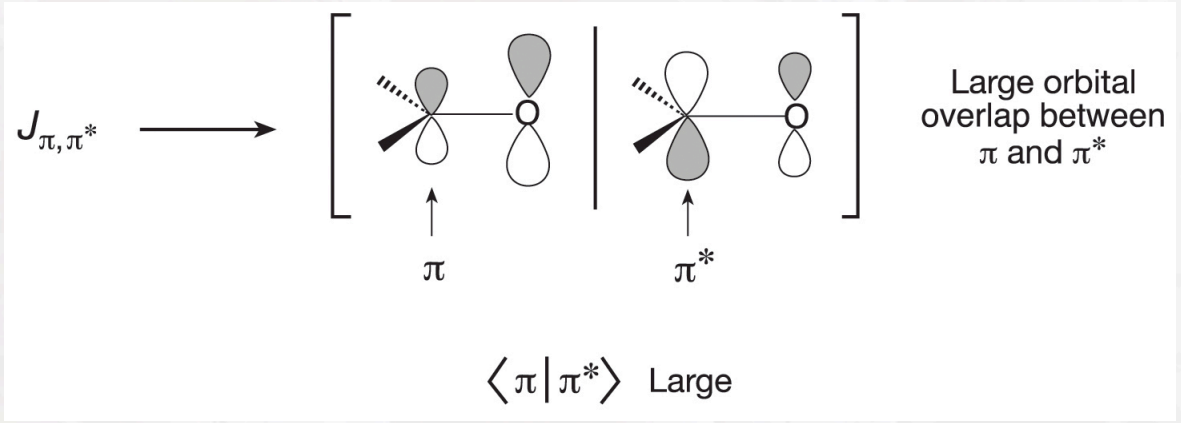
$$J(n,\pi^*) \sim e^2/r_{12} \langle n\phi(1)\pi^*(2)|n\phi(2)\pi^*(1) \sim \langle \phi(1)|\phi(2)\rangle$$

overlap integral controls the gap

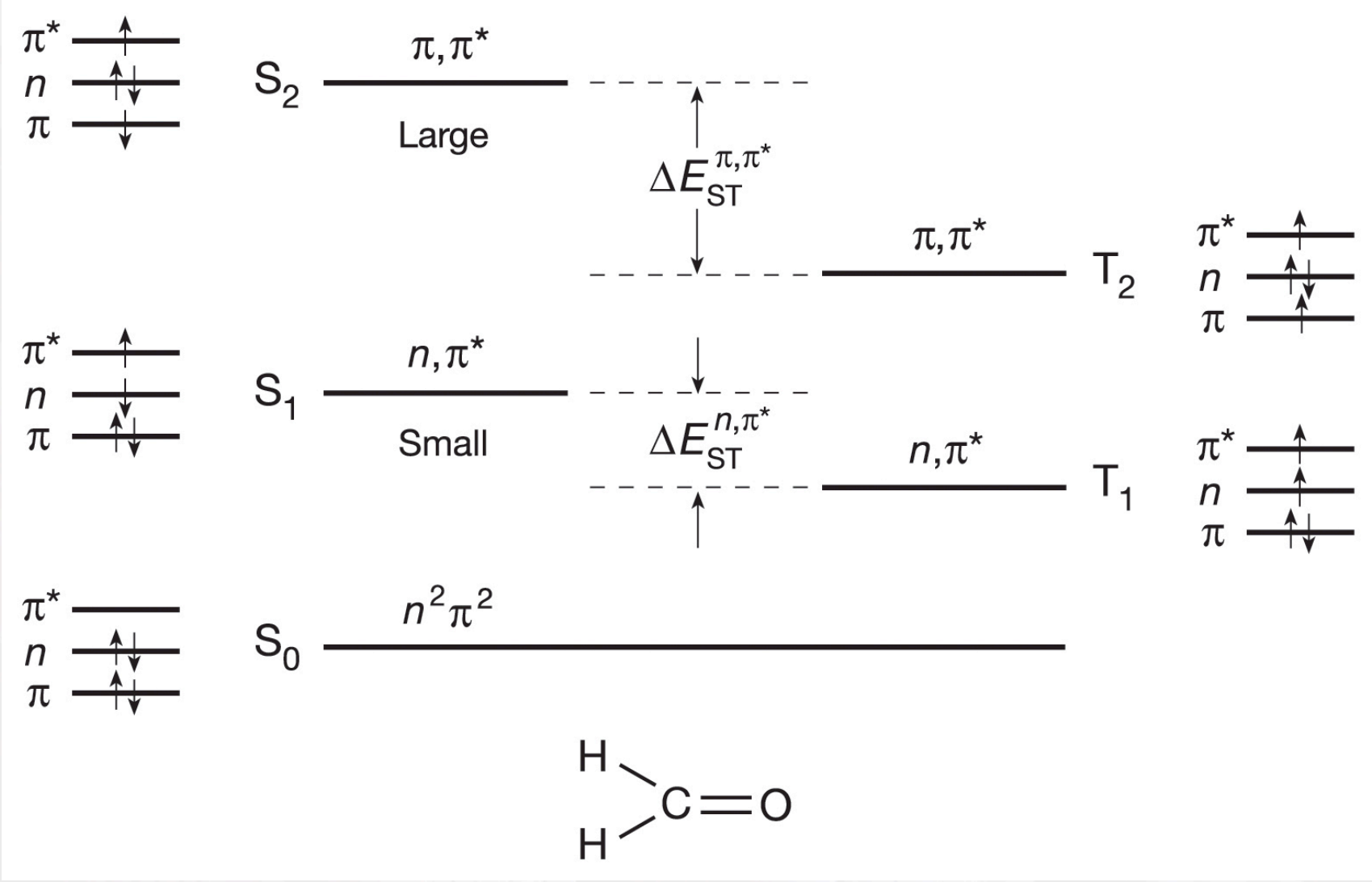
$J(n,\pi^*) = \langle n(1)\pi^*(2)|e^2/r_{12}|n(2)\pi^*(1)\rangle$

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

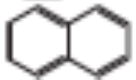
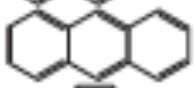




Energies of singlet and triplet states



S_1-T_1 energy gap: Examples

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.