Molecular and Supramolecular Photochemistry

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Fundamental Research:
The presentations/reports are **not "subject"** to the EAR – Fundamental Research as per EAR Part 734.8 (a) and (c).

1

2

Molecular and Supramolecular Photochemistry

Videos of all lectures are posted in my website. You should watch them if you have problems in following the lectures:

https://chemistry.as.miami.edu/research-groups/ramamurthy-group/video-lectures/video-lectures-miami/index.html

3

This Course

Deals with interaction of Light with Materials, Molecules, Electrons

What is light?

What is a material?

What is a molecule?

What is an electron?

How do light and an electron interact?

What are the consequences of interaction?

How to control the interaction and its cosequences?

What are the uses of light in our everyday life?

4

Photo(n)chemistry

Chapters 1 & 2

TRS, Principles of Molecular Photochemistry:

An Introduction

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

5

What is matter or material?

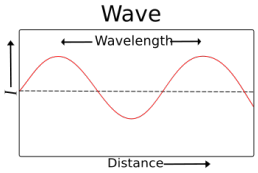
- **Matter is a collection of molecules**
- **Molecule is a collection of atoms**
- **Atom is a collection of nuclei and electrons**
- **The fundamental components of matter and molecules are nuclei and electrons**
- **To understand matter and molecule one needs to know the location and energies of nuclei and electrons.**

6

Photon?

Photon (Light) has dual characteristics: a particle and a wave

Wavelength	**λ**	**c/ν**
Wavenumber:	**υ**	**1/λ**
Frequency:	**ν**	**c/λ**
Energy	**hν**	**hc/λ**
Einstein:	**Nhν**	**Mole of photons (one Avagadro number of photons)**
Velocity:	**186,281 miles/sec; 2.9979 x 10^{10} cm/sec**	
Momentum:	$p = \frac{h}{\lambda}$	
Mass ((relativistic mass):	$m = \frac{E}{c^2} = \frac{h/\lambda}{c}$	**Momentum/c**
Charge:	**0 (no charge)**	
Spin:	**1$\hbar$**	



7

Electron

- **It has dual wave and particle properties, just like photon**
- **Negatively charged, does not change with energy**
- **Electric charge oscillates with time**
- **It has spin of 1/2 $\hbar$**
- **Because it is spinning and charged, it can be considered to be a small magnet**
- **Coupled with protons and neutrons it holds atoms, molecules and everything in the world**
- **It is small, radius of 0.00028 nm.**

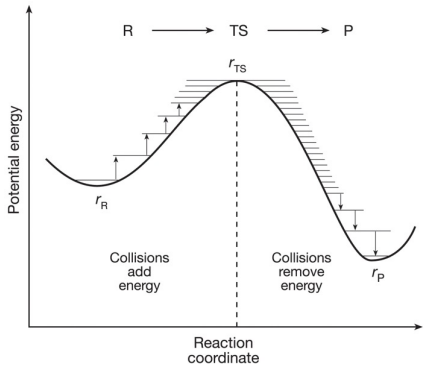
8

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 only

9

Visualization of Thermal Reactions



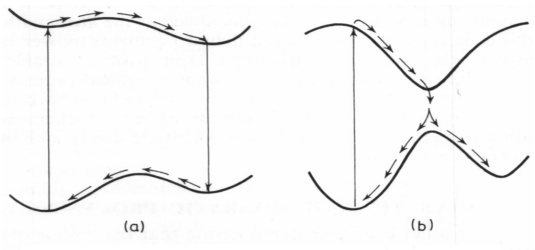
- Transition state connects a single reactant to a single product (intermediate) and it is a saddle point along the reaction course.
- Collisions are a reservoir of continuous energy (~ 0.6 kcal/mol per impact).
- Collisions can add or remove energy from a system.
- Concerned with a single surface.

10

Visualization of Photochemical Reactions

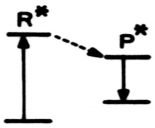
We need to deal with two surfaces (ground and excited state.

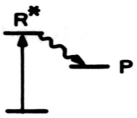
Adiabatic



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

Diabatic





11

The Basic Laws of Photochemistry

Grotthuss-Draper law

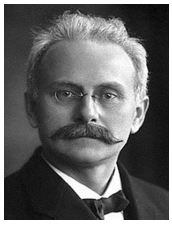
The First Law of Photochemistry: light must be absorbed for photochemistry to occur.

Grotthus

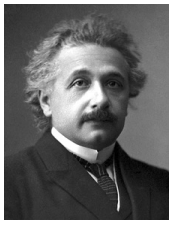
Drapper

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



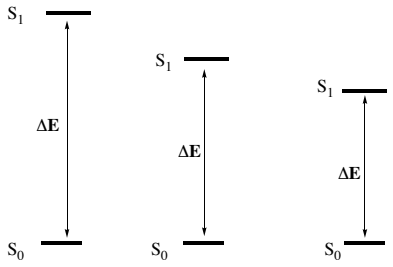
Einstein

12

Third law of photochemistry

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

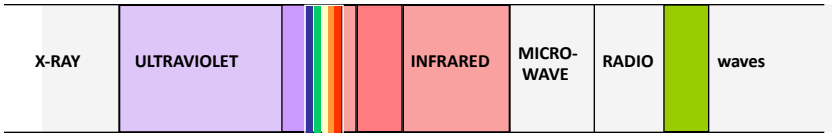
The *energy conservation rule* (Eq. 4.8): There must be an exact matching of the energy difference that corresponds to the energy required for the transition (ΔE) between orbitals and the energy of the photon ($h\nu$); that is, ΔE must exactly equal $h\nu$ (Eq. 4.8).



ΔE (kcal mol^{-1}) = [2.86 x 10^4 kcal mol^{-1} nm]/λ nm

13

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

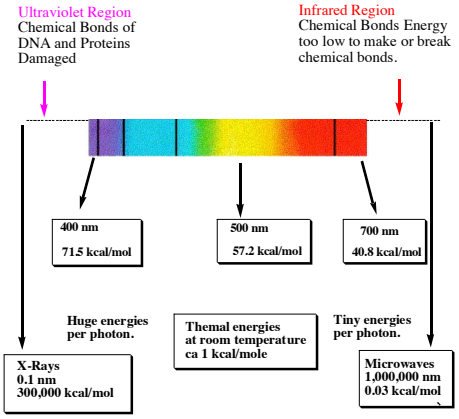
14

Light and Energy Scales

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

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

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



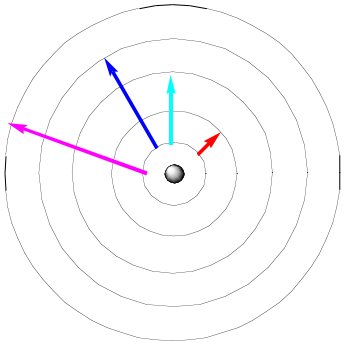
15

Where are the electrons in atoms and molecules?

Niels Bohr
Nobel Prize 1922

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

Atomic orbitals: s, p, d, f



16

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.

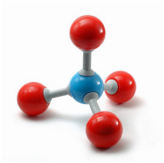
17

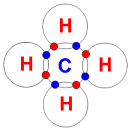
Born – Oppenheimer Approximation

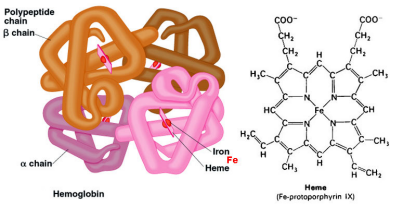
- Electronic motion and nuclear motion can be separated (Born-Oppenheimer approximation)
- To understand molecules, first focus on the location and energies of electrons
- Understand: Ψ_o(electronic) independent of χ and S

18

Molecule, a collection of atoms is defined by Ψ







Nobel Prize in Physics (1933)

$$H\Psi = E\Psi$$

Operator — Eigenvalue

Schrödinger equation

19

What is Ψ ?

Ψ defines a molecule in terms of nuclei and electrons

Ψ is made of three parts

$$\Psi = \Psi_o \; \chi \; S$$

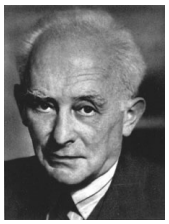
Electronic Nuclear Spin

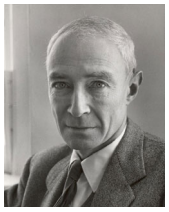
The three parts are interconnected. So, it is hard to define a molecule precisely in terms of Ψ

20

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.

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

Electronic Nuclear Spin

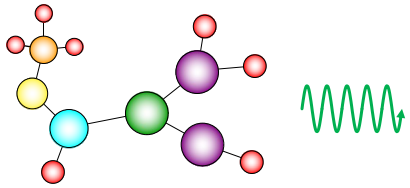
Time scale matter

21

Natural Oscillation Frequencies of Atoms and Molecules

Electrons vibrate in their motion around nuclei
High frequency: ~10^{14} - 10^{17} cycles per second.

Nuclei in molecules vibrate with respect to each other
Intermediate frequency:
~10^{11} - 10^{13} cycles per second.



Nuclei in molecules rotate
Low frequency: ~10^{9} - 10^{10} cycles per second.

Accelerating charges (positive or negative) emit light.

22

Atomic to Molecular Orbitals

Books

- Valence, C. A. Coulson, 1952
- Molecular Orbital Theory for Organic Chemists, Andrew Streitwieser, 1961
- Notes on molecular orbital calculations, John D Roberts, 1962
- The Molecular Orbital Theory of Conjugated Systems, Lionel Salem, 1966
- The importance of antibonding orbitals, Milton Orchin, 1967
- Hückel Molecular Orbital Theory, Keith Yates, 1978

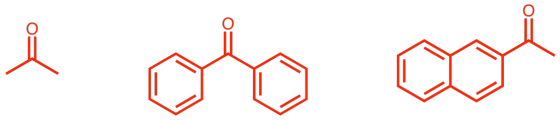
A classic book on chemical bonds

- The Nature of the Chemical Bond, L. Pauling, 1939

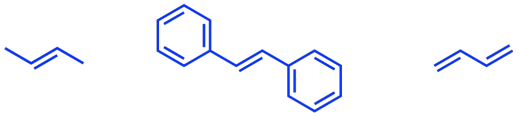
23

Examples of Common Organic Chromophores

Carbonyls



Olefins



Enones

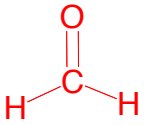
Aromatics

24

Viewing electrons in atoms and molecules

Atoms: Electrons are present in atomic orbitals (Bohr)

Molecules: Electrons are present in molecular orbitals (Mulliken)



Inner orbitals

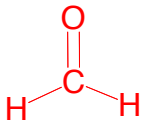
Bonding orbitals

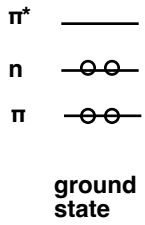
Frontier orbitals

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

25

Types of transitions in formaldehyde

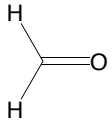




Orbital diagram

26

Common Chromophores
Carbonyl Compounds



n ⟶ π*

290 nm

ε = 10

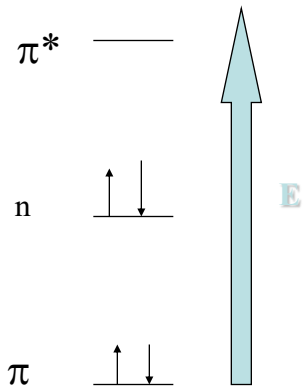
forbidden

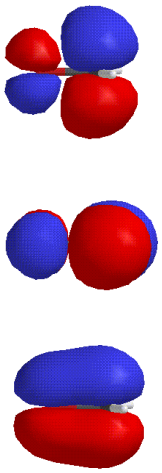
π ⟶ π*

170 nm

ε = 100

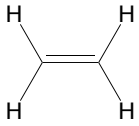
allowed

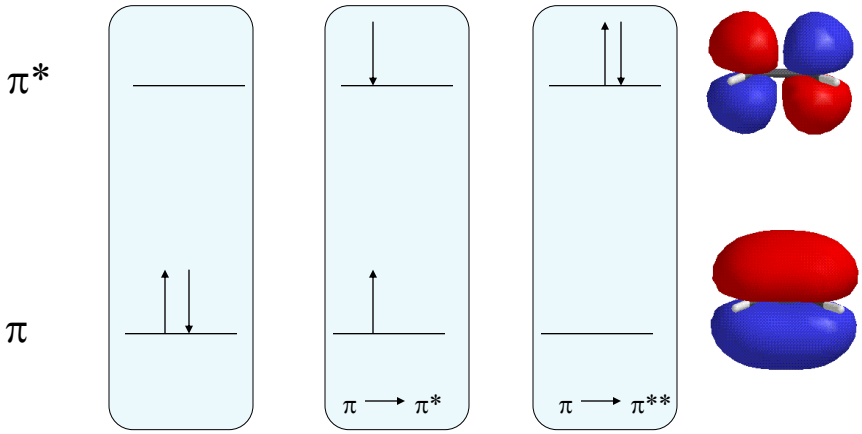




27

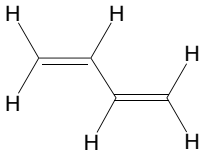
Common Chromophores: Olefins
Ethylene

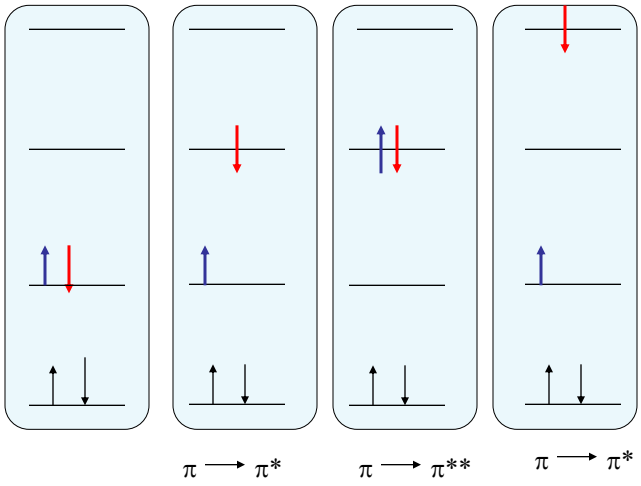


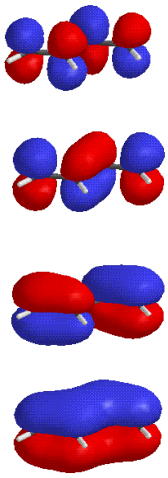


28

Common Chromophores: Olefins
1,3-Butadiene

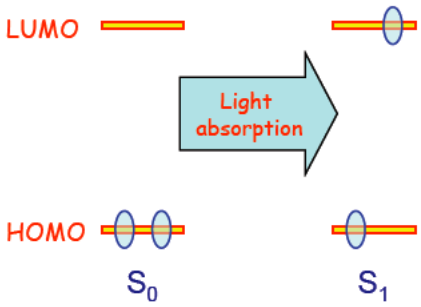






29

Light absorption and electron movement



State diagram

30

Excited state energies

The energy required to produce an electronically excited state

$$R\ (E_1) + h\nu \rightarrow R^*\ (E_2)$$

is obtained by inspecting the absorption spectrum of the molecule.

$$\Delta E = |E_2 - E_1| = |E_2(^*\mathrm{R}) - E_1(\mathrm{R})| = h\nu = hc/\lambda$$

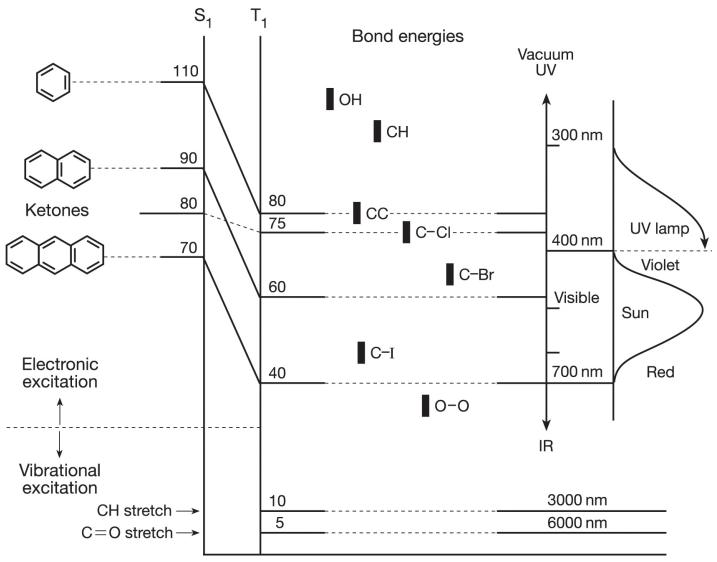
h is Planck's constant (1.58×10^{-34} cal s)

λ is the wavelength at which absorption occurs (commonly given in units of nanometers, nm),

c is the speed of light (3×10^{8} cm s^{-1})

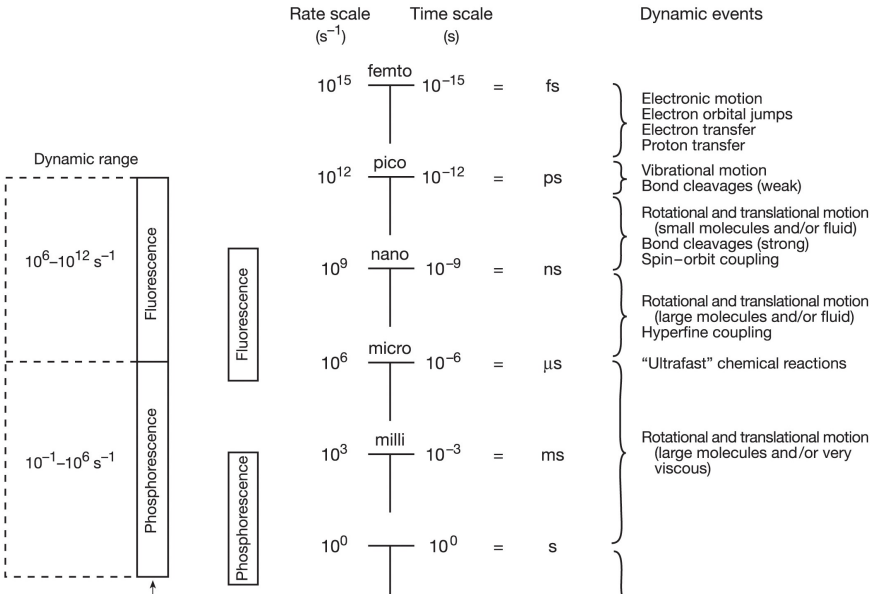
31

Excitation energy, bond energy and radiation wavelength



32

Time scales



33

Nobels in Photochemistry

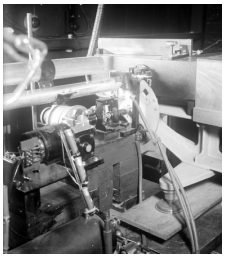
Development of Flash Photolysis and Femtosecond Chemistry


Norrish

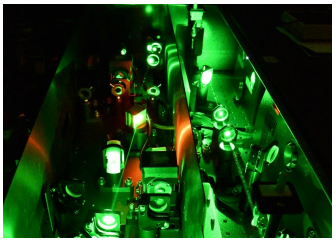

Porter


Zewail

The Nobel Prize in Chemistry 1967



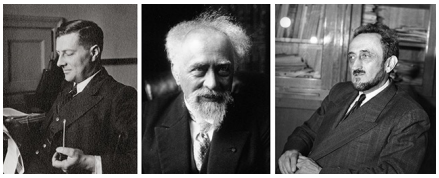
The Nobel Prize in Chemistry 1999



34

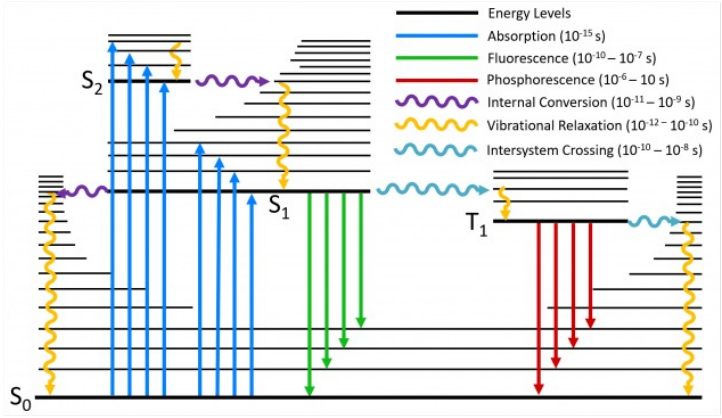
Perrin-Jablonski Diagram

A. Jablonski (1898-1980)



F. Perrin (1901-1992)

J. Perrin 1870-1942
Nobel Prize, 1926



35

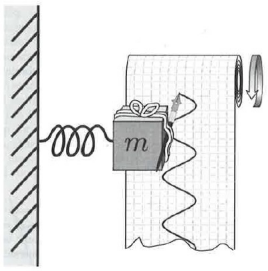
Born-Oppenheimer Approximation

Motions of electrons in orbitals are much more rapid than nuclear vibrational motions

$$\Psi \sim \Psi_0 \chi \mathbf{S}$$

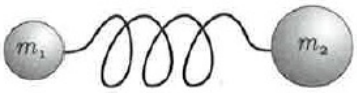
"true" molecular wavefunction — **(electronic)** **(nuclei)** **(spin)**

36



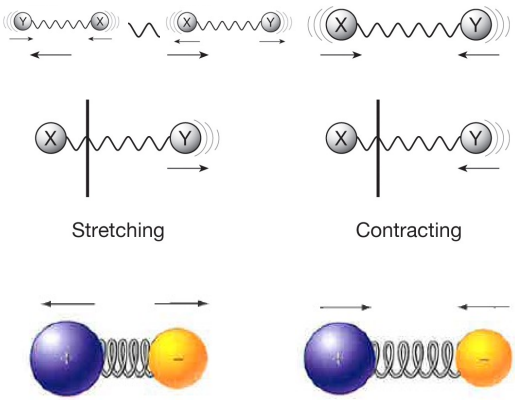
$$F = - k \Delta r \quad = \quad -k \left| r - r_e \right|$$

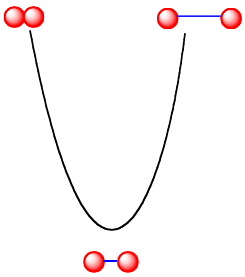
k is the force constant, Δr is the distance of displacement from equilibrium, F is the restoring force



37

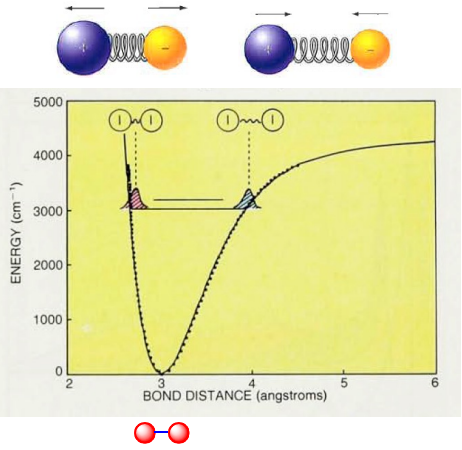
A Model for Vibrational Wavefunctions
The Classical Harmonic Oscillator

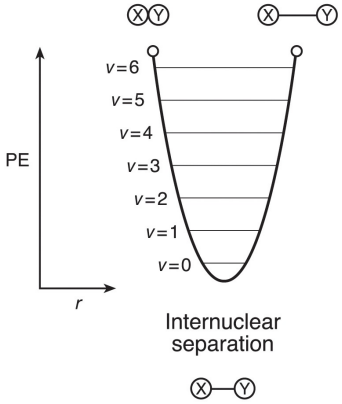




38

A Model for Vibrational Wavefunctions
The Classical Harmonic Oscillator





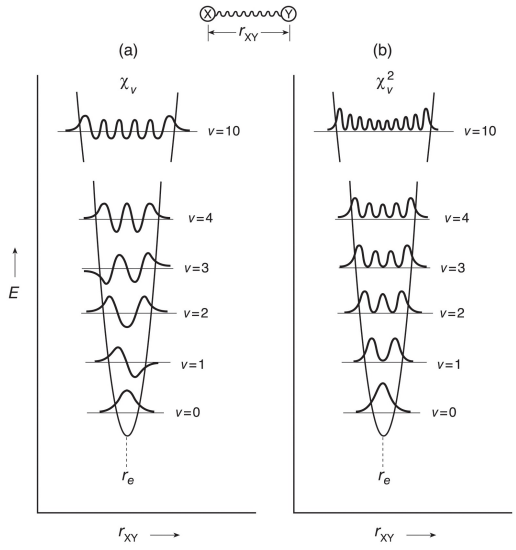
E_v = PE + KE

Quantized Harmonic Oscillator

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

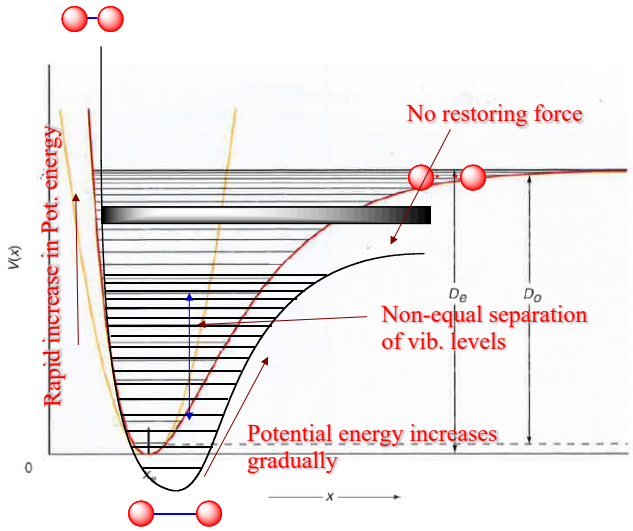
39

The Quantum Mechanical Version of the Classical Harmonic Oscillator



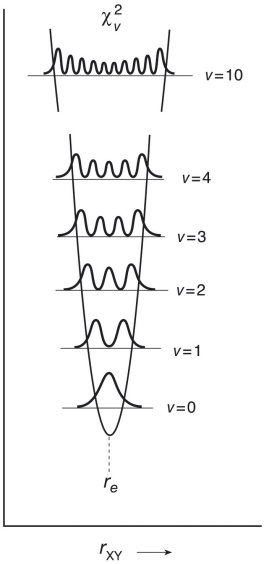
40

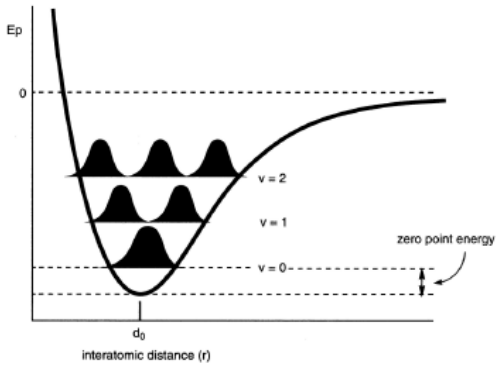
The Anharmonic Quantum Mechanical Oscillator



41

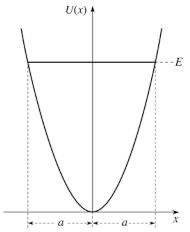
Anharmonic Oscillator-Probablity Density



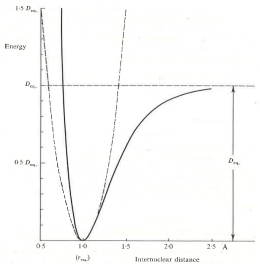


42

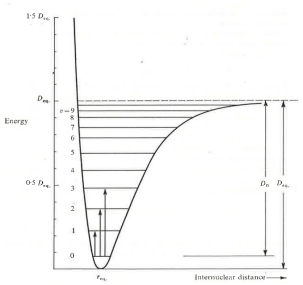
Harmonic and Anharmonic Oscillator



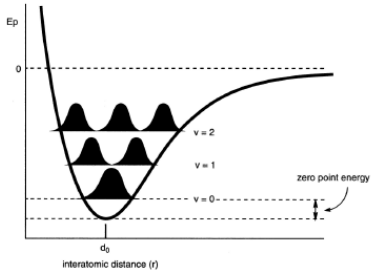
Harmonic



Anharmonic



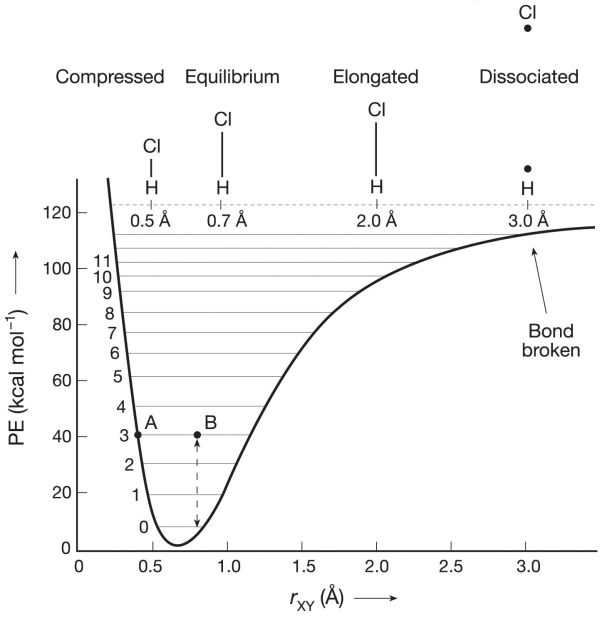
Anharmonic Quantized



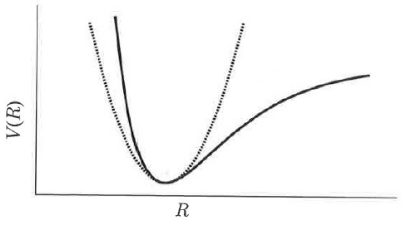
- Anharmonic
- Quantized energy level
- Probablity of location of the nuclei

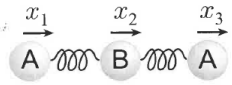
43

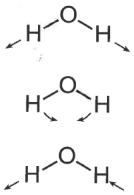
The Anharmonic Oscillator: e.g., HCl



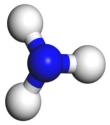
44



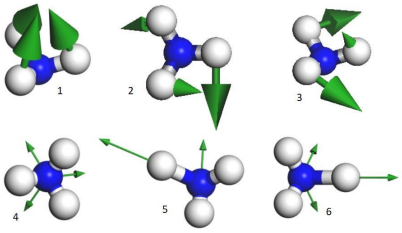




To represent molecules with more than three atoms one needs 3N–6 space

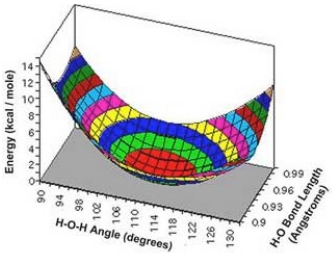


Ammonia

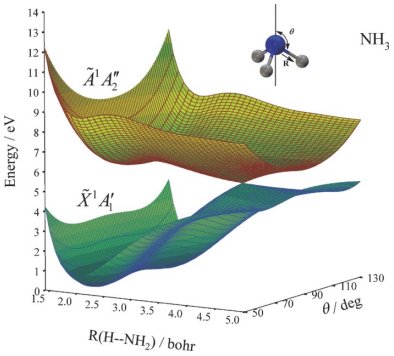


45

Representation of Polyatomic Molecules



Water



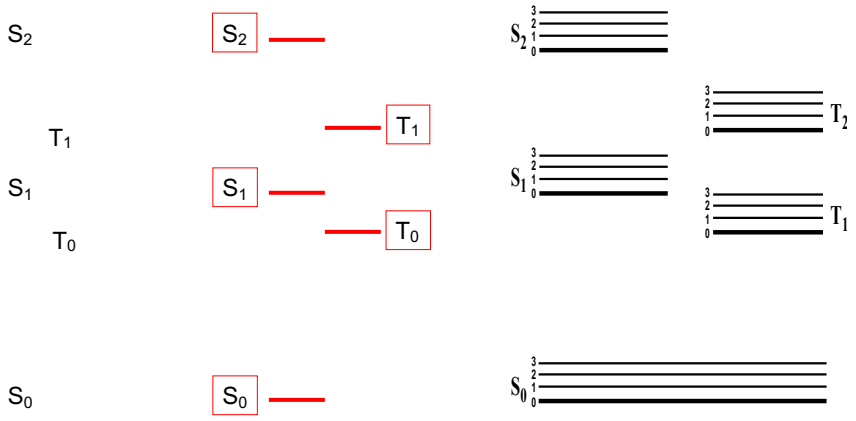
To represent molecules with more than three atoms one needs 3N–6 space

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

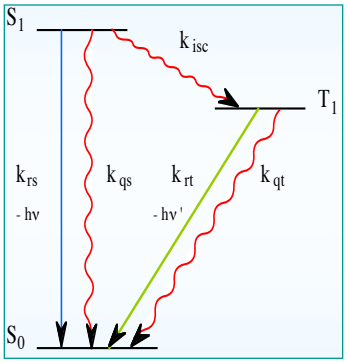
46

Energy level diagram of molecules

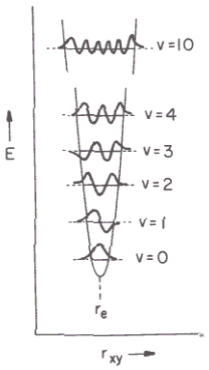


47

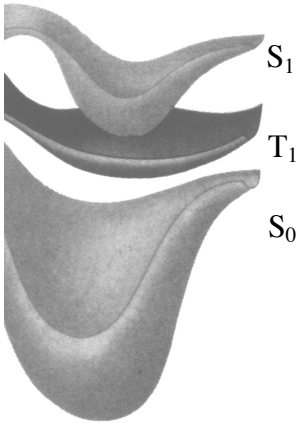
Visualizing molecules in ground and excited states



Molecule represented in one dimension



Molecule represented in two dimensions



Molecule represented in three dimensions

48

Spin

Chapters 1 & 2

Principles of Molecular Photochemistry: An Introduction

NJT, VR and JCS

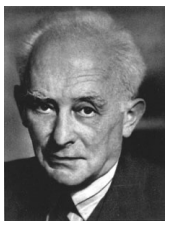
p.56 - 69 (sec. 2.9 - 2.15)

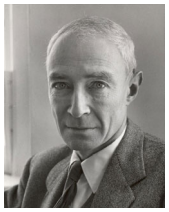
p.82 - 108 (sec. 2.21 - 2.39)

49

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.

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

Electronic Nuclear Spin

Time scale matter

50

The Four Quantum Numbers

- 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.

51

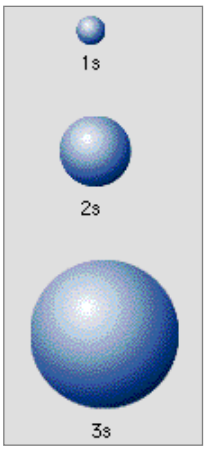
1. Principal Quantum Number (*n*)

Energy level

Size of the orbital

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

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



52

2. Angular Momentum Quantum # (l)

Energy sublevel

Shape of the orbital

s

- 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**

p

d

53

3. Magnetic Quantum Number (m_l)

Orientation of orbital

Specifies the number and shape of orbitals within each sublevel

- the third of a set of quantum numbers
- tells us ***how many*** orbitals there are of a particular type and ***their orientation in space of a particular orbital***
- only ***two electrons*** can fit in an orbital

54

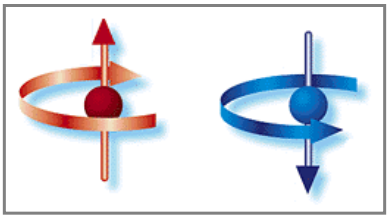
Visualization of Spin Chemistry

- 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 itis important to note "correct" mathematical representations fail for complex systems as molecules

55

Visualization of Spin Chemistry

Visualize spin by resorting to a classical analogy of a spherical object executing a spinning motion about an axis, *i.e.*, a top or a gyroscope.



Develop a model which associates specific magnetic properties, *i.e.*, a magnetic moment, with the electron's spin angular momentum

56

A bit of History

http://www.lorentz.leidenuniv.nl/history/spin/goudsmit.html

Stern and Gerlach: How a Bad Cigar Helped Reorient Atomic Physics, B. Friedrich and D. Herschbach, *Physics Today*, December, 53-59, **2003**

George Uhlenbeck and Discovery of Electron Spin, A. Pias, *Physics Today*, December, 34-40, **1989**

Fifty years of spin: It might as well be spin
Samuel A. Goudsmit, *Physics Today* **29**, 6, 40, **1976**

57

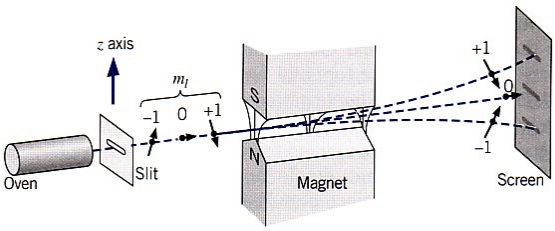
What is "intrinsic spin"?

- Also called "spin", or spin angular momentum, or S
- It's a "degree of freedom", or quantum number: a "state" the particle has
- Does interact with magnetic fields like L
- NOT a physical rotation
- INTRINSIC property – like charge and mass! We have no model for what "makes it up/causes it" for fundamental particles
- Shows up most simply in Pauli exclusion principle

58

Expectation and Observation
Stern & Gerlach ~1922

Otto Stern
Nobel Prize, 1943



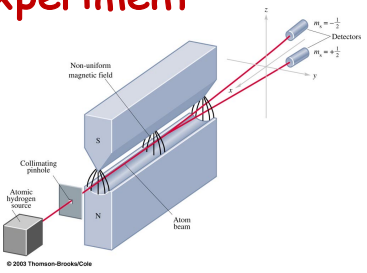
[1]It is because an atom's behavior in a magnetic field depends on m_ℓ that it is known as the "magnetic quantum number."

[2]In the original Stern–Gerlach experiment of 1922, two lines were seen, but neutral *silver* atoms were used. Although the silver atoms, having one 5*s* electron beyond a closed $n = 4$ shell, should behave as atoms of $\ell = 0$, the Stern–Gerlach apparatus was later used with hydrogen (1925, Phipps and Taylor), to rule out any complication multiple electrons might introduce.

59

The Stern-Gerlach experiment

- Experiment was confirmed using:



Element	*Electronic Configuration*
H	$1s^1$
Na	$\{1s^2 2s^2 2p^6\}3s^1$
K	$\{1s^2 2s^2 2p^6 3s^2 3p^6\}4s^1$
Cu	$\{1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}\}4s^1$
Ag	$\{1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}\}5s^1$
Cs	$\{[Ag]5s^2 5p^6\}6s^1$
Au	$\{[Cs]5d^{10} 4f^{14}\}6s^1$

- In all cases, $l = 0$ and $s = 1/2$.

60

Stern-Gerlach and spin

O. Stern and W. Gerlach saw a beam of silver atoms split into two beams!

G. Uhlenbeck and S. Goudsmit suggested that each electron has its own intrinsic angular momentum – "spin" – with only two eigenvalues.

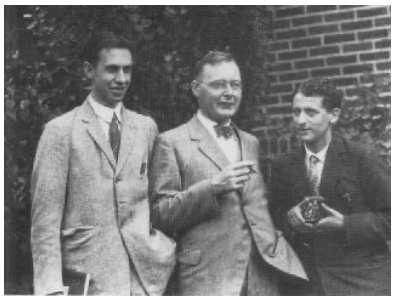
But electron spin has odd features. For example, its magnitude never changes, just its direction – and it has only two directions.

Thus far every eigenstate of an atom was associated with three quantum numbers n, l and m. But now we have to introduce a fourth quantum number, the spin: $m_s = \pm ½$.

Note: The nucleus, too, has spin angular momentum. But its magnetic moment is relatively tiny because the mass of a proton is about 2000 times the electron mass.

61

Some history titbits
Uhlenbeck & Goudsmit ~ 1925

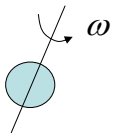


The discovery note in *Naturwissenschaften* is dated 17 October 1925. One day earlier **Ehrenfest** had written to Lorentz to make an appointment and discuss a "very witty idea" of two of his graduate students. When Lorentz pointed out that the idea of a spinning electron would be incompatible with classical electrodynamics, Uhlenbeck asked Ehrenfest not to submit the paper. Ehrenfest replied that he had already sent off their note, and he added: "**You are both young enough to be able to afford a stupidity**!"

http://www.lorentz.leidenuniv.nl/history/spin/spin.html

62

Across the continent: Ralph Kronig & Spinning Electron



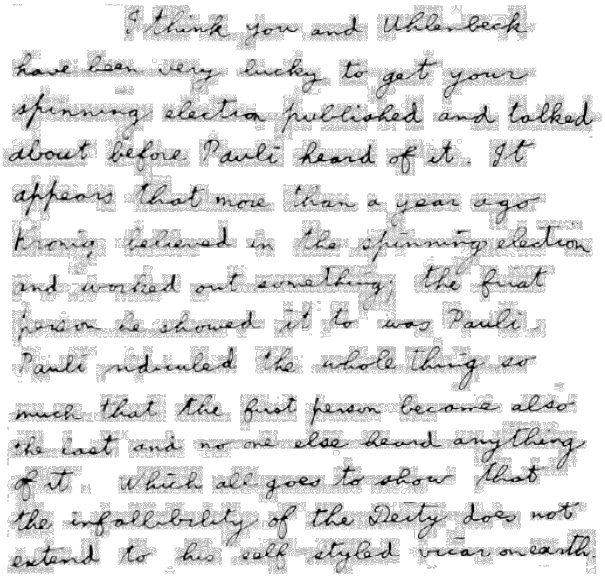
Ehrenfest's encouraging response to his students ideas contrasted sharply with that of Wolfgang Pauli.

At the same time, Ralph Kronig, a young Columbia University PhD who had spent two years studying in Europe, had come up with the idea of electron spin several months before Uhlenbeck and Goudsmit. He had put it before Pauli for his reactions, who had ridiculed it, saying that "it is indeed very clever but of course has nothing to do with reality. No, it's quite impossible." Pauli completely crushed Kronig. He did not publish his ideas on spin.

http://www.lorentz.leidenuniv.nl/history/spin/spin.html

63

Letter from Thomas to Goudsmit



I think you and Uhlenbeck have been very lucky to get your spinning electron published and talked about before Pauli heard of it. It appears that more than a year ago Kronig believed in the spinning electron and worked out something. The first person he showed it to was Pauli. Pauli ridiculed the whole thing so much that the first person became also the last and no one else heard anything of it. Which all goes to show that the infallibility of the Deity does not extend to his self styled vicar on earth.

Part of a letter by L.H. Thomas to Goudsmit (25 March 1926). Reproduced from a transparency shown by Goudsmit during his 1971 lecture. The original is presumably in the Goudsmit archive kept by the AIP Center for History of Physics.

http://www.lorentz.leidenuniv.nl/history/spin/goudsmit.html

64

The Pauli Exclusion Principle

No two electrons can have identical quantum numbers. With three quantum numbers *n, l, m* two electrons in an orbital will have identical quantum numbers.

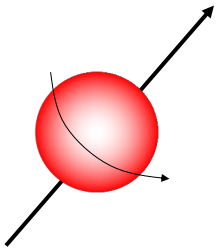
Wolfgang Pauli
Nobel Prize, 1945

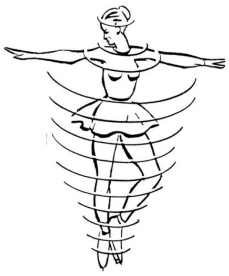
An empty orbital is fully described by the three quantum numbers: n, *l* and m_l

An electron in an orbital is fully described by the four quantum numbers: n, *l*, m_l and m_s

65

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

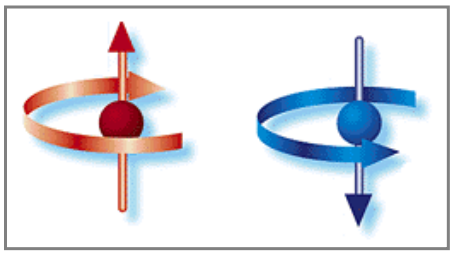
- Classically angular momentum is a property of a macroscopic object which is in rotation about an axis

66

4. Spin Quantum Number (m_s)

Electron spin $\Rightarrow$ +½ or -½

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



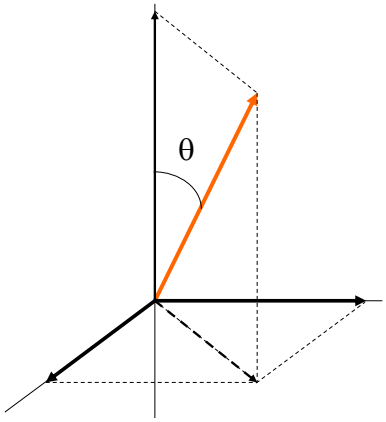
67

Scalars and Vectors

- Some physical quantities are completely described by a magnitude (a single number): they are termed **scalar**
- Some other quantities have a directional property, and their description requires both a magnitude and a direction: they are termed **vectors**

68

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.

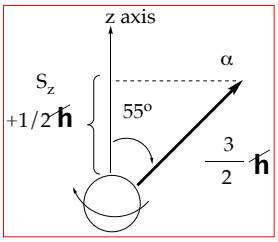
69

Spin angular momentum

- Electron possesses a fixed and characteristic spin angular momentum of ½ $\hbar$

$\hbar$: Planck's constant/2π

$\hbar$ = h/2π = 1.0545717 × 10−34 J·s eV·s



This is fixed value ½ $\hbar$ 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.

70

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

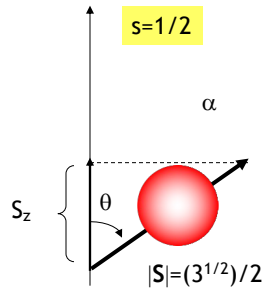
- **M_s** (**spin multiplicity**) related to the orientation of the spin vector

Spin multiplicity= 2S+1

71

s=1/2

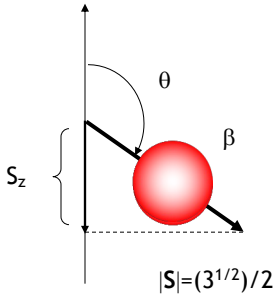
Spin multiplicity= 2S+1 = 2



In particular for

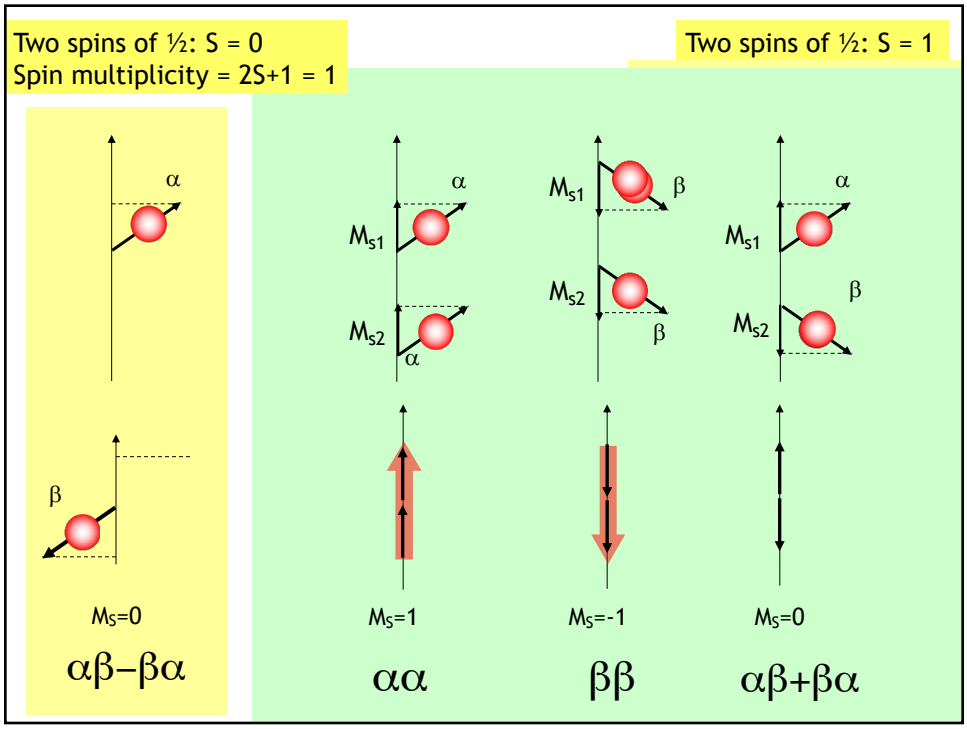
S=1/2 →|S|=$(3^{1/2})/2$

θ=55° for M_s= 1/2



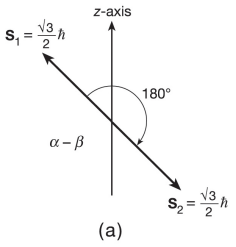
θ=125° for M_s=-1/2

72



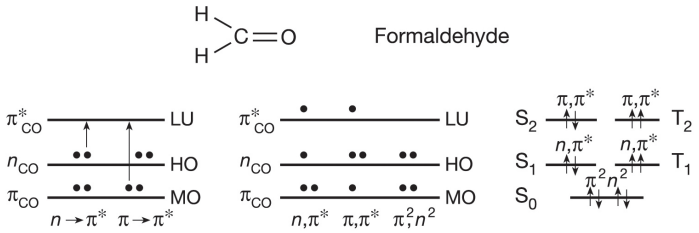
73

2D Vector representations for two interacting electrons



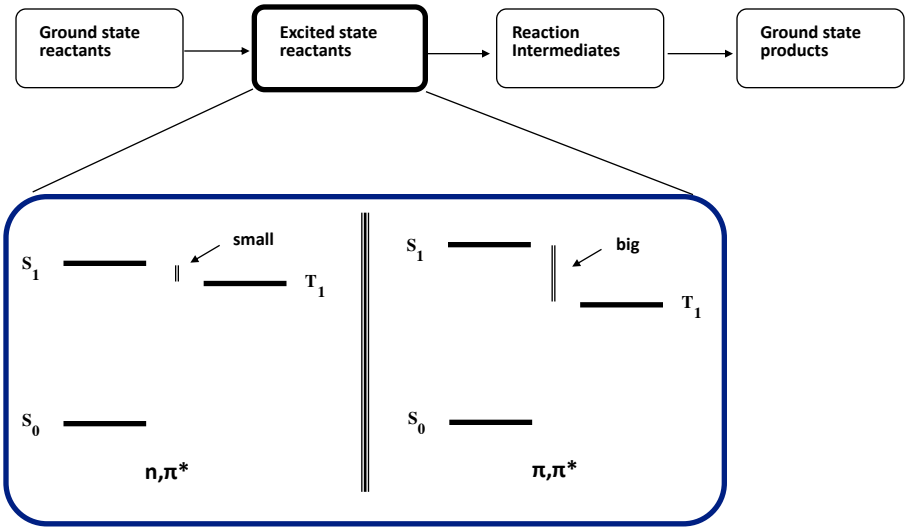
74

Electronic and Spin Configuration of States



75

S_1-T_1 energy gap



76

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

Role of exchange integral (J)

77

Why triplets are lower in energy than singlets?

What controls the singlet-triplet energy gap?

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

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

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

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

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

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

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

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

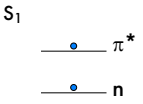
78

The Electron-Exchange Interaction in Molecules

The Singlet and the Triplet states are split apart in energy by the *electron-exchange interaction.*

Electron-exchange interaction has the form of repulsive columbic interaction between the two charged particles (electrons).

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



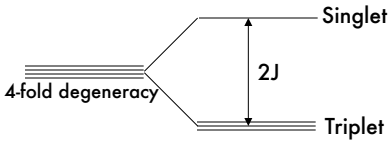
Factorizing out from the integral the columbic term, the intensity of interaction is proportional to the overlap integral between the two states.

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

overlap integral controls the gap

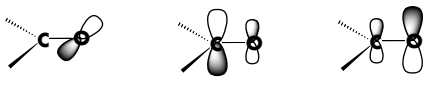
79

The repulsive interaction lowers the energy of the Triplet state, since the electrons are farther apart.



Large exchange splitting (J) reflects the fact that the unpaired electrons can approach quite closely.

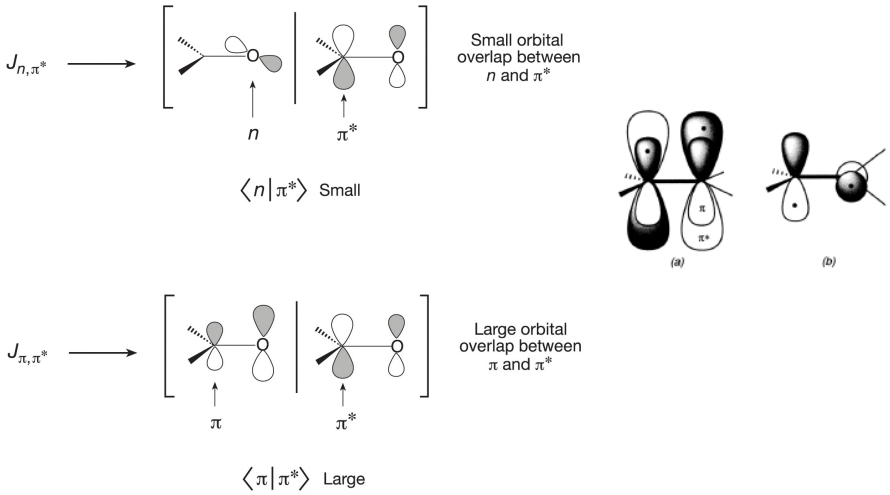
The Singlet-Triplet energy spacing depends on the overlap between the molecular orbital wavefunctions involved: $J(n,\pi^*) < J(\pi,\pi^*)$



80

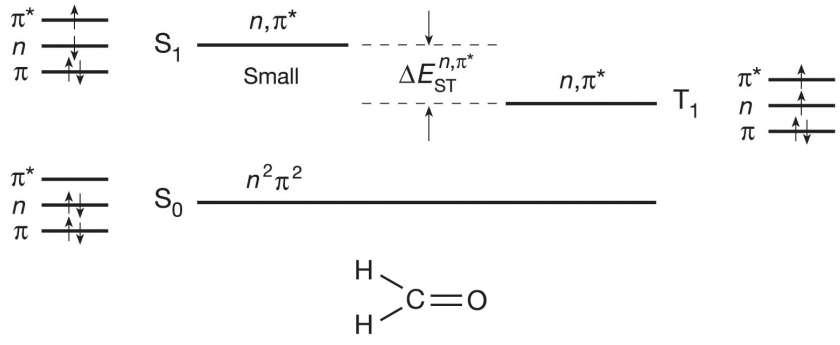
$J(n,\pi^*) = \langle n(1)\pi^*(2)|e^2/r_{12}|n(2)\pi^*(1)\rangle$

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



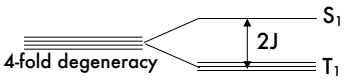
81

Energies of singlet and triplet states

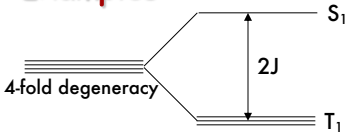


82

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.

83