

Fotochimica

UniFE

LM in Scienze Chimiche, A.A. 2012/13

F. Scandola

<http://docente.unife.it/franco.scandola/materiale-didattico/>

Stati elettronici. Approssimazione di Born-Oppenheimer. Orbitali molecolari, configurazioni elettroniche, stati. Vibrazioni in molecole poliatomiche.

Assorbimento di radiazioni. Momento di transizione. Regole di selezione di simmetria e di spin. Principio di Franck-Condon. Struttura delle bande di assorbimento

Processi unimolecolari in stati eccitati: Disattivazioni radiative. Rilassamento vibrazionale. Fluorescenza e fosforescenza. Fattori di Franck-Condon e relazioni fra assorbimento ed emissione. Distorsione degli stati eccitati e Stokes shift. **Transizioni non-radiative.** Fermi golden rule. Conversione interna e intersystem crossing. Fattori di Franck-Condon. Energy-gap law, effetti di deuterazione. Intersezioni e avoided crossings. **Processi chimici in stati eccitati.** Diagrammi di correlazione di orbitali e stati. Dissociazione di legame s. Twisting di legami p. Reazioni pericliche. Fotosostituzione in complessi ottaedrici di metalli di transizione

Processi bimolecolari in stati eccitati. Cinetica di Stern-Volmer. Trasferimento di energia fra molecole. Sovrapposizione spettrale. Meccanismi coulombiano e di scambio. Quenching e sensibilizzazione. Trasferimento fotoindotto di elettroni. Proprietà redox di stati eccitati. Modelli cinetici. Regione "invertita". Separazione di carica e ricombinazione. Chemiluminescenza.

Fotochimica in sistemi biologici. Fotoni come quanti di energia e bits di informazione. La fotosintesi. Aspetti generali dell'energia solare. Modi di conversione. Sistemi fotosintetici naturali. Struttura generale: le antenne, i centri di reazione. Architettura, termodinamica e cinetica. La visione. Fotorecettori. Processi fotochimici primari. Generazione di segnali. Amplificazione.

Fotochimica in sistemi supramolecolari artificiali. Dispositivi molecolari nanometrici. Approcci "top-down" e "bottom-up". Verso una fotosintesi artificiale. Triadi per separazione di carica. Antenne artificiali. Dispositivi fotovoltaici ed elettro-ottici. Conversione fotovoltaica. Celle a semiconduttori sensibilizzati. Luce e informazione. Sensori. Sistemi "write-read-erase" e memorie molecolari. Macchine molecolari, elettronica molecolare, logica molecolare.

PHOTOCHEMISTRY IN NATURE

Biological systems

- Photosynthesis
- Photomorphogenesis
- Light-dependent rhythms
- Phototaxis
- Phototropism
- Vision
- Photodamage

Atmosphere

- Ozone cycle
- Photochemical smog

APPLICATIONS OF PHOTOCHEMISTRY

<i>Atmospheric chemistry</i>	modeling of troposphere, stratospheric ozone depletion, photochemical smog control
<i>Environment</i>	mineralization of organic pollutants, water purification
<i>Immunology</i>	fluoro- and chemiluminescence-detectable immunoassays
<i>Isotope enrichment</i>	multiphoton dissociation, photoionization
<i>Microelectronics</i>	photoresists, microlithography
<i>Lasers</i>	cw or pulsed, from UV to IR, applications in physics, chemistry, medicine, engineering, etc.
<i>Materials science</i>	photochromic materials
<i>Medicine</i>	photodynamic therapy of tumors, phototherapy of jaundice
<i>Molecular biology</i>	DNA intercalation, cleavage, conformation probing
<i>Optics</i>	nonlinear optics, electro-optic materials, second-harmonic generation, optical waveguides
<i>Synthesis - fine chemicals</i>	vitamins, antibiotics, steroids, prostaglandins, fragrances
<i>Synthesis - large scale</i>	photohalogenations, photooxidations, caprolactam
<i>Photoimaging</i>	photography, xerography
<i>Photocatalysis</i>	heterogeneous photooxygenation, photohydrogenation, homogeneous photooxidations
<i>Polymer chemistry</i>	photopolymerization, photocrosslinking, photodegradation, stereolithography
<i>Solar energy</i>	photovoltaic devices, photogeneration of fuels, energy storage

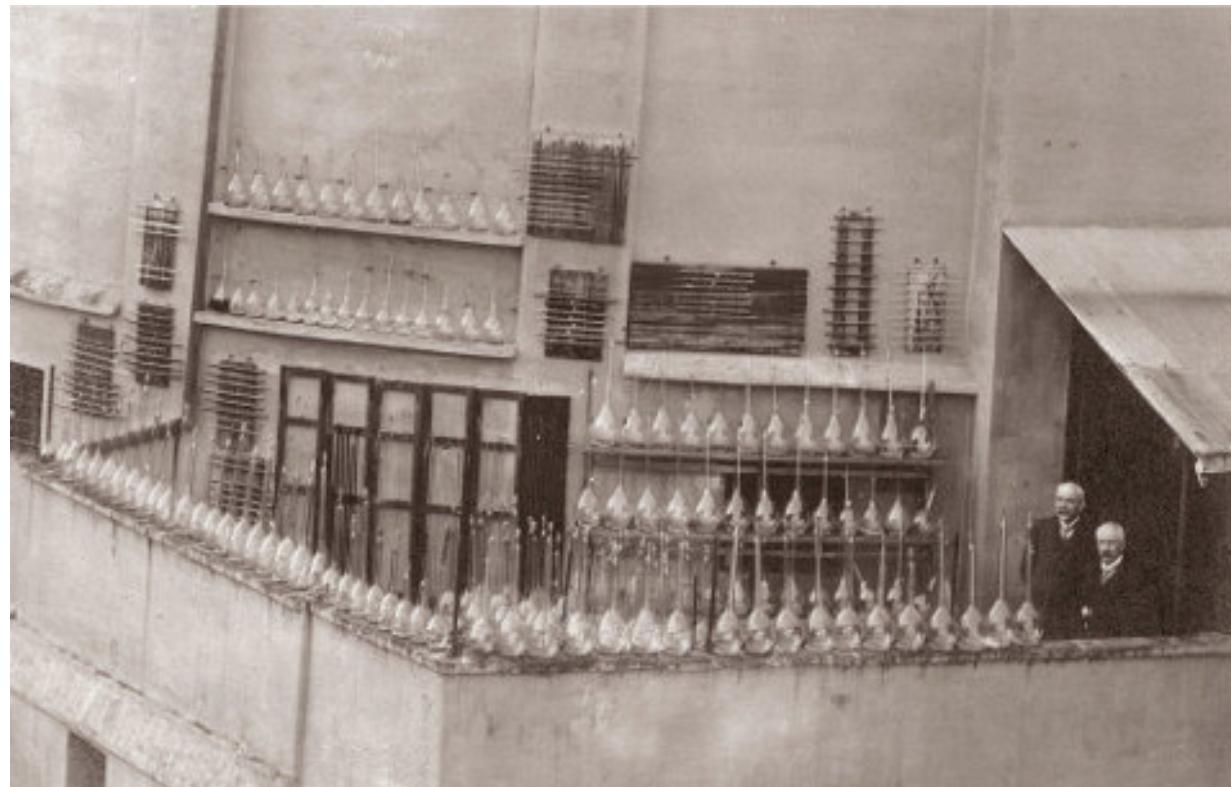
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Giacomo Ciamiciani

Professor of Chemistry
University of Bologna (1889 -1921)



Résultats des expériences pour les tubes circulaires avec la lumière blanche. -- Elles ont été faites principalement en mesurant le gaz dégagé avec des tubes de 14^{mm} placés verticalement.

502

Mélanges
de liquides actifs.

Dates des expériences.

Normaux. $\frac{1}{2}$ N. $\frac{1}{4}$ N. $\frac{1}{8}$ N.

$\epsilon =$ rapport des axes de l'ellipse déterminée par les rayons du Soleil qui traversent le tube vertical (d'après la mesure des ombres).

Expériences : rapports entre les fractions de décomposition ($\frac{Y}{P}$) pour un même temps dans des tubes circulaires de 14^{mm} de diamètre, placés verticalement.

Déterminations d'après la mesure du gaz dégagé.....	Mélanges de liquides actifs.	Normaux. $\frac{1}{2}$ N. $\frac{1}{4}$ N. $\frac{1}{8}$ N.	ϵ .	Dates des expériences.	
				1	2,16
		1	4,63?	27 mai 1884, de 10 ^h 54 à 11 ^h 52 : ciel magnifique.	2,1
		1	4,44?	6 août 1884, de 2 ^h 55 à 3 ^h 44 : très beau temps.	1,3
		1	4,67?	8 août 1884, de 3 ^h 22 à 4 ^h : beau temps.	1,25
		1	4,65	22 octobre 1884, de 11 ^h 25 à 12 ^h 30 : beau temps.	1,2
		1	4,47	23 octobre 1884, de 10 ^h 20 à 10 ^h 55 : très beau temps.	1,1
		1	4,56	24 octobre 1884, de 11 ^h 45 à 12 ^h 38 : très beau temps.	1,1
		1	4,67	25 octobre 1884, de 1 ^h 15 à 2 ^h 23 : très beau temps.	1,1
		1	4,66	4 juin 1885, de 3 ^h 35 à 4 ^h 30 : beau ciel.	1,2
		1	4,77	11 juin 1885, de 2 ^h 07 à 3 ^h 17 : ciel magnifique.	1,55
		1	4,54	24 juin 1885, de 2 ^h 43 à 3 ^h 08 : ciel magnifique.	1,5
		1	4,60	25 juin 1885, de 2 ^h 25 à 3 ^h 16.	1,5
		1	2,32	24 juin 1886, de 3 ^h 42 à 4 ^h 26 : soleil assez pur.	1,25
		1	1,96	21 août 1886, de 1 ^h 44 à 2 ^h 16 : soleil assez pur.	1,4
		1	1,90	21 août 1886, de 4 ^h 25 à 5 ^h .	1,1
		1	2,04	28 août 1886, de 12 ^h 16 à 12 ^h 58 : beau temps.	1,5
		1	2,01	5 août 1887, de 11 ^h 55 à 12 ^h 51.	1,8

Fig. 2 - Old days photochemistry: a table taken from a paper of G. Lemoine [3] reporting the results obtained upon irradiation with sunlight of ferric oxalate solutions

In a famous lecture entitled "The photochemistry of the Future" delivered in New York at the VIII International Congress of Applied Chemistry (**1912**), at the apex of coal technology, Ciamician pictured a future society based on the sun as direct energy source:

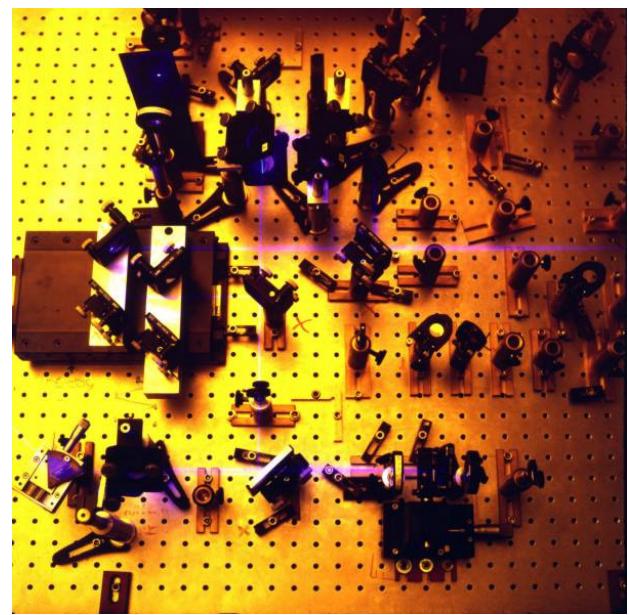
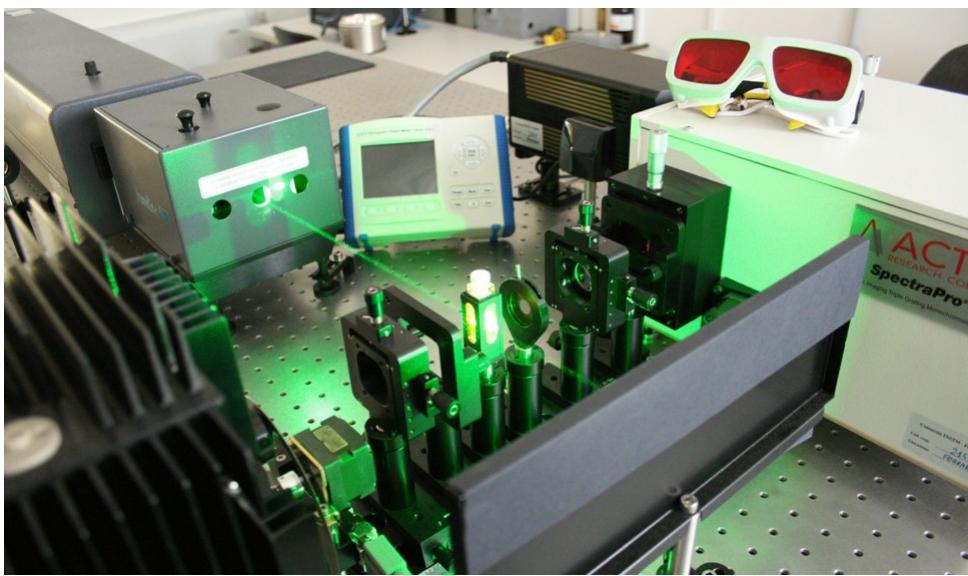
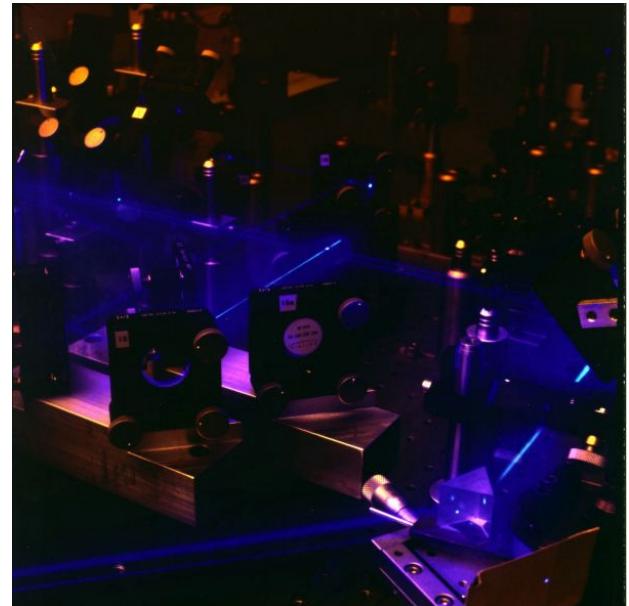
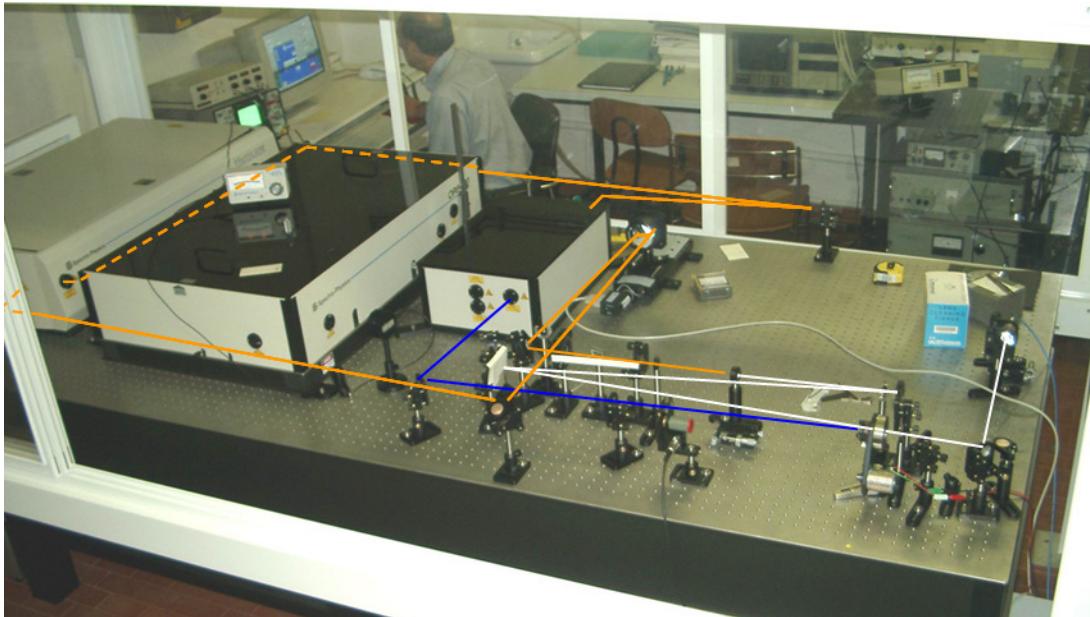
"So far human civilization has made use almost exclusively of fossil solar energy. Would it not be advantageous to make better use of radiant energy?"

.....

"On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines!"

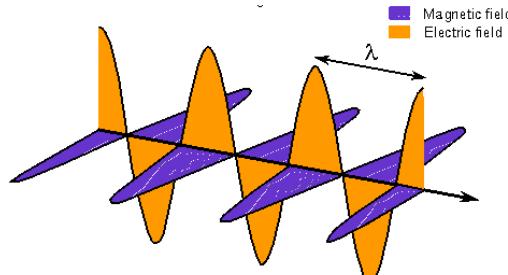
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"If our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to the progress and to human happiness."



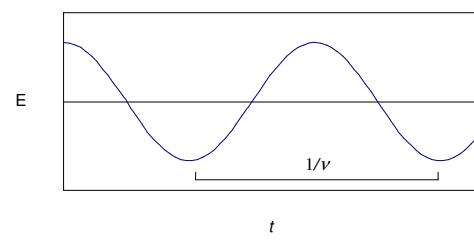
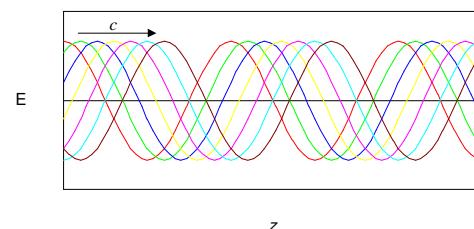
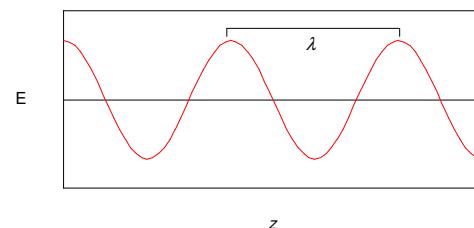
Stati elettronici. Approssimazione di Born-Oppenheimer. Orbitali molecolari, configurazioni elettroniche, stati. Vibrazioni in molecole poliatomiche.

Radiazione Elettromagnetica aspetti ondulatori



$$E = E_0 \cos 2\pi\nu(t - z/c)$$

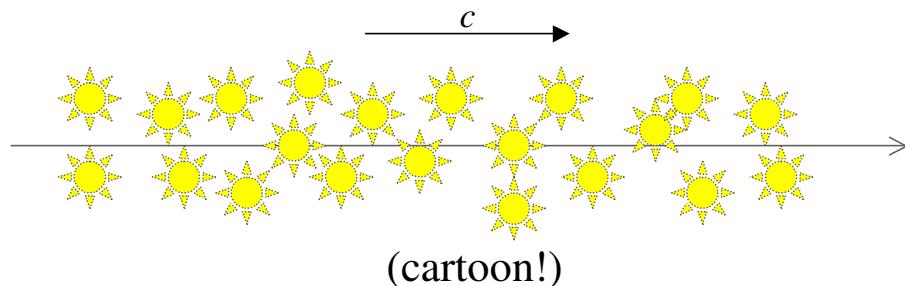
$$\nu = c/\lambda$$



E' il modello usato nella descrizione dei fenomeni dell'ottica classica (riflessione, rifrazione, interferenza)

Radiazione Elettromagnetica aspetti corpuscolari

Radiazione elettromagnetica = flusso di **fotoni**



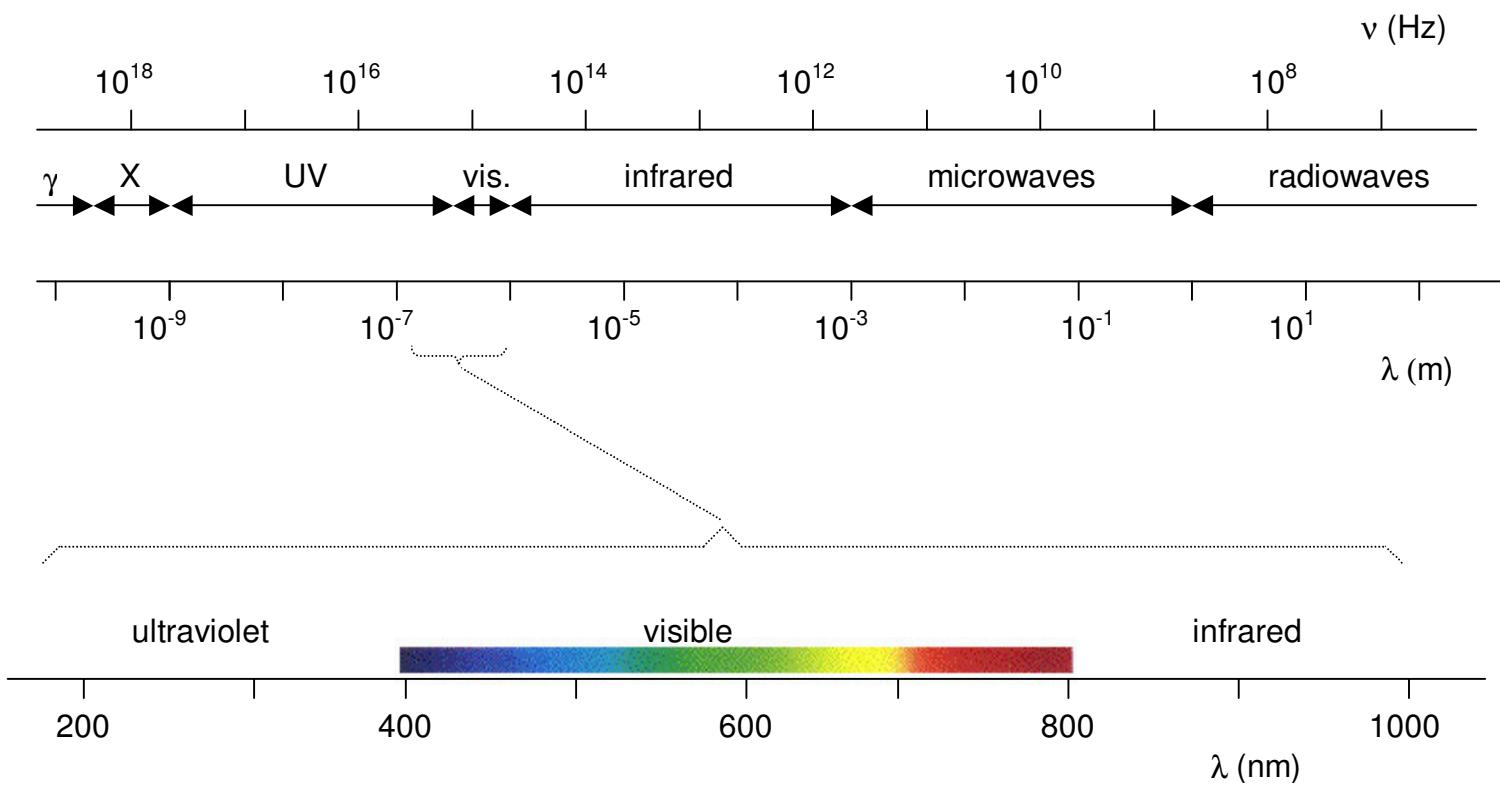
Fotone = pacchetto elementare di energia

$$E = h\nu$$

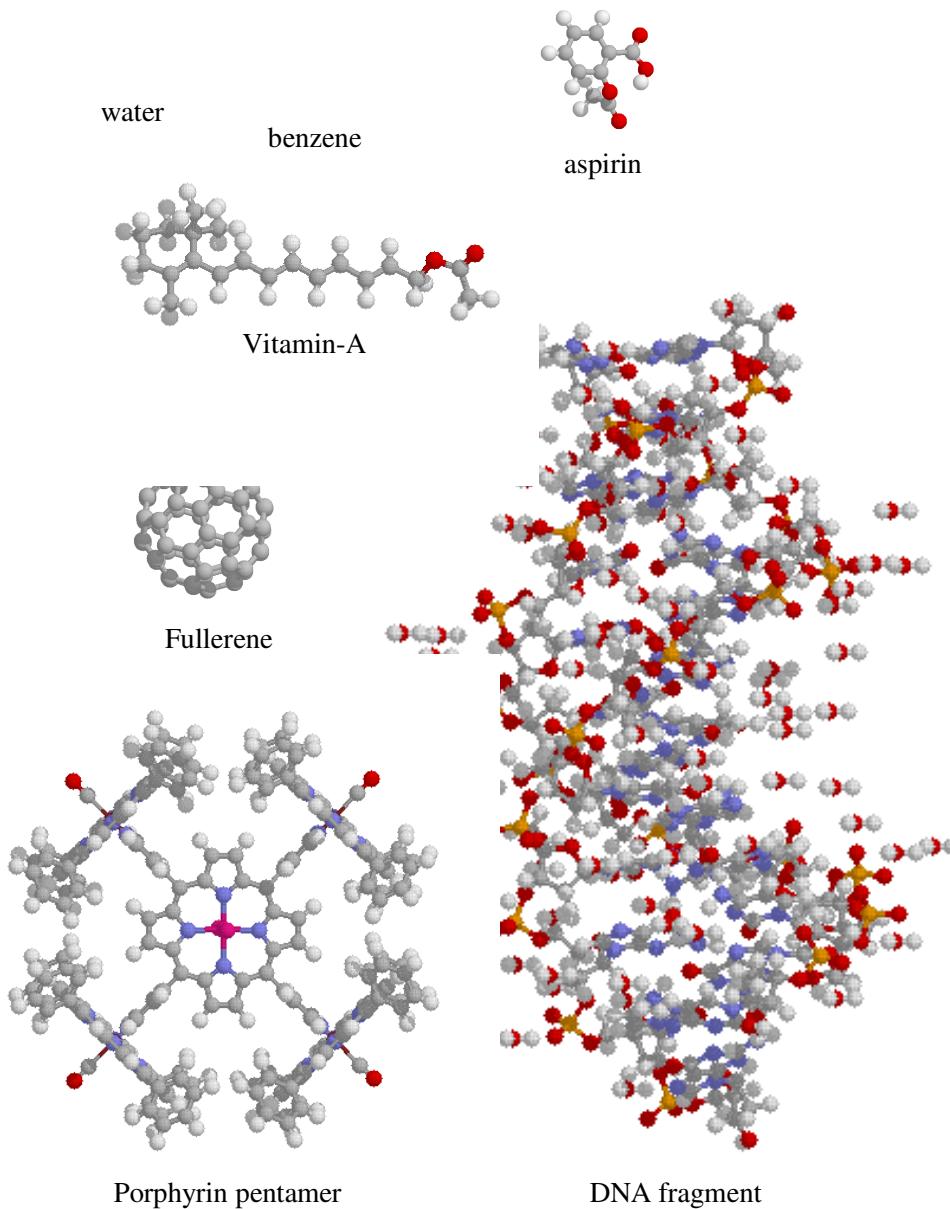
$$p = h/\lambda$$

E' il modello più utile nella descrizione a livello microscopico delle interazioni fra radiazione elettromagnetica e materia (assorbimento, emissione)

Spectral Ranges of Electromagnetic Radiation



Interaction of light with molecular species: generation of **electronically excited states**



Description of electronically
excited states



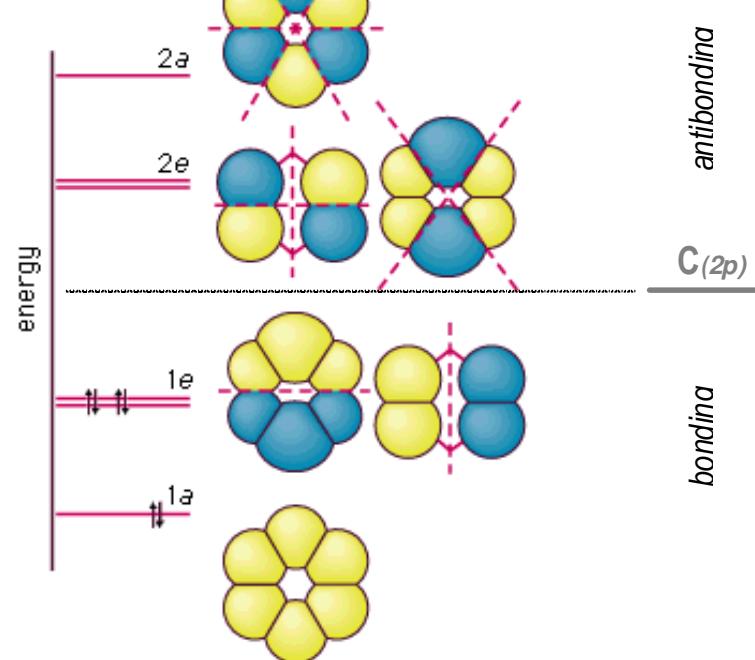
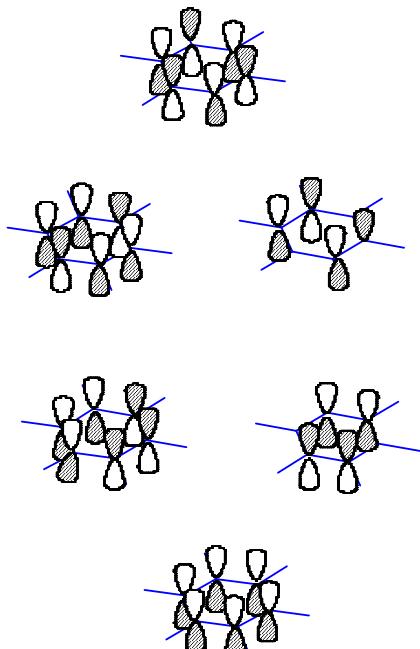
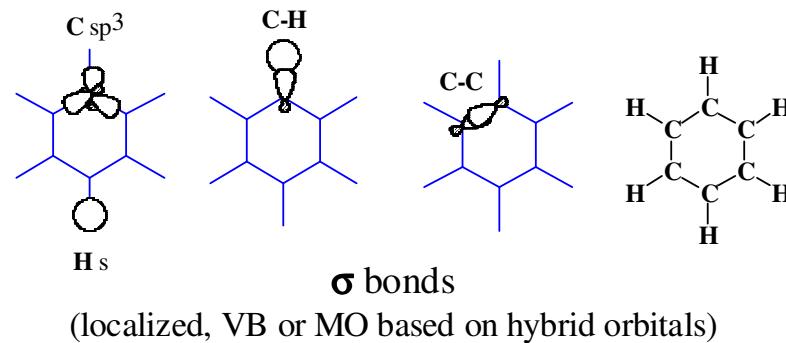
Molecular Orbitals

Benzene

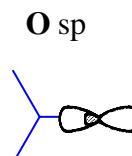
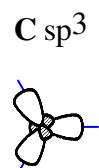
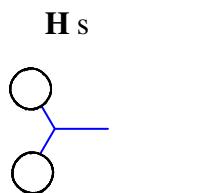
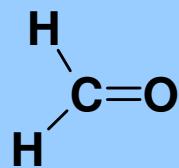
Focus on frontier orbitals



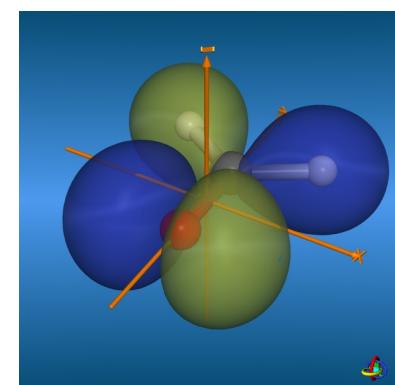
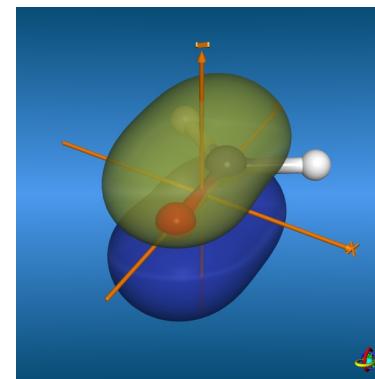
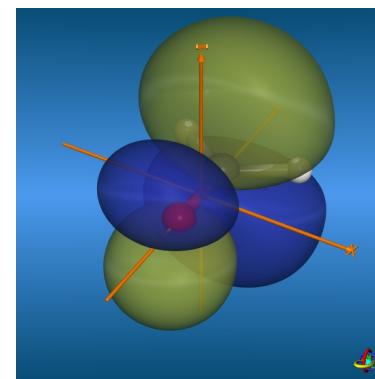
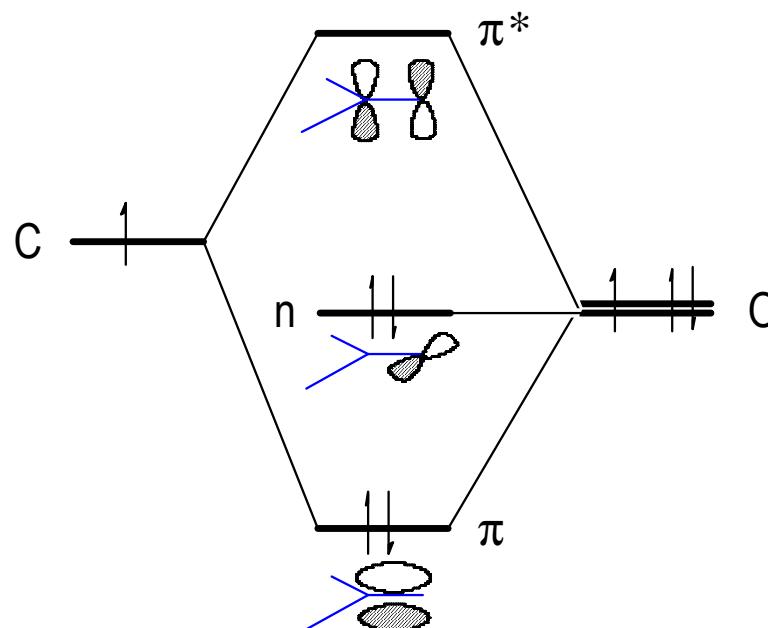
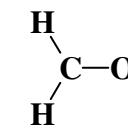
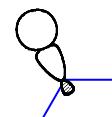
σ -framework, localized, VB
p-system, delocalized MO



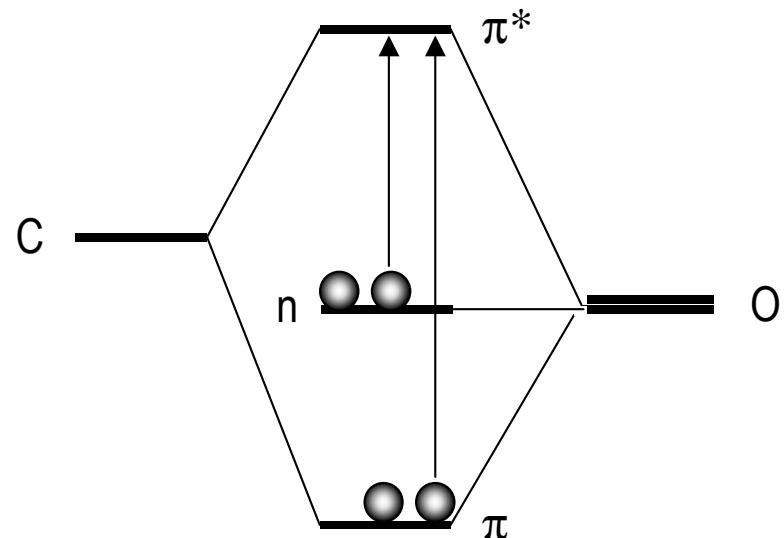
Formaldehyde



σ bonds



Configurazioni elettroniche e transizioni elettroniche



Transizioni:

$$n \rightarrow \pi^*$$

$$\pi \rightarrow \pi^*$$

Configurazioni:

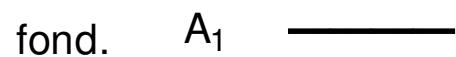
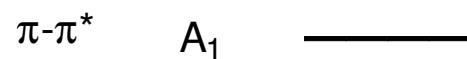
fondamentale
 $\pi^2 n^2$

eccitate
 $\pi^2 n \pi^*$ “ $n-\pi^*$ ”
 $\pi n^2 \pi^*$ “ $\pi-\pi^*$ ”

.....

Appr. di Ordine Zero

$$E = \sum_i n_i E_i$$

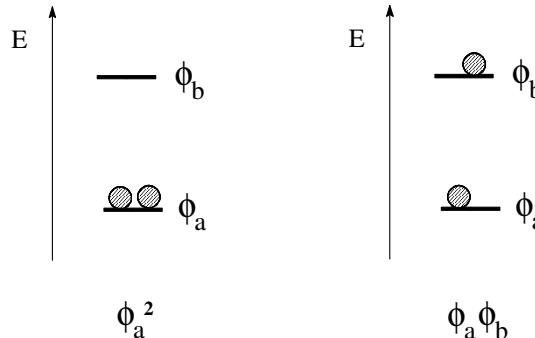


Appr. di Primo Ordine

$$E = \sum_i n_i E_i + E_{\text{rep.el.}}$$

L'aggiunta delle **repulsioni interelettroniche** modifica *qualitativamente* il diagramma degli stati di energia?

Configurazioni elettroniche, spin, e stati elettronici



Stati Elettronici

$$\phi_a^2$$

$$\Psi(S_0) = (1/\sqrt{2}) [\phi_a(1)\phi_a(2)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

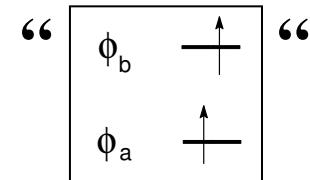
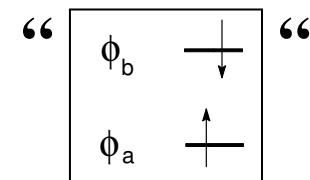
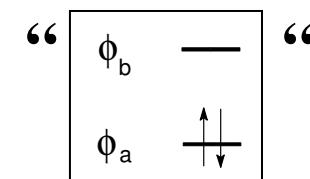
$$\phi_a \phi_b$$

$$\Psi(S_1) = (1/\sqrt{2}) [\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

$$\Psi(T_1^1) = (1/\sqrt{2}) [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] [\alpha(1)\alpha(2)]$$

$$\Psi(T_1^0) = (1/\sqrt{2}) [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] [\beta(1)\beta(2)]$$

$$\Psi(T_1^{-1}) = (1/\sqrt{2}) [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$



$$\Psi(S_1) = (1/\sqrt{2}) [\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

$$\Psi(T_1^1) = (1/\sqrt{2}) [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] [\alpha(1)\alpha(2)]$$

$$\Psi(T_1^0) = (1/\sqrt{2}) [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] [\beta(1)\beta(2)]$$

$$\Psi(T_1^{-1}) = (1/\sqrt{2}) [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

$$E = E_a + E_b + E_{\text{rep}}$$

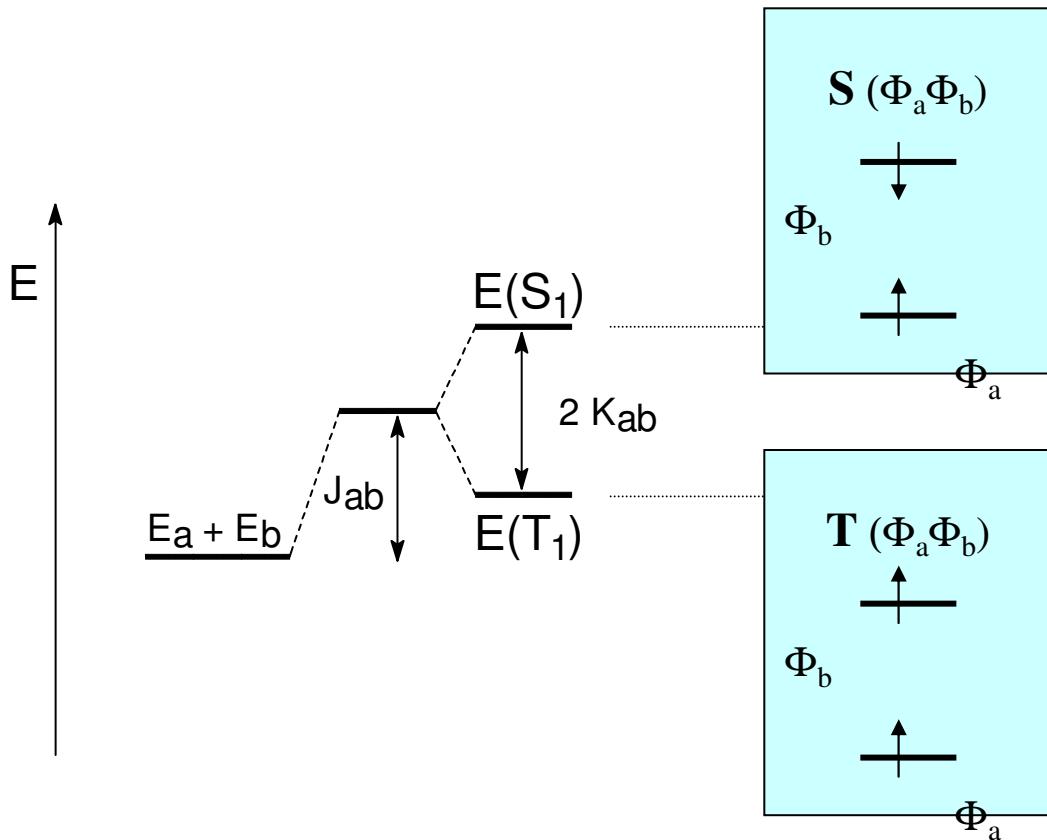
exchange K_{ab}

$$E_{\text{rep}} = \langle \Psi_* | (e^2/r) | \Psi \rangle = (1/2)^{1/2} \langle [\phi_A(1)\phi_B(2) \pm \phi_A(2)\phi_B(1)] | (e^2/r_{12}) | [\phi_A(1)\phi_B(2) \pm \phi_A(2)\phi_B(1)] \rangle$$

Coulomb J_{ab}

$$E_{\text{rep}}(S_1) = J_{ab} + K_{ab}$$

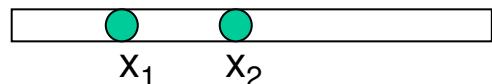
$$E_{\text{rep}}(T_1) = J_{ab} - K_{ab}$$



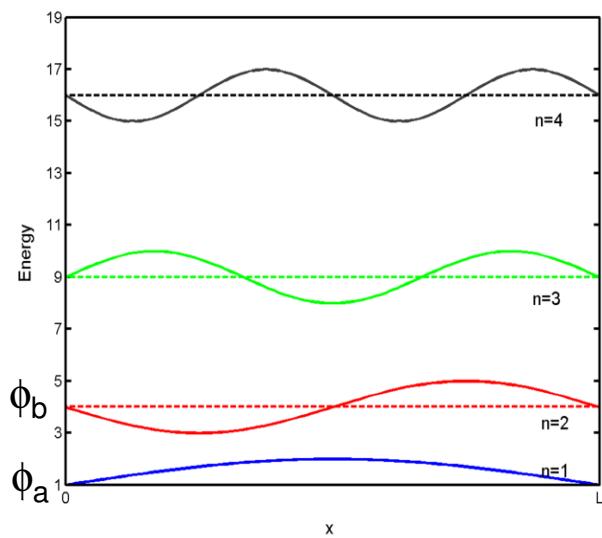
Il moto individuale di ogni elettrone è dettato dal proprio orbitale,
ma quello ***relativo*** dei due è controllato dallo ***spin***:

- con spin antiparalleli, gli elettroni hanno tendenza a "viaggiare insieme" (\Rightarrow maggiori repulsioni)
- con spin paralleli, gli elettroni hanno tendenza a "evitarsi" (\Rightarrow minori repulsioni)

Esempio: 2 elettroni in una scatola monodimensionale



Con diverse autofunzioni (“in orbitali diversi”),
ad es., ϕ_a ($n=1$) e ϕ_b ($n=2$)



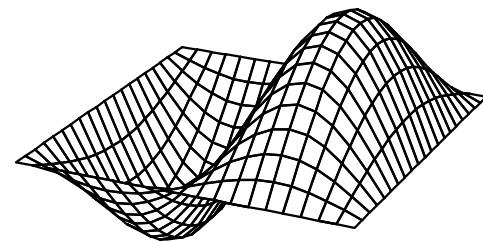
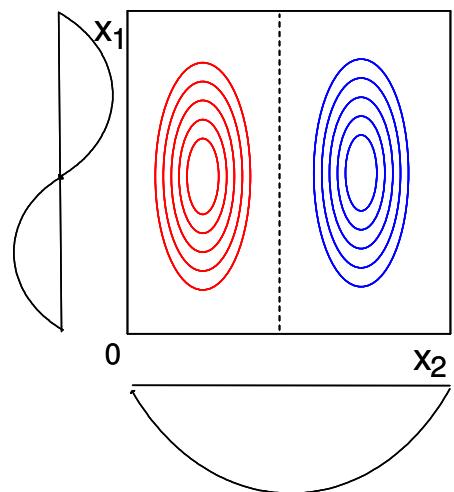
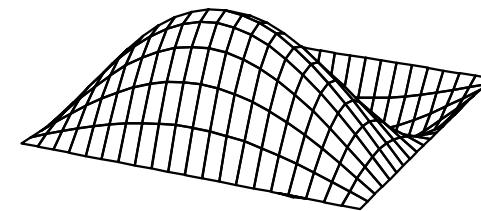
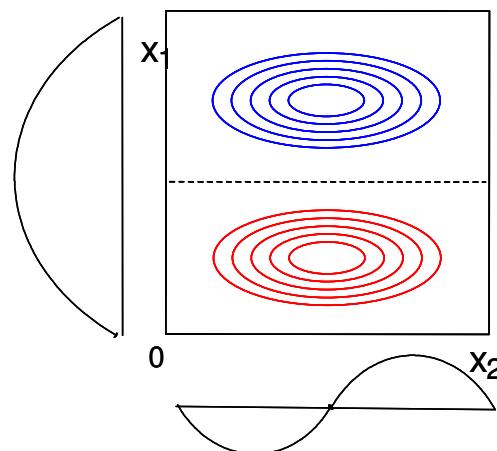
$$\Psi(S_1) = (1/\sqrt{2}) [\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

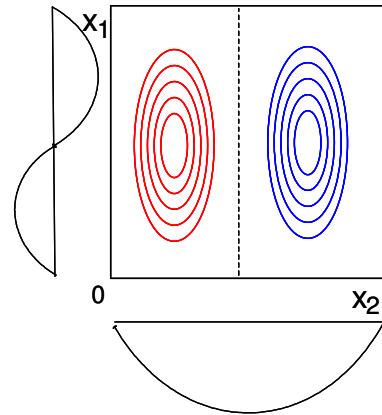
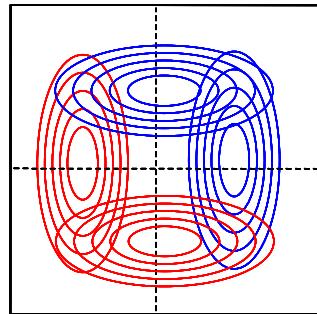
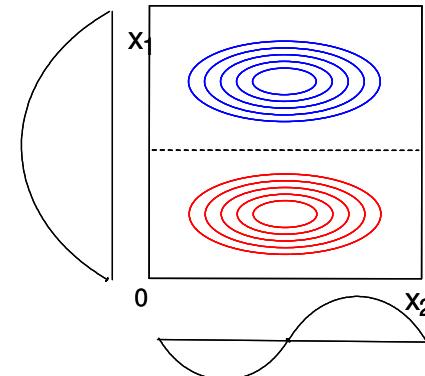
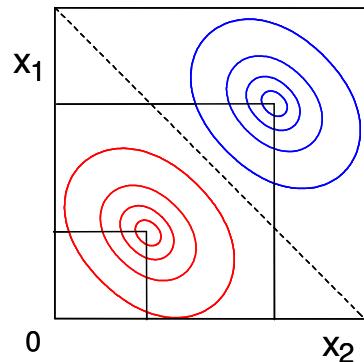
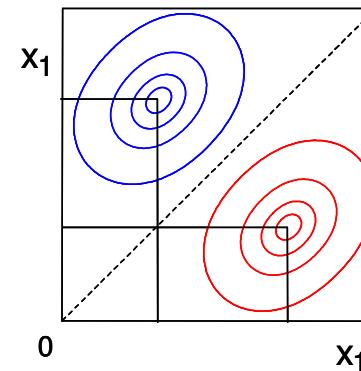
$$\Psi(T_1^1) = (1/\sqrt{2}) [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] [\alpha(1)\alpha(2)]$$

$$\Psi(T_1^0) = (1/\sqrt{2}) [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] [\beta(1)\beta(2)]$$

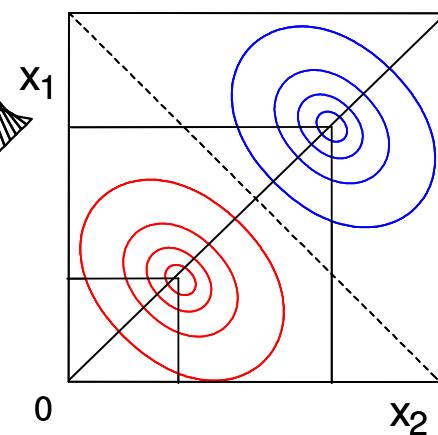
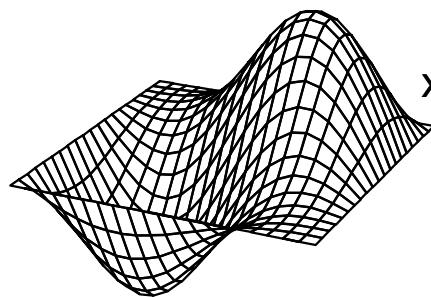
$$\Psi(T_1^{-1}) = (1/\sqrt{2}) [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

Come cambia il moto **relativo** dei due elettroni a seconda dello spin (parallelo o antiparallelo, tripletto o singoletto)?

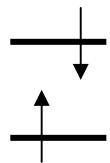
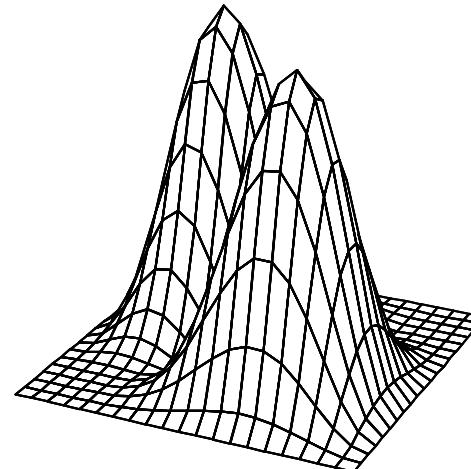
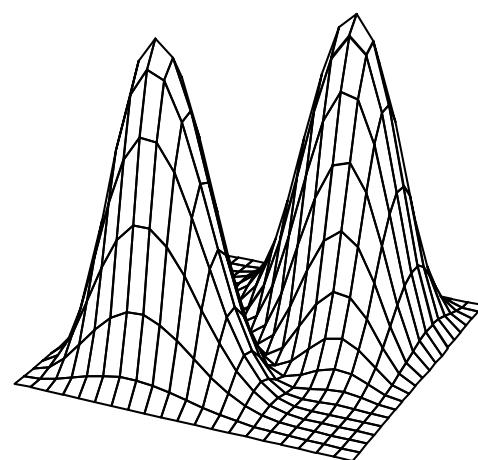
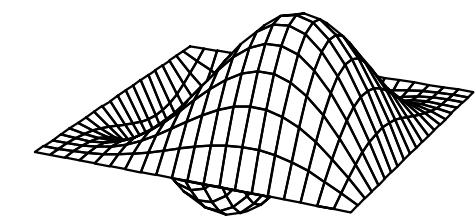
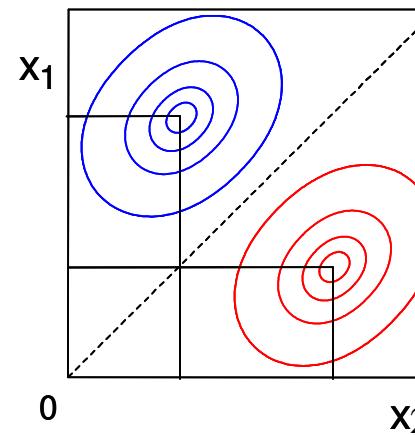
$\phi_a(2)\phi_b(1)$  $\phi_a(1)\phi_b(2)$ 

$\phi_a(2)\phi_b(1)$  $\phi_a(1)\phi_b(2)$  $\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)$  $\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)$ 

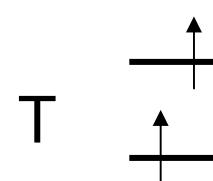
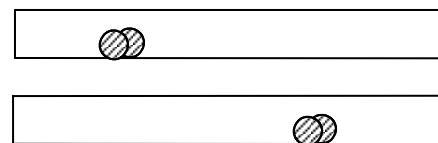
$$\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)$$



$$\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)$$



S



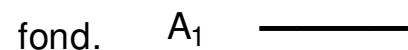
T

configurazioni elettroniche

stati elettronici

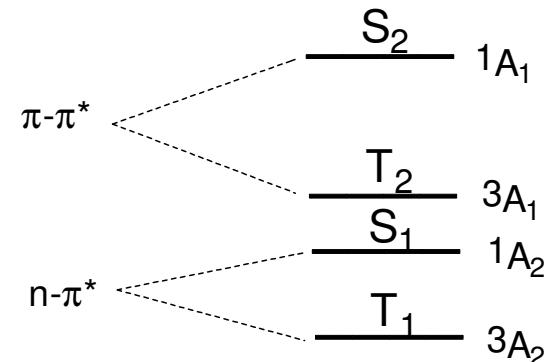
Appr. di Ordine Zero

$$E = \sum_i n_i E_i$$

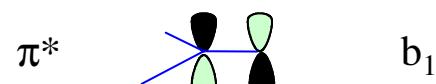
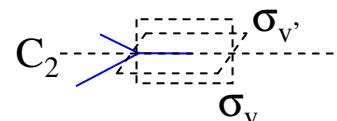


Appr. di Primo Ordine

$$E = \sum_i n_i E_i + E_{\text{rep.el.}}$$

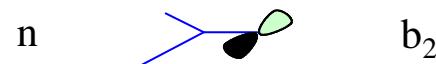


C_{2v}	E	C_2	$\sigma_v (xz)$	$\sigma'_v (yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

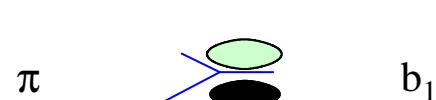


b_1

$$n - \pi^* \quad b_2 \times b_1 = A_2$$



b_2



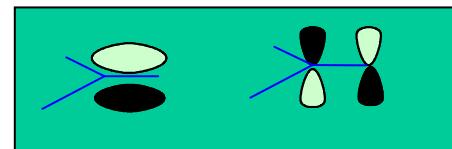
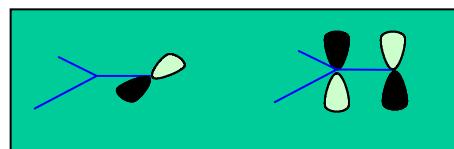
b_1

$$\pi - \pi^* \quad b_1 \times b_1 = A_1$$

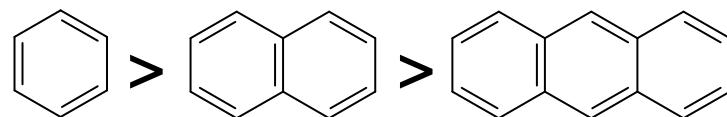
$$\text{Separazione S-T} = 2 J_{ab}$$

Dipende da (i) sovrapposizione fra densità elettroniche dei due orbitali e (ii) grado di delocalizzazione

-e.g., è maggiore per stati $\pi-\pi^*$ che per $n-\pi^*$



-e.g., per stati $\pi-\pi^*$ diminuisce all'aumentare della delocalizzazione degli MO



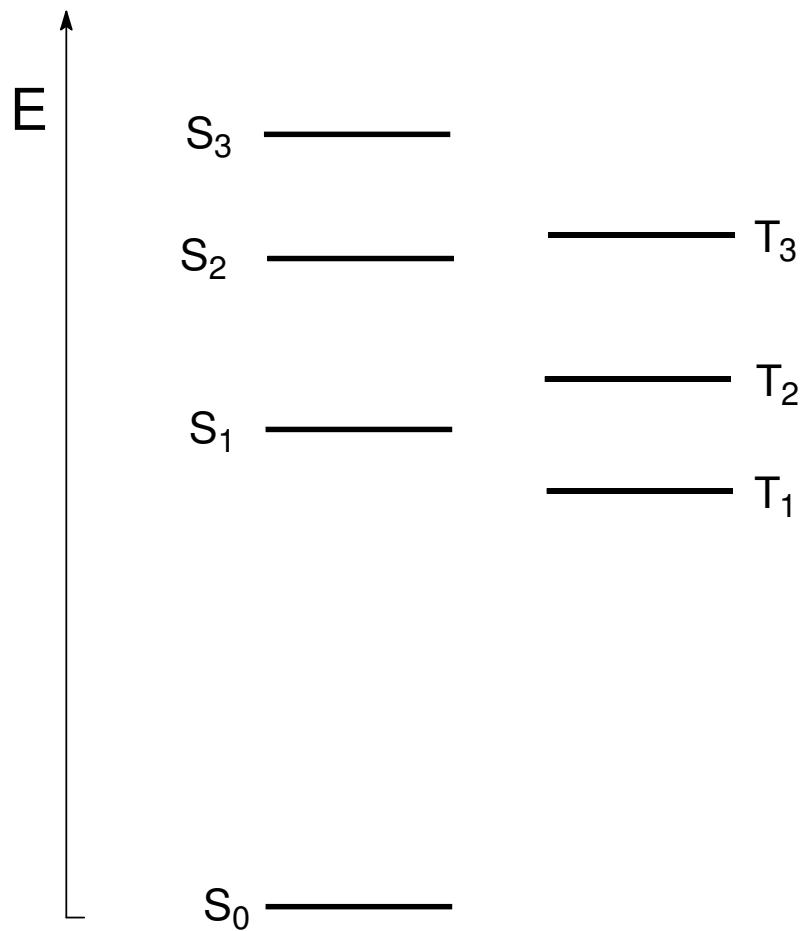
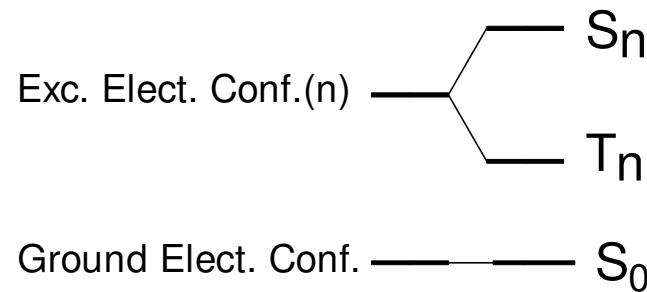


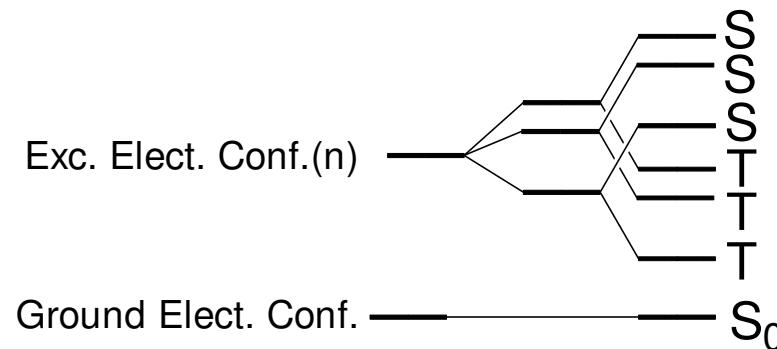
Diagramma di Jablonski

MO \Rightarrow Electro Configurations \Rightarrow Electronic States

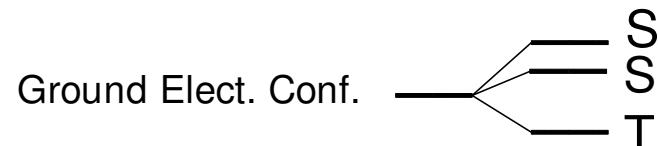


General: Closed-shell systems, non-degenerate MO

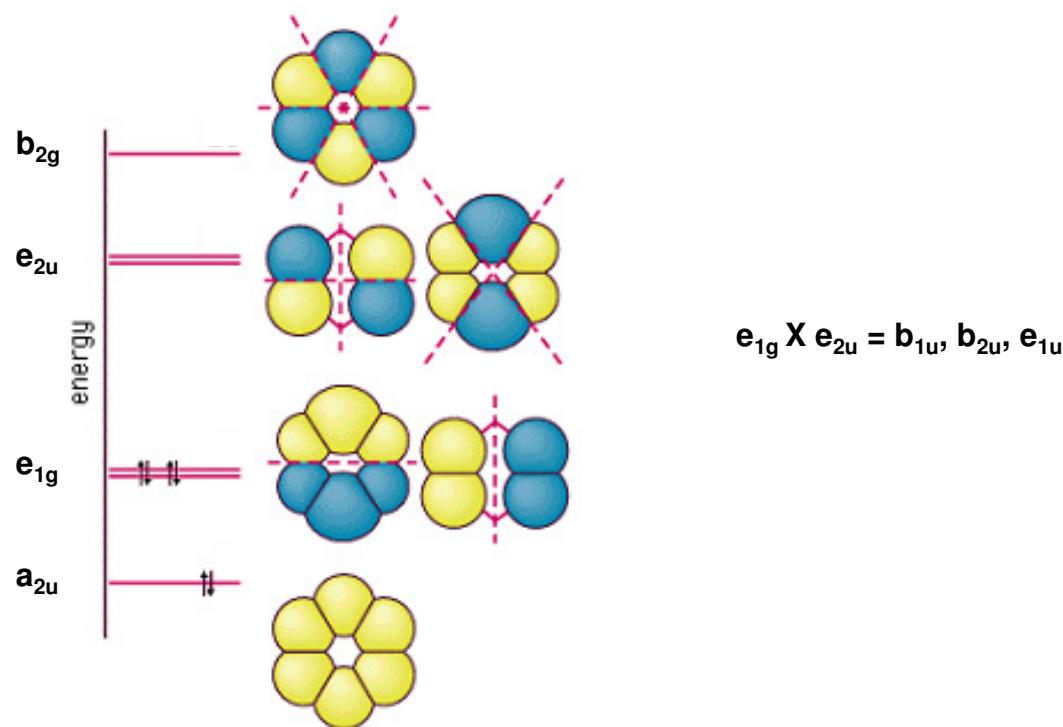
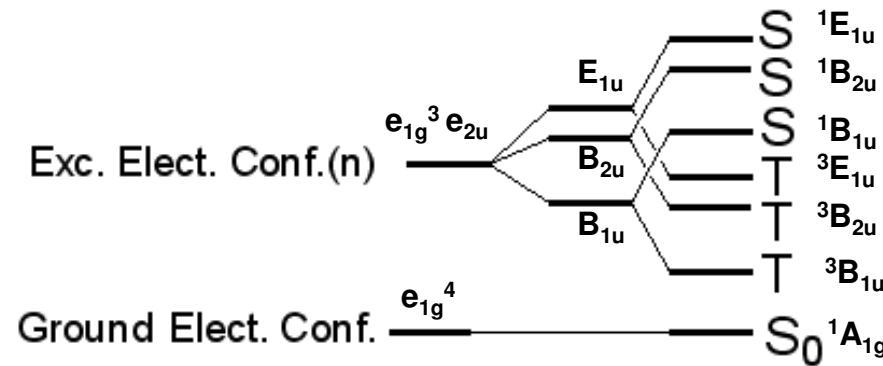
Exceptions: 1) Closed-shell systems, degenerate MO



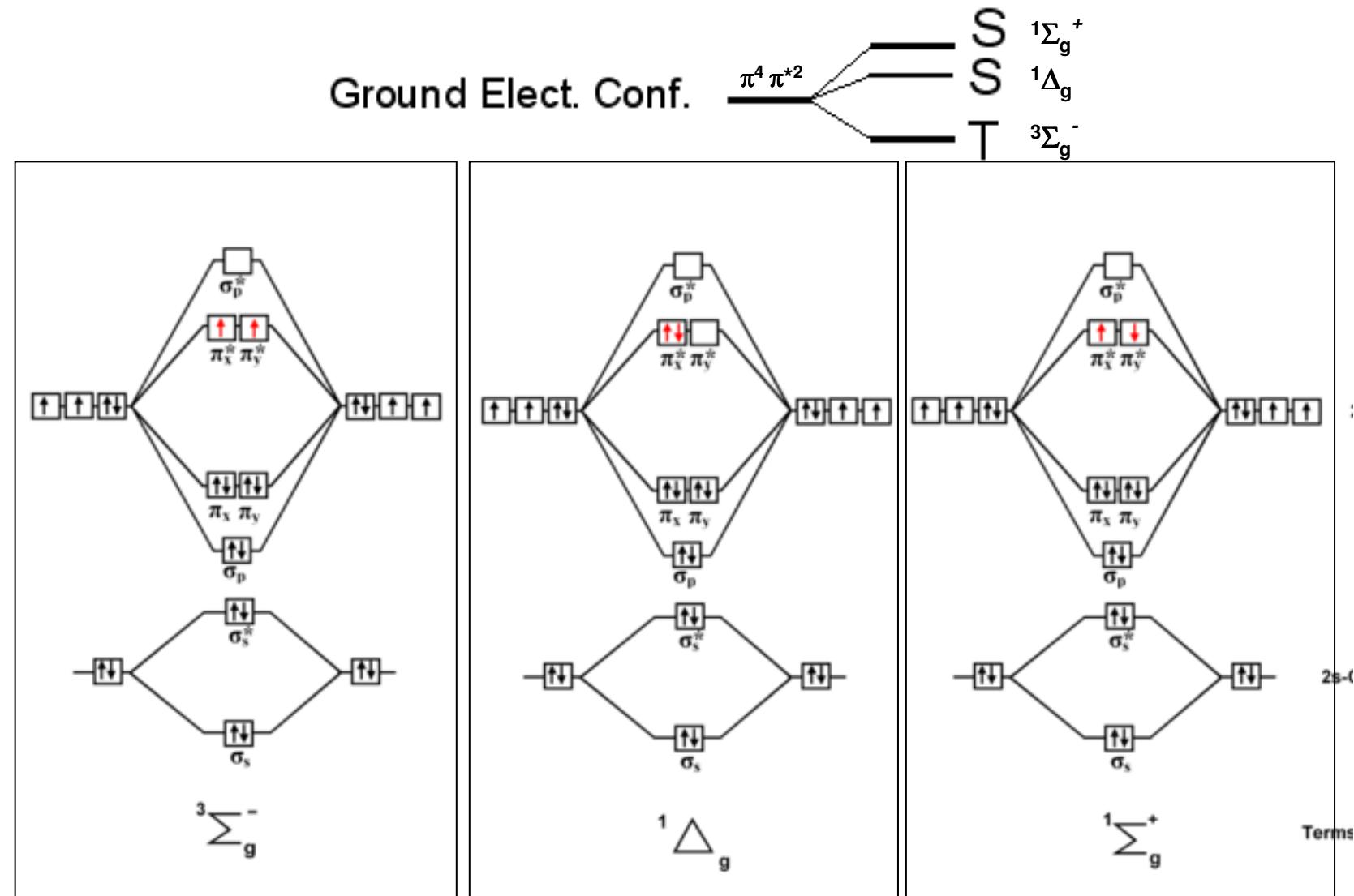
Exceptions: 2) Open-shell systems



Exceptions: 1) Closed-shell systems, degenerate MO, e.g., benzene



Exceptions: 2) Open-shell systems, e.g., O₂



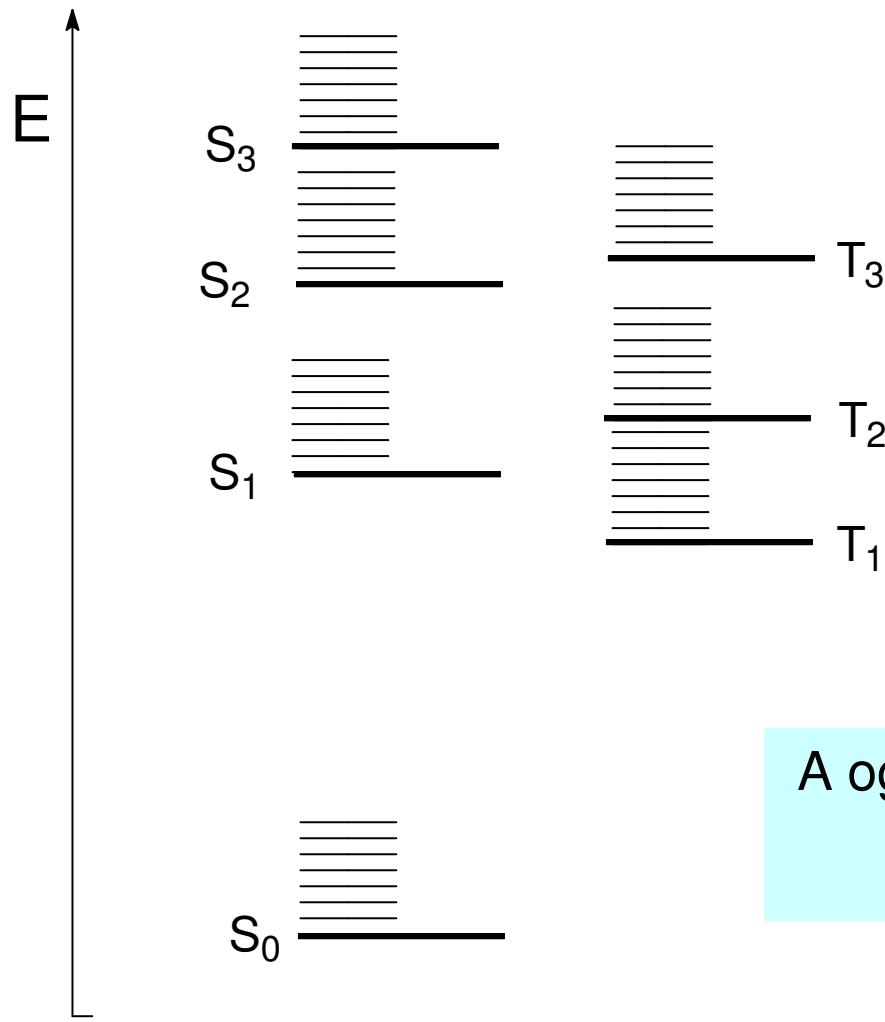


Diagramma di Jablonski

A ogni stato elettronico sono associati
livelli vibrazionali

the Born-Oppenheimer Approximation

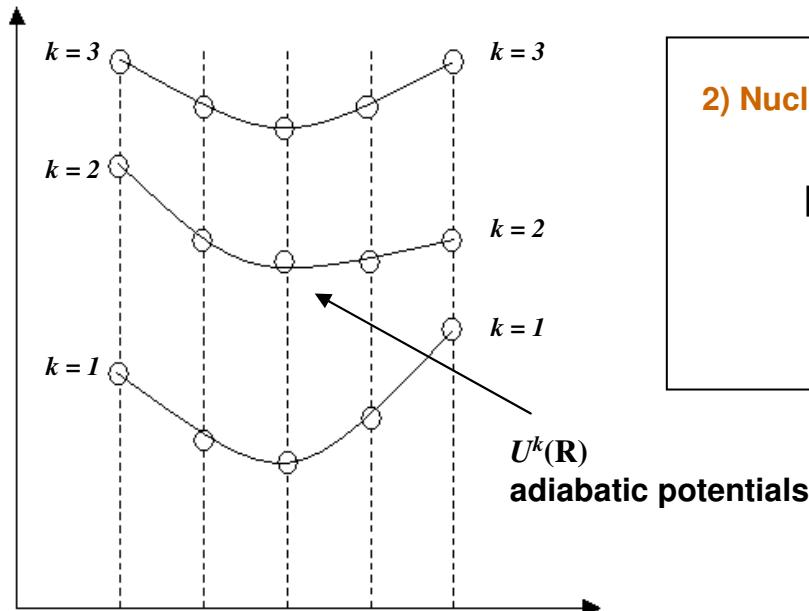
$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}), \quad \text{total Hamiltonian}$$

1) Electron motion: at fixed nuclear geometry

$$\hat{T}_N(\mathbf{R}) \quad \text{neglected} \quad \hat{V}_{NN}(\mathbf{R}) \quad \text{constant}$$

$$\hat{H} = \hat{T} \quad \hat{H}_{el} = \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}), \quad \text{electronic Hamiltonian}$$

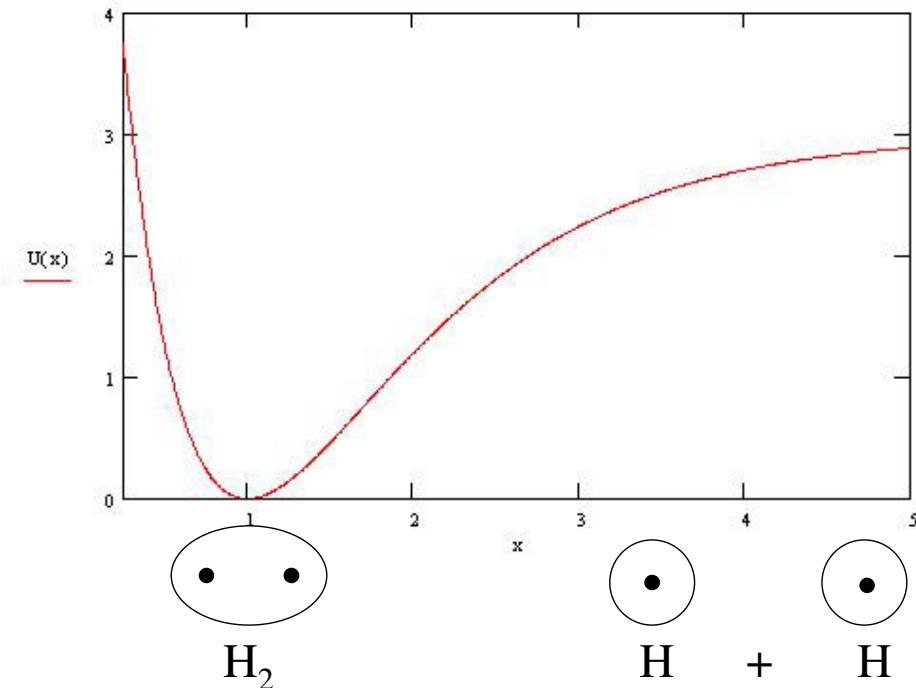
$$\hat{H}_{el}\Psi(\mathbf{r}; \mathbf{R}) = E_{el}\Psi(\mathbf{r}; \mathbf{R}) \quad \text{electronic Schroedinger eq.} \quad \psi^k(\mathbf{r}, \mathbf{R}) \quad \text{electronic eigenfunction}$$



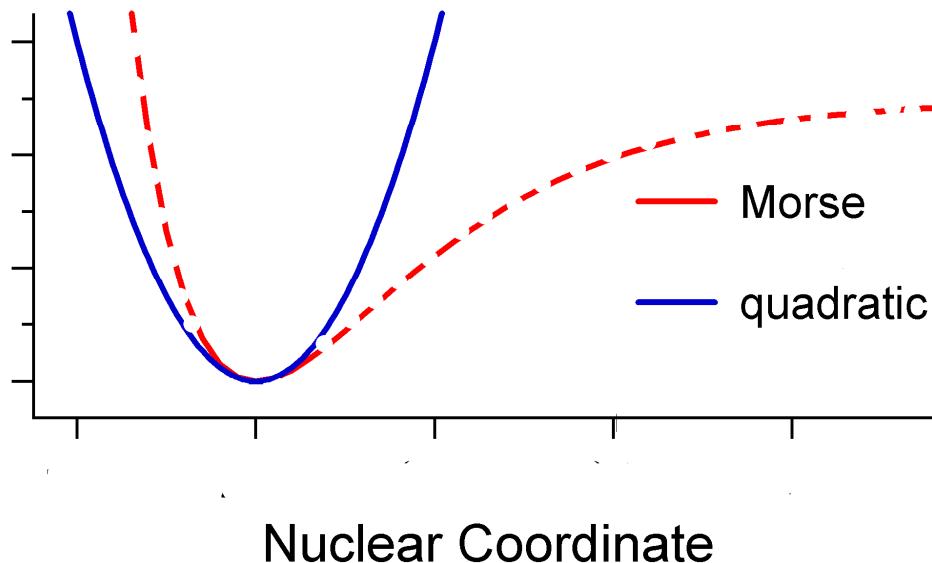
2) Nuclear motion: vibration in adiabatic potentials

$$[T_N + U^k(\mathbf{R})] \chi_k(\mathbf{R}) = E \chi_k(\mathbf{R}) \quad \text{nuclear Schroedinger eq.}$$

$$\chi_v^k(\mathbf{R}) \quad \text{nuclear (vibrational) eigenfunctions}$$



Potential Energy of a Diatomic Molecule (Morse function)



“Harmonic Oscillator”
Approximation

Quantum mechanical harmonic oscillator

Quantum mechanical hamiltonian for a diatomic molecular oscillator (equilibrium at $x = 0$).

$$H = \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + V(x)$$

For the harmonic oscillator, $V(x) = \frac{1}{2} kx^2$, so

$$H = \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2$$

The Schrodinger equation is $H\Psi = E\Psi$

The general solution is

$$\Psi_v = N_v H_v(\alpha^{1/2}x) e^{-\alpha x^2/2}$$

$N_v = \left(\frac{\alpha^{1/2}}{2^v v! \pi^{1/2}} \right)$ is the normalization

$H_v(\alpha^{1/2}x)$ are Hermite polynomials

Some of the Hermite polynomials are:

$$\begin{aligned} H_0(y) &= 1 \\ H_1(y) &= 2y \\ H_2(y) &= 4y^2 - 2 \\ H_3(y) &= 8y^3 - 12y \\ H_4(y) &= 16y^4 - 48y^2 + 12 \end{aligned}$$

The constant α is related to the classical vibrational frequency ω , reduced mass μ , and force constant k by

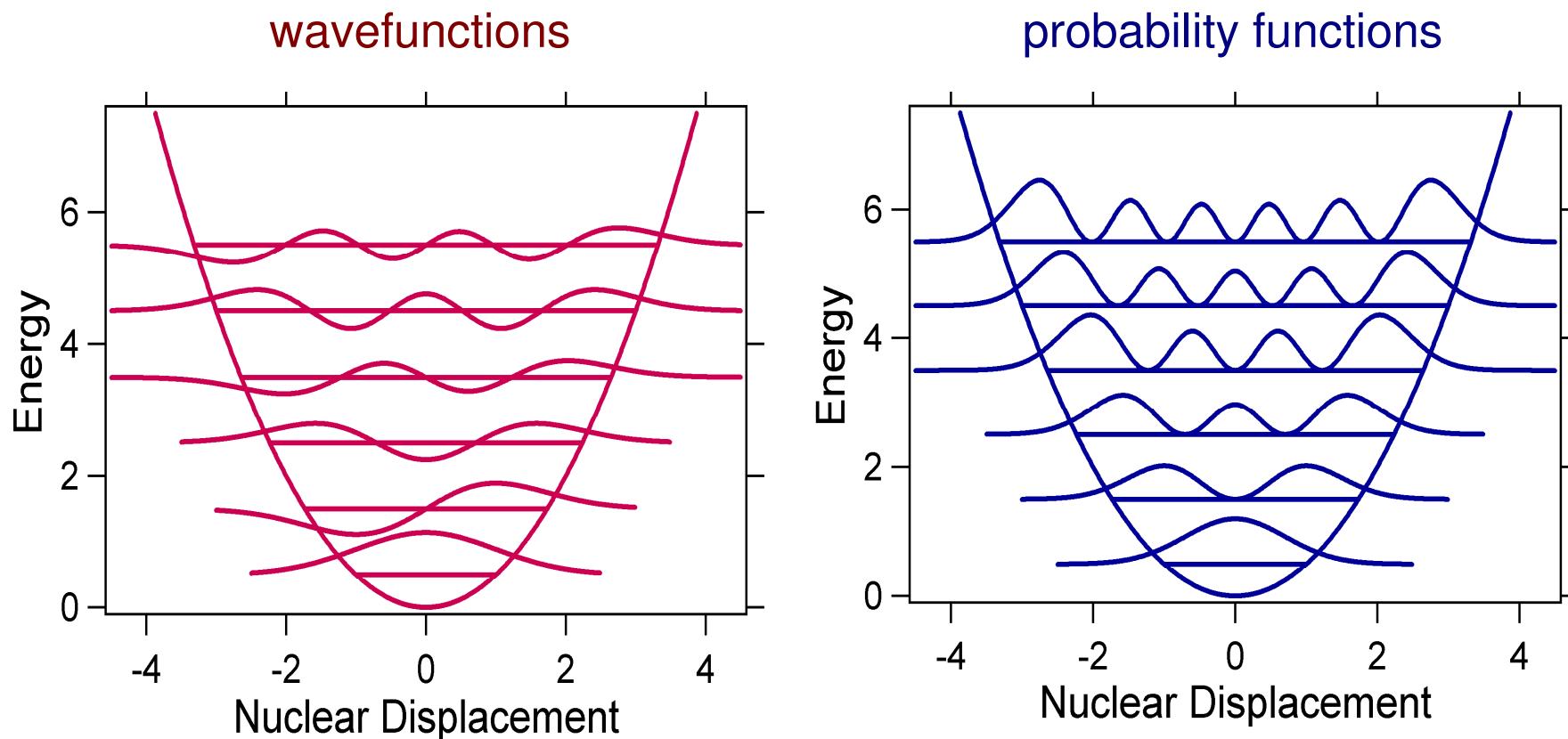
$$\alpha = \frac{\mu\omega}{\hbar} = \frac{\sqrt{\mu k}}{\hbar}$$

The energies are

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega$$

where v is a vibrational quantum number.

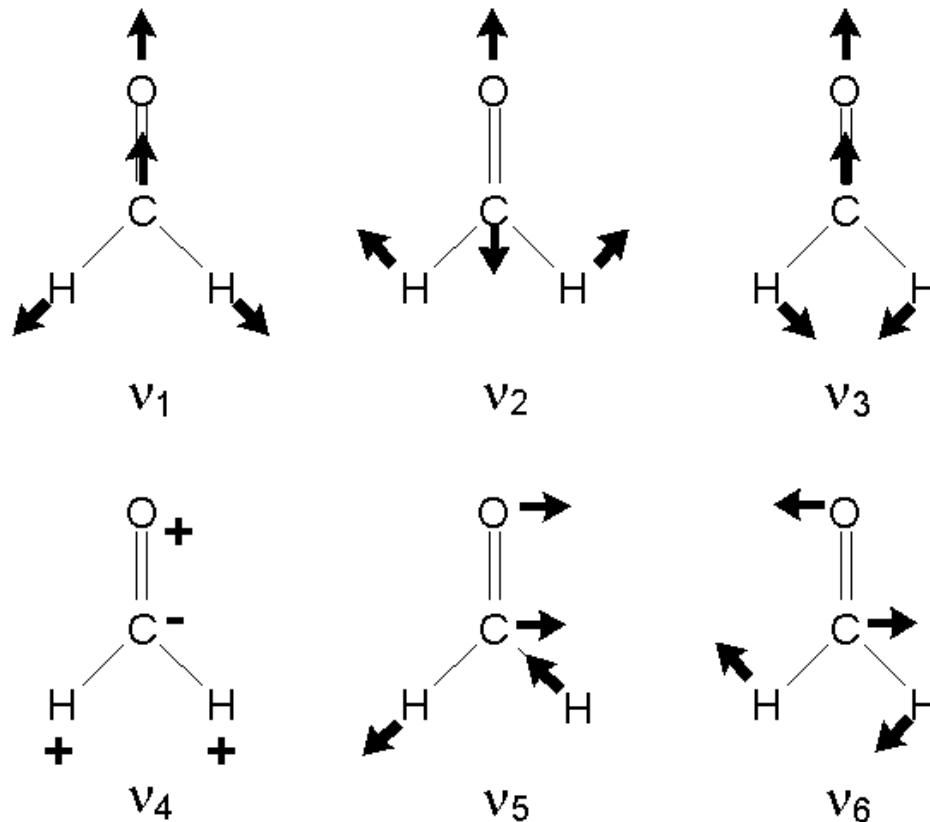
Harmonic Oscillator



Vibrations in Polyatomic Molecules

The complex nuclear motion of a (non-linear) N-atomic molecule can be viewed as the superposition of $(3N-6)$ **normal modes** of vibration.

For Formaldehyde:



For each electronic state, a potential **hypersurface** (in $3N-5$ dimensional space). **Sections** can be represented as surfaces (all coordinates constant, except for two) or curves (all coordinates constant, except for one)

