



# Excited States

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# *Excited States*

## **1.- Excited States. Spectroscopy, Photophysics and Photochemistry:**

*Processes and magnitudes: what to compute*

## **2.- Quantum-Chemical Methods for Excited States:**

*Potential energy surfaces (PES) and transition probabilities:  
how to compute them. CASSCF, CASPT2, CASSI*

## **3.- Towards a Nonadiabatic Photochemistry:**

*PES MEPs, crossings, and conical intersections*



# Concept of Potential Energy (Hyper)Surface (PES)



- Represent molecular potentials for the nuclear motion
- Built by solving the time-independent Schrödinger equation

$$H \Psi(\mathbf{R}, \mathbf{r}) = E \Psi(\mathbf{R}, \mathbf{r})$$

$$H = T_n + T_e + V_{ne} + V_{ee} + V_{nn} = T_n + H_e$$

Born-Oppenheimer approach

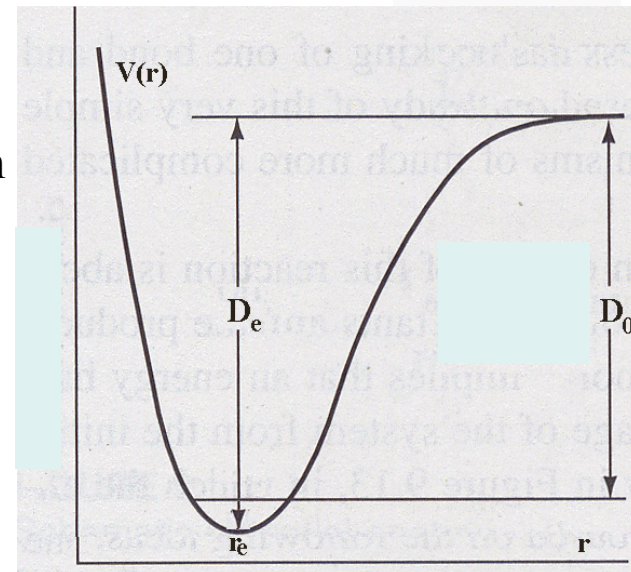
$$\Psi(\mathbf{R}, \mathbf{r}) = \Psi^n(\mathbf{R}) \Psi^e(\mathbf{r}; \mathbf{R})$$

$$H_e \Psi_i^e(\mathbf{r}; \mathbf{R}) = E_i^e(\mathbf{R}) \Psi_i^e(\mathbf{r}; \mathbf{R})$$

Electronic Schrödinger equation

$$[T_n + E_i^e(\mathbf{R})] \Psi_j^n(\mathbf{R}) = E_j^n \Psi_j^n(\mathbf{R})$$

Nuclear Schrödinger equation

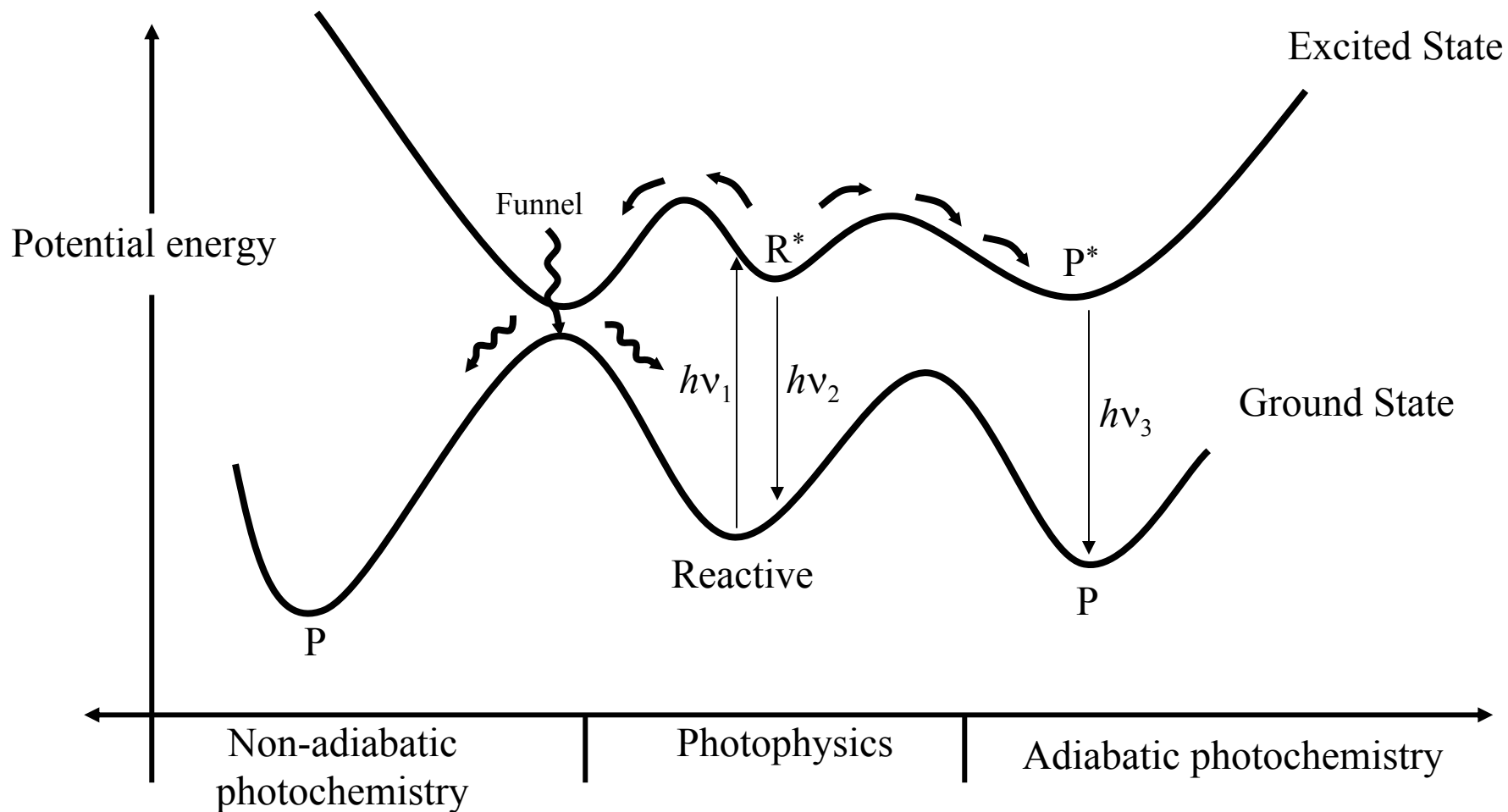


$E_i^e(\mathbf{R})$  eigenvalue of  $H_e$  for each nuclear configuration  $\mathbf{R}$

$E_j^n(\mathbf{R})$  eigenvalue of nuclear  $H$

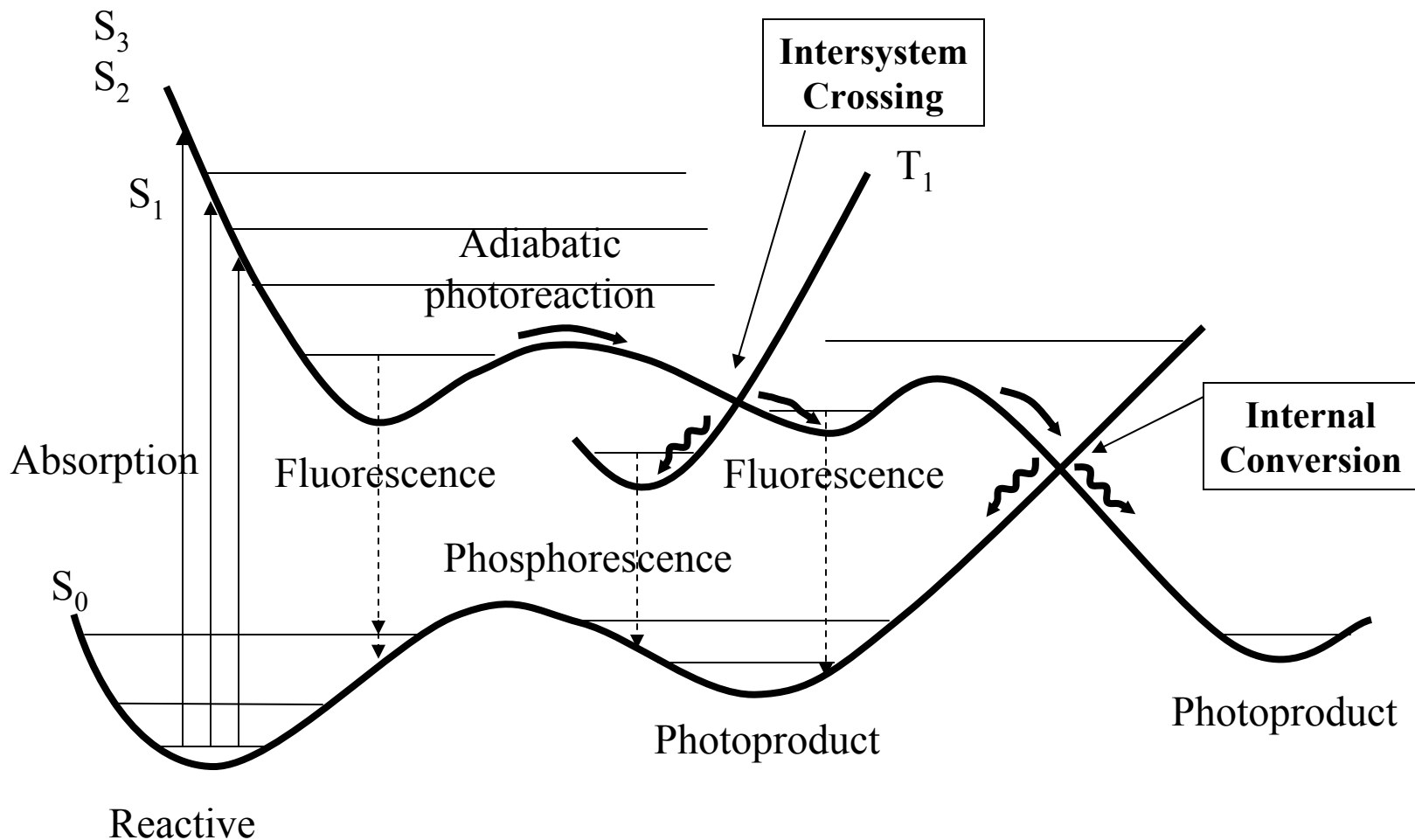


# Photophysics and photochemistry



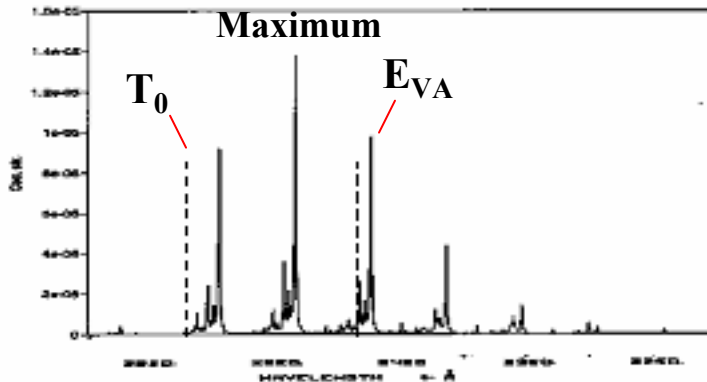
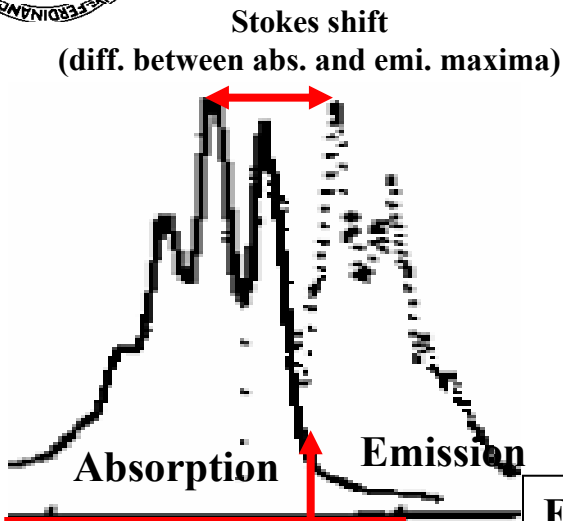


# *Nonadiabatic photochemistry*





# Band maxima and origin: theory-experiment



Depending on the system:

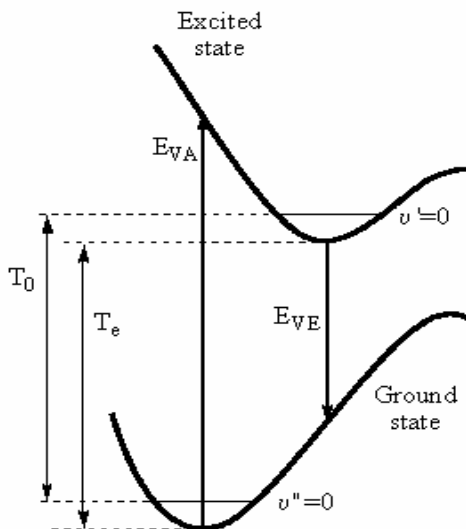
The maximum change with the experimental conditions

Max.  $\approx E_{VA}$ : 0.1-0.2 eV

**Band origin**  
(without vibrational accuracy)

$E_{VA}$ ,  $T_e$  y  $E_{VE}$  (CASPT2//CASSCF): with no experimental analogous

To compare with experiment we have to add to each point in the surface the *zero-point vibrational correction (ZVE)*. By using ground vibrational states we obtain  $T_0$ , band origin or  $0-0 \text{ ó } 0_0^0$  transition.



$$T_0 = T_e + ZVE_{ij} = T_e + E_{i,vib}(0) - E_{j,vib}(0) = T_e + \frac{1}{2} \sum_Q \omega_{i,Q} - \frac{1}{2} \sum_Q \omega_{j,Q}$$

where ZVE (o ZPVE) is usually computed by using the harmonic approach:

$$E_v = (v + \frac{1}{2})h\omega \quad \longrightarrow \quad E_{v=0} = \frac{1}{2} \sum_Q \omega_Q$$

Is enough with the band positions? What about intensities?

**Transition probabilities**



# Probability of electronic transitions



- Semiclassical model for radiation-matter interaction: the effect of the radiative field is reduced to a small perturbation added to the nuclear hamiltonian  $H'(t)$
- Time dependent perturbation : resonance condition  $h\nu = E_1 - E_2$
- *Fermi Golden rule*: the transition probability related with the Einstein coefficient

$$B_{if} \propto \langle \phi_i | H' | \phi_f \rangle^2, \text{ square of the transition moment } M$$

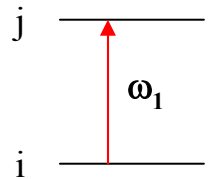
- Dipole approach:  $H'(t) = -\mu E(t) \longrightarrow \mu = e \sum r_\alpha$
- Higher approaches:  $H'(t) = -P_\alpha^{(k)} E(t) \longrightarrow P_\alpha^{(k)} = \sum_k r_\alpha^{(k)}$   $k=1$  dipole,  $k=2$  quadrupole,...

One-photon transition dipole moment between two electronic states  $i, j$

RASSI

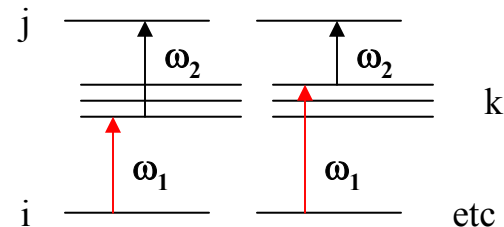
$$M_e^{i \rightarrow j} = \sum_{\alpha=x,y,z} \langle \phi_i | \mu_\alpha | \phi_j \rangle \quad \mu, \text{ dipole moment}$$

$\omega_1$  energy of photon.  $M_e$  doesn't depend on  $\omega_1$



Two-photon transition dipole moment between two electronic states  $i, j$

$$S_e^{i \rightarrow j} = \sum_{\alpha, k} \left[ \frac{\langle \phi_i | \mu_\alpha^{\omega_1} | \phi_k \rangle \langle \phi_k | \mu_\beta^{\omega_2} | \phi_j \rangle}{\omega_k - \omega_1} + \frac{\langle \phi_i | \mu_\beta^{\omega_2} | \phi_k \rangle \langle \phi_k | \mu_\alpha^{\omega_1} | \phi_j \rangle}{\omega_k - \omega_2} \right]$$



$k$  all intermediate states between  $i$  and  $j$   
 $\omega_1$  energy of photon 1;  $\omega_2$  energy of photon 2

$\omega_1 + \omega_2 = \text{total transition energy}$



# Absorption probability: oscillator strength



## Estimation of band intensity: oscillator strength (AREA BENEATH THE BAND)

By analogy to classical theory: the oscillator strength  $f$  measures the number of electron oscillating around its equilibrium position when the molecule is placed in a radiation field. It is adimensional (au)

Theoretical  $f = \frac{2}{3} \Delta E |M(Q_0)|^2$

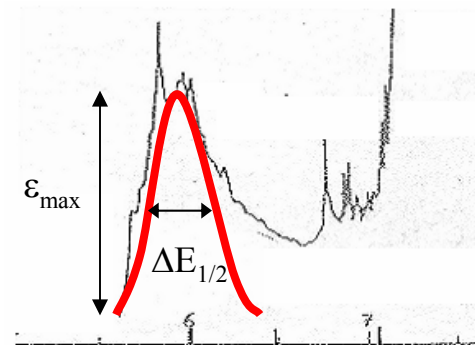
$$M(Q_0)^2 = M_x^2 + M_y^2 + M_z^2$$

$$f_{v'v''} = \frac{2}{3} \Delta E_{v'v''} |M_{v'v''}|^2$$

$f$  between vibrational states

Experimental  $f = 4.32 \cdot 10^{-9} F \int_{\nu_1}^{\nu_2} \epsilon d\nu$

$F \sim 1$  (refraction factor)  
Basic approach: band half-width



Thomas-Reiche-Kuhn rule:  $\sum_e f = N_e$ , that is  $\sum f = 1$  per electron

$$\int_{\nu_1}^{\nu_2} \epsilon d\nu = \epsilon_{\max} \Delta E_{1/2}$$

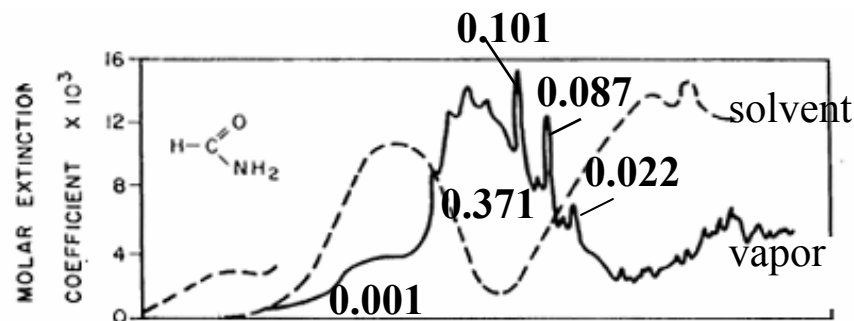
### Values of $f$ :

Valence transitions  $\pi\pi^*$  (0.01-1.0)

Valence transitions  $n\pi^*, \sigma\sigma^*$  (0.001-0.1)

Rydberg transitions (0.0001-0.05)

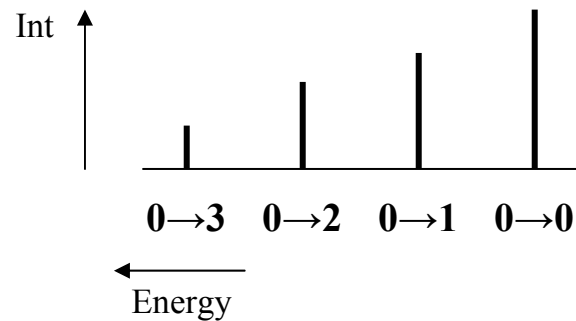
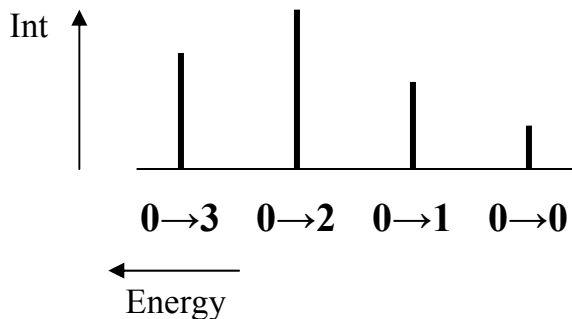
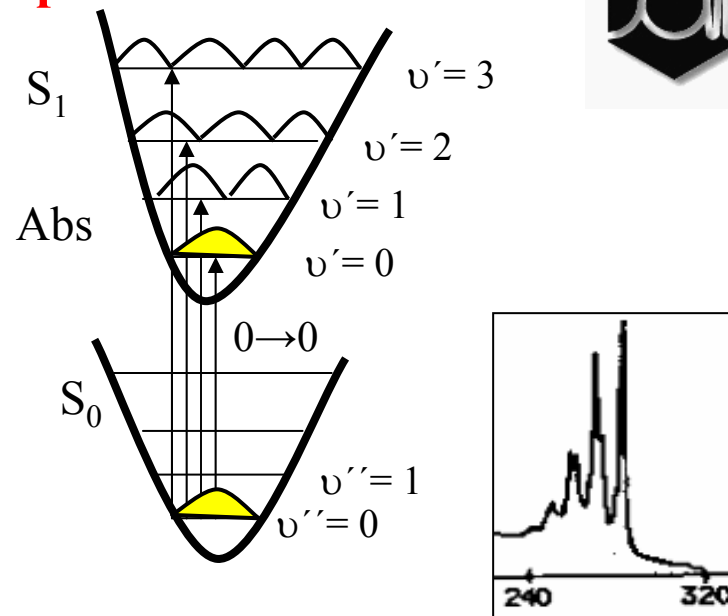
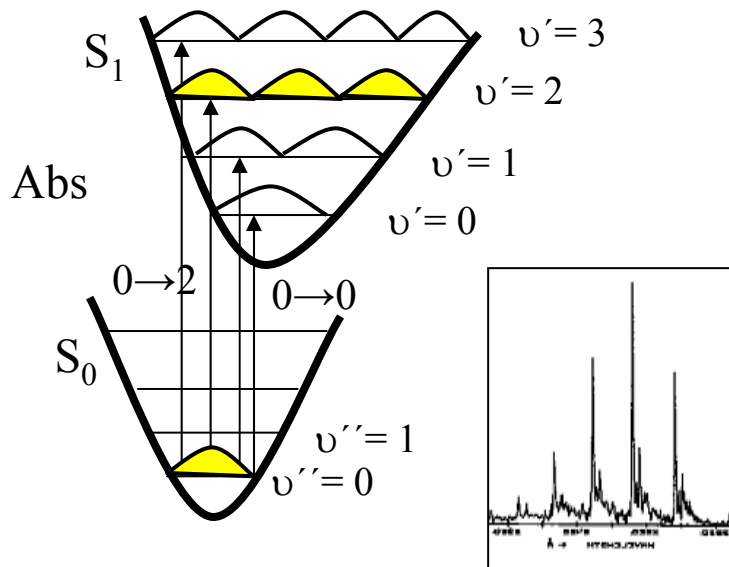
Is  $f$  enough? → vibrational profiles







# Vibrational profiles: Vibrational Transition Dipole Moments



***Herzberg-Teller expansion for the vibrational transition moment***

$$M_{gi,fj} = M(Q_0) \langle \chi_i(Q) | \chi_j(Q) \rangle + \sum_k \left( \frac{\partial M(Q)}{\partial Q_k} \right)_{Q_0} \langle \chi_i(Q) | Q_k | \chi_j(Q) \rangle + \dots$$



## Vibrational profiles: Vibrational Transition Dipole Moments



$$M_{gi, fj} = M(Q_0) \langle \chi_i(Q) | \chi_j(Q) \rangle + \sum_k \left( \frac{\partial M(Q)}{\partial Q_k} \right)_{Q_0} \langle \chi_i(Q) | Q_k | \chi_j(Q) \rangle + \dots$$

zeroth order  
*Condon approximation*

first order and higher (one is typically enough)  
*Herzberg-Teller coupling terms*

$$M_{gf}(Q_0) = \langle \varphi_g | \mu | \varphi_f \rangle$$

Electronic transition moments (TDM) between  $g$  and  $f$

$$\langle \chi_i(Q) | \chi_j(Q) \rangle$$

Vibrational overlap

$$\langle \chi_i(Q) | \chi_j(Q) \rangle^2: \text{Franck-Condon factors (FC)}$$

*HT couplings*

Geometrical dependence of TDM and FC

Requirements for calculation with MOLCAS:

- Optimize initial and final states (CASSCF) and compute electronic energies (CASPT2)
- Compute Hessians (polyat) or higher (small molec.) (MCKINLEY, MCLR)
- Compute TDM derivatives (RASSI, MCLR)
- Solve Schrödinger vibrat. eq. and compute vib. osc. strengths and Boltzmann state pop. (MULA)



# Energy relaxation processes: kinetic constants ( $k$ ) and radiative lifetimes ( $\tau$ )



$$k_{decay} = k_{radiative} + k_{nonradiative}$$

$$\frac{1}{\tau_i} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{norad}}$$

Quantum yield  $\phi$ : ratio total relaxation time ( $\tau_F, \tau_P$ ) and radiative time ( $\tau_{rad}$ )

$$\phi_i = \frac{\tau_i}{\tau_{rad}} = \frac{k_{rad}}{k_i}$$

$i = F = \text{Fluorescence}$   $\tau_{rad} \approx 10^{-9}-10^{-7}$  s

$i = P = \text{Phosphorescence}$   $\tau_{rad} \approx 10^{-3}-10^2$  s

$\phi \approx 1$  intense emission  
 $\phi \approx 0$  mostly nonradiative processes

Theoretical calculation:  $\tau_{rad}$  from  $M(Q_0)$  y  $T_0$   
 $\tau_{total}$  from reaction dynamics

## Radiative relaxation: Fermi's Golden Rule

**Radiative lifetime:**  $\tau_i = 1/k_i$

For the radiative emission the rate constant  $k_{Frad}$  or  $k_{Prad}$  is related to the Einstein coefficient for spontaneous emission  $A_{if}$ . Its inverse is the radiative lifetime:

$$k_r = A_{if} = \frac{1}{\tau_{rad}} = 2.142005 \cdot 10^{10} M(Q_0)^2 E^3$$

$M(Q_0)$ , TDM (transition dipole moment)  
 $E$ , emission energy ( $T_0$ )

### Strickler-Berg relationships

For phosphorescence, TDM is computed for states including Spin-orbit coupling:

$$M_e^{i \rightarrow j} = \sum_{\alpha=x,y,z} \langle \phi_i | \mu_\alpha | \phi_j \rangle$$

$$\theta_S = {}^1\psi + \sum_k a_k {}^3\psi_k + \sum_l a_l {}^1\psi_l$$

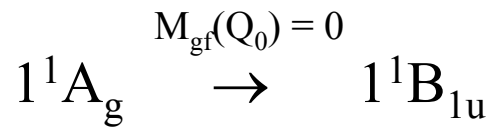
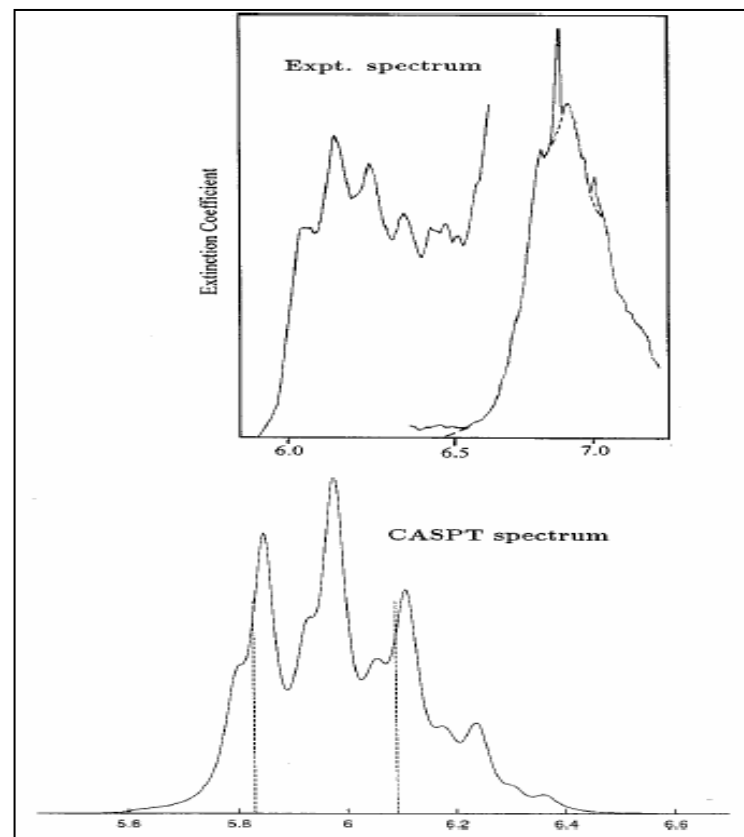
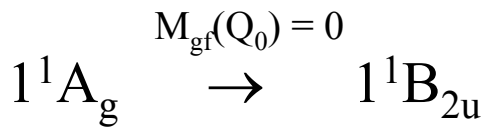
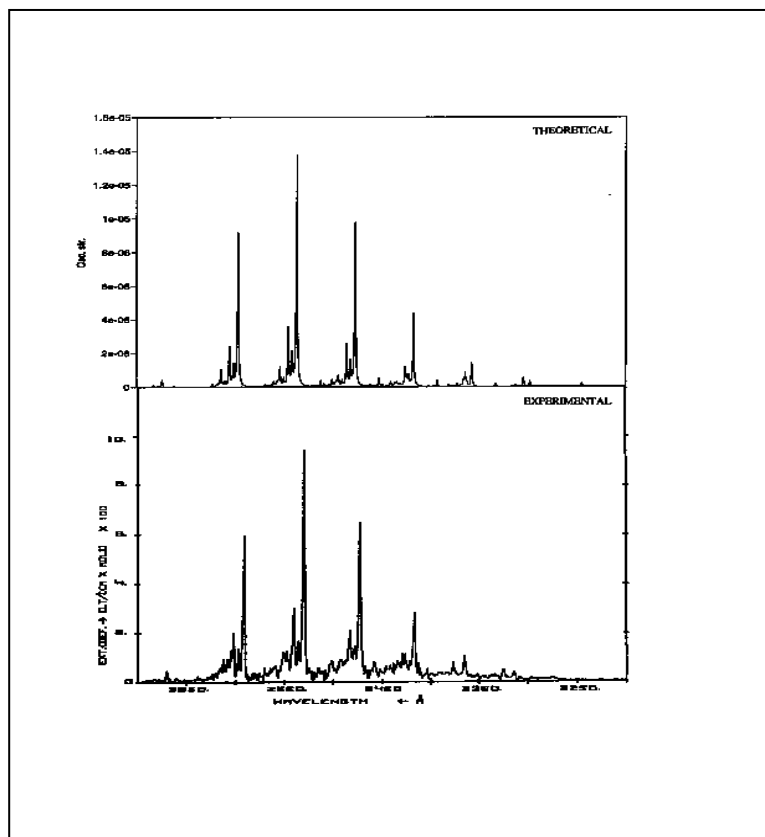
$$\theta_T = {}^3\psi + \sum_l a_l {}^1\psi_l + \sum_k a_k {}^3\psi_k$$



# Vibrational profiles of electronic transitions



## Two low-lying transitions in the spectrum of benzene





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## *Types of electronic transitions*



Valence states:

Compact, large dynamical correlation effects, large valence basis sets needed

Rydberg states:

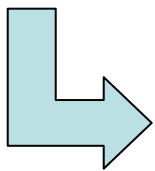
Diffuse, perturbable, near-degeneracy correlation effects, specific basis sets

Anionic resonances (shape, core-excited):

Large and diffuse basis needed, stabilization of the results

Multipole-bound anionic states:

Extremely diffuse states, small bond energies, specific basis functions



Quantum-chemical methods for excited states  
(just the most commonly used)

Ab initio

Time-Dependent Density Functional



## *Ab initio methods*



- Variationals
- Perturbationals
- Variational-perturbation techniques
- Others

Hartree-Fock Method:

$$\Psi_0 = |\chi_1 \chi_2 \cdots \chi_a \chi_b \cdots \chi_N\rangle$$

$$E_0 = \frac{\langle \Psi_0 | H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}$$

No  
Elect. Correl.

CI Method (*Configuration Interaction*):

$$\Phi_0 = C_0 |\Psi_0\rangle + C_S |\Psi_S\rangle + C_D |\Psi_D\rangle + C_T |\Psi_T\rangle + C_Q |\Psi_Q\rangle + \dots$$

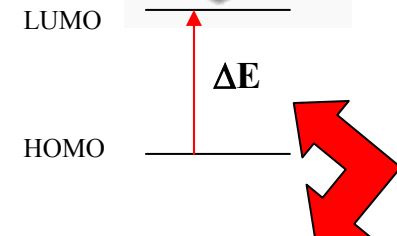
$$\varepsilon_0 = \frac{\langle \Phi_0 | H | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle}$$

Electronic Correlation Energy:

$$E_{\text{CORR}} = \varepsilon_0 - E_0$$



# *Ab initio methods for excited states*



## **ΔSCF methods**

Excitation energy in the HF/SCF model:  $\Delta E_{\text{orbital}} (E_{\text{LUMO}} - E_{\text{HOMO}}, \text{etc.})$

Electronic correlation energy

What's left? Multiconfigurational description of the transitions (within the MO model a transition must be described by many excitation among the orbitals)

- **Single-configuration methods:**

*Applicability:* near closed-shell ground-state geometry, nondegenerated situations

- CIS (CI-Singles)
- Propagators (Response methods): RPA, SOPPA
- Coupled-Cluster Methods: EOM-CCSD(T), CC3, SAC-CI

- **Multi-configuration methods:**

*Applicability:* all type of situations

- Multireference CI: MRCI, MR-SC<sup>2</sup>CI
- Multireference perturbation: MR-PT (CASPT2, ...)
- Multireference Coupled-Cluster: MRCC





# *Ab initio methods for excited states*



## Multi-reference methods:

$\Psi_0 = |\chi_1 \chi_2 \cdots \chi_a \chi_b \cdots \chi_N\rangle$  Single configurational reference (Hartree-Fock, HF)

$$\Psi_0 = \sum_i c_i \Phi_i = c_0 |\varphi_0\rangle + \sum_i c_{iS} |\varphi_{iS}\rangle + \sum_i c_{iD} |\varphi_{iD}\rangle + \dots$$

Multiconfigurational reference (MCSCF), where  $\Phi_i = |\chi_2 \cdots \chi_a \chi_b \cdots \chi_N \chi_i\rangle, \dots$

HF: variationally optimized MOs ( $\chi_i$ )

MCSCF: variationally optimized MOs ( $\chi_i$ ) and CI coefficients ( $c_i$ )



Static or nondynamic correlation included  
Quasi-degenerated configurations

CASSCF, Complete Active Space SCF implies the selection of an space of active electrons and orbitals

On top of the reference:

CI up to the desired excitation, MRCI: MRCI(SD), MRCI(SDTQ)+Q, etc

MP up to the desired perturbation order, MPMP: CASPT2, CASPT3, MR-MP2, etc

CC up to the desired excitation order: MRCC: MRCCSD, MRCCSD(T)



Dynamic correlation



# *Ab initio methods for excited states*



## Multi-reference methods:

$$\Psi_0 = \sum_i c_i \Phi_i = c_0 |\varphi_0\rangle + \sum_i c_{iS} |\varphi_{iS}\rangle + \sum_i c_{iD} |\varphi_{iD}\rangle + \dots$$

So far, with MCSCF (in general CASSCF) the electronic correlation named static is included, and one set of optimized MOs and other set of optimized CI coefficients per state are obtained

On top of this reference other methods compute the *dynamical correlation*:

Singles, doubles, triples... CI excitations: MRCI(SDT), ...

Non size-extensive method (Davidson correction +Q, SC<sup>2</sup>CI)

Only applicable to very small systems (otherwise the errors reach several eVs)

Coupled-cluster excitations CC with triples: MRCC(SDT)...

Very expensive methods still under development (avoid the errors of CCSD(T))

Only applicable to small systems

Moller-Plesset Perturbations MRMP: CASPT2, CASPT3, etc

Generality and precision in medium-large-size systems

Problems in the selection of the reference (size, intruder states, etc): LS techniques, etc

Non-orthogonality of the states

***Applicability:*** no restrictions, except limitations in the selection of the reference  
(all type of states, degeneracies, conical intersections, etc)



# *Ab initio methods for excited states*



## CASPT2

### Multiconfigurational Second-Order Perturbation Theory

$$(\hat{H}^{(0)} - E^{(0)})\Psi^{(k)} = -\hat{H}'\Psi^{(k-1)} + \sum_{j=0}^{k-1} E^{(k-j)}\Psi^{(j)}$$
$$E^{(2)} = \langle \Psi^{(0)} | \hat{H}' | \Psi^{(1)} \rangle$$
$$\Psi^{(1)} = (1 - |\Psi^{(0)}\rangle\langle\Psi^{(0)}|)(\hat{H}^{(0)} - E^{(0)})^{-1}(E^{(1)} - \hat{H}')|\Psi^{(0)}\rangle$$

CASPT2: standard  $H_0$  Hamiltonian

CASPT2(g1,g2,IPEA): modified  $H_0$  for open-shell cases

LS-CASPT2: Level-Shift CASPT2 (standard or imaginary), addition of a penalty parameter to avoid weakly perturbing states

MS-CASPT2: Multi-State CASPT2, multiconfigurational multidimensional methods, includes the coupling of several electronic states through an effective Hamiltonian. Recommended for valence-Rydberg mixings and crossing regions



# *Ab initio methods for excited states*



## MS-CASPT2

HF      CASSCF

↓      ↓

MP2      CASPT2

$$\mathbf{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \cong \begin{pmatrix} E_1 & \frac{H_{12} + H_{21}}{2} \\ \frac{H_{12} + H_{21}}{2} & E_2 \end{pmatrix} = \begin{pmatrix} E_1 & \Delta \\ \Delta & E_2 \end{pmatrix}$$

Wave functions corrected to first-order. Non orthogonal

$$E_{(+)} = E + \Delta \quad \Psi_{(+)} = \frac{1}{\sqrt{2}} (\Psi_1 + \Psi_2)$$

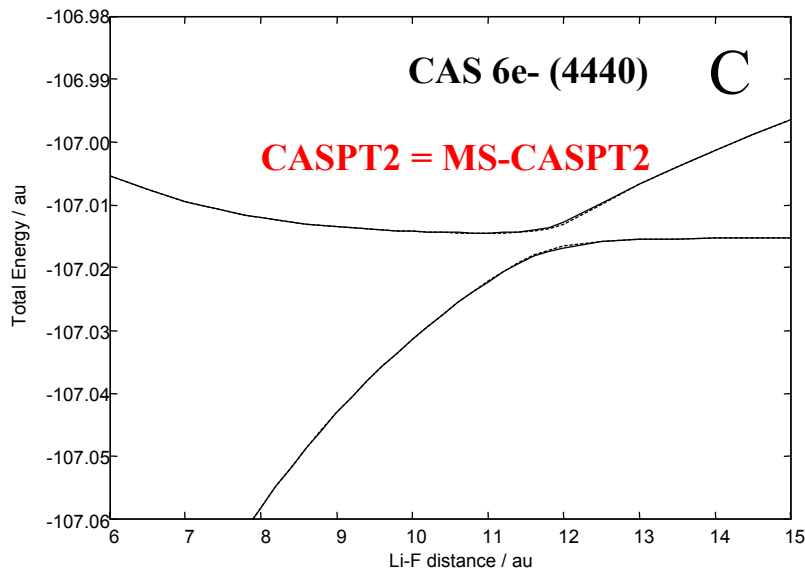
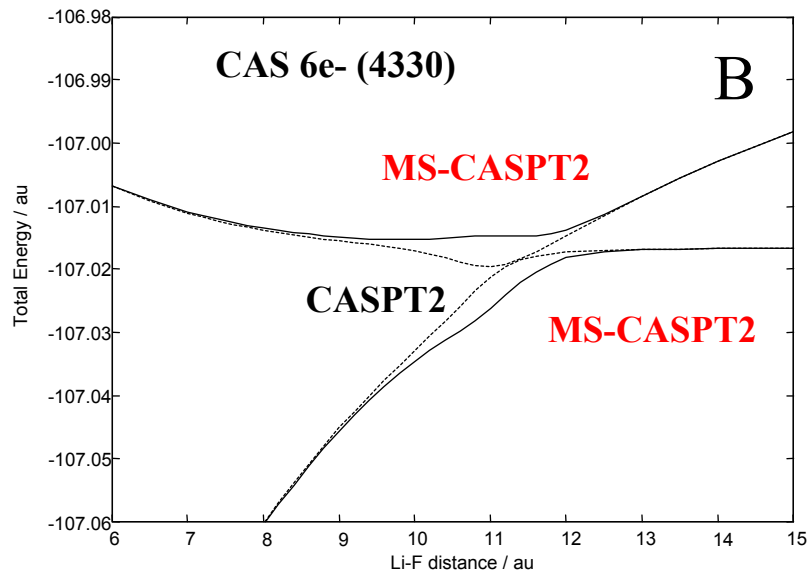
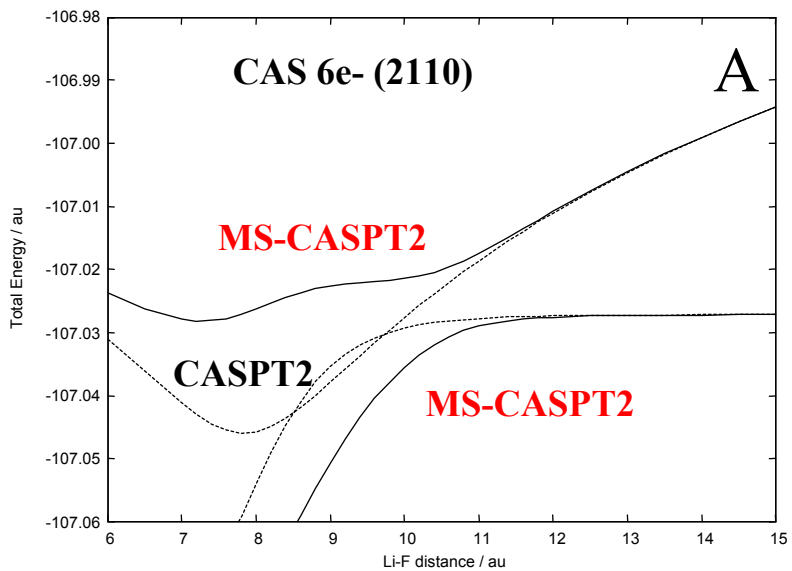
$$E_{(-)} = E - \Delta \quad \Psi_{(-)} = \frac{1}{\sqrt{2}} (\Psi_1 - \Psi_2)$$



# Ab initio methods for excited states



## MS-CASPT2



LiF: avoided crossing between  $^1\Sigma_g^+$  states

L. Serrano-Andrés, M. Merchán, R. Lindh, JCP (2005)

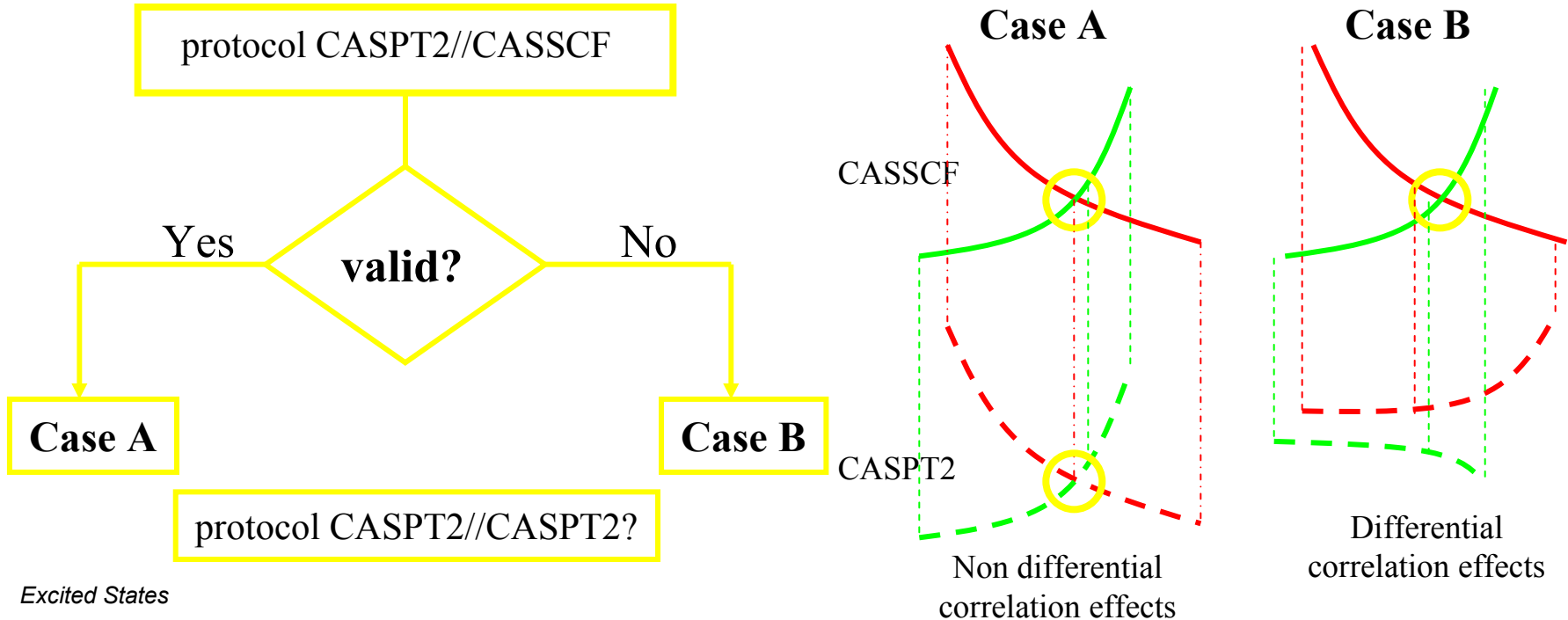


# The problem of the differential correlation energy

## Ex. Location of conical intersections



- Geometry determinations (locating singular points):  
CASSCF: reference, multiconfigurational descriptions (static correlation)  
Minima, TS (Transition State), MEP (Minimum Energy Paths),  
MECP (Minimal Energy Crossing Points), and CI (Conical Intersections)
- Point calculations at the optimized geometries:  
CASPT2 (or MRCI): treatment of dynamical correlation  $\Rightarrow$  quantity





# One-electron basis sets for excited states



Building of Molecular Orbitals (MO):

Numerically: network of points

Analytically: expansion of one-electron functions

Type of expansion:

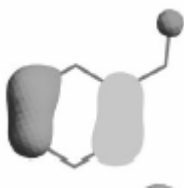
Single center: not flexible enough in molecules (specific use: *Rydberg, bond functions*)

Polycentric: on each atom (AIM, *atoms-in-molecules expansion*)

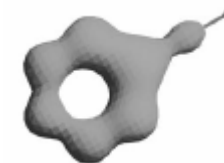
Type of functions:

Elipsoidals, hydrogenoids, Slater, etc: not practical

Gaussians (GTF, *Gaussian-type functions*)



$$g^{a,b,c}(x,y,z;\zeta,r_A) = N_A N_B N_C (x-x_A)^a (y-y_A)^b (z-z_A)^c \exp(-\zeta |r-r_A|^2)$$



$N$  normalization factors;  $a, b, c$ , positive integers changing with the type of functions

The function is centered on atom  $A$  in  $r_A$ , and it is combined with others in the remaining atoms

$\zeta$ , positive orbital exponent, represents the extension of the represented orbital

It is more efficient to use atom-centered functions as linear combination of primitive cartesian gaussians:

$$\text{OA: } \chi_r^{a,b,c}(x,y,z; r_A) = \sum c_i g^{a,b,c}(x,y,z;\zeta,r_A)$$

$$\text{OM: } \Psi_j(\mathbf{r}) = \sum a_i \chi_r^{a,b,c}(x,y,z; r_A)$$



# One-electron basis sets for excited states



## Which conditions make a basis set optimal?

- (a) Simple evaluation of the Hamiltonian elements
  - (b) Fast convergence
  - (c) Systematic extension until completion
- Numerical stability  
Simple differentiability  
Fast integration

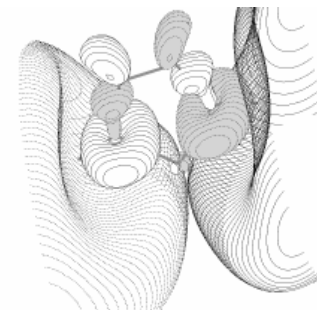
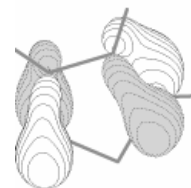
## Do the excited states require one-electron basis sets different than those used for the ground state?

- (a) Basis sets must deal simultaneously with states of different nature
- (b) Some situations require specific functions of diffuse character

## Características generales:

- (a) Polarization functions required in any method including correlation energies  
6-311G\*\* (low-lying states), cc-pVDZ (at least), ANO 4s3p1d (better)
- (b) Addition of diffuse functions to deal with diffuse states, Rydberg or anionics  
6-311+G\*\*, aug-cc-pVDZ, ANO 4s3p1d+1s1p1d, ANO 4s(1s)3p(1p)1d(1d)

Typical $\zeta$ exponents:	core orbitals	20 (C) – 400 (Zn)
	valence orbitals	0.5 (C) - 5 (Zn)
	polarization orbitals	0.1-0.01
	Rydberg orbitals	0.01-0.001







# One-electron basis sets for excited states



## Differences of the one-electron basis sets:

### Pople et al. type: STO-3G, 4-31G, 6-311G\*\*, 6-311++G\*\*,...

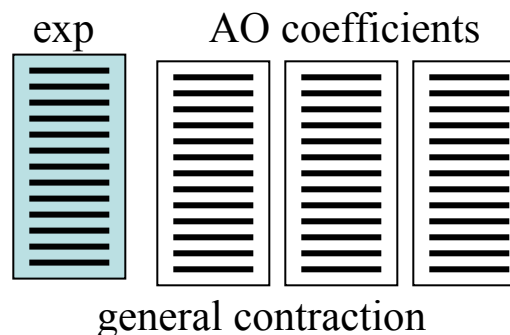
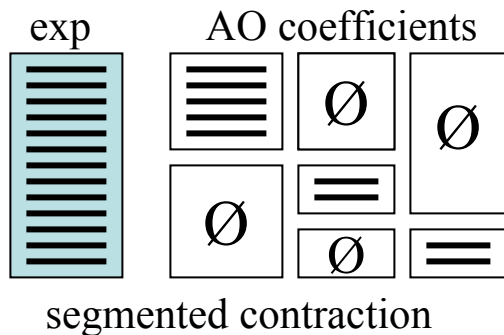
optimized with methods without correlation energy for atoms in ground states  
segmented contraction  
less accurate than others, useful for ground state and low-lying excited states

### Dunning correlation-consistent (cc) type: cc-pVDZ, cc-pVTZ, aug-cc-pVDZ,...

optimized with methods with correlation energy for atoms in ground states  
segmented contraction  
good for ground states, and for valence and Rydberg when adding diffuse functions (*aug*)

### ANO (Atomic Natural Orbitals) type: 3s2p1d, 4s3p1d, 5s4p2d1f+1s1p1d,...

optimized with methods with correlation energy for atoms in different situations:  
ground and excited atomic states, cations, anions, electric fields, ...  
general contraction  
good in all cases, more flexible with less functions, and high accuracy. More expensive too







# Time-Dependent DFT methods for excited states



## Time Dependent DFT

- TD Kohn-Sham Method

$$\left(-\frac{1}{2}\nabla^2 + V_S[\rho(t)]\right)\phi_i(t) = i\frac{\partial\phi_i(t)}{\partial t} \quad \rho(t) = \sum_i n_i |\phi_i(t)|^2$$

$$V_S(t) = V_N + \int \frac{\rho(2,t)}{r_{12}} d\tau_2 + V_{XC}[\rho(t)] + V_{ext}(t)$$

**Time Dependent  
External Perturbation**

- Linear or Non-Linear Response

$$\mu(t) = \int \alpha(t-t')E(t')dt'$$

**Dynamic Polarisability**

$$\alpha(\omega) = \sum_n \frac{|\langle\Psi_0|\mu|\Psi_n\rangle|^2}{\omega - \Delta E_{n0}}$$

**Excitation Energies  
Oscillator Strengths**



# Time-Dependent DFT methods for excited states



Ex.: C<sub>70</sub> excitation energies in eV

State	LSDA	B3LYP	RPA	CIS	Experiment
<sup>1</sup> E <sub>1</sub> '	1.87	2.22	3.48	3.67	1.9
<sup>3</sup> E <sub>1</sub> '	1.74	1.77		2.16	1.4-1.6

G. E. Scuseria et al. J. Chem. Phys. 109, 8218 (1998)

Most employed method: B3LYP

21 molecules: average deviation 0.4 eV

J. Fabian et al. Theochem. 594, 41 (2002)



# Failures in multiconfigurational situations



## CC methods

	EOM-CCSD	(T)	(T)
$2^1A_g$ state of butadiene:	1.0	0.7	0.5 eV with respect to CASPT2
$2^1A_g$ state of hexatriene:	1.2	0.5(CC3)	with experiment
$2^1A_1$ state of ozone:	5-6 eV		with experiment
$1^1E_g$ state of ferrocene:	1.5 eV		with experiment
Some states of $C_2$ :	2.05	0.86(CC3)	0.41(CCSDT) with FCI

Improvements: CR-CCSD(T)

## TD-DFT methods

MC situations, S-T gaps, diradicals (>8% doubly or higher excitations): deviations from experiment (eV)

$1^1\Pi_u$ state of $C_3$	0.76	$1^1A_g - 1^3B_{1u}$ in ethene	-0.79
$2^1A_1$ state of ozone	5.55	$1^1A_g - 1^3B_u$ in butadiene	-0.96
$2^1A_g$ state of butadiene	1.44	$1^1A_g - 1^3B_u$ in hexatriene	-1.29
$2^1E_{2g}$ state of benzene	1.86	$1^1A_g - 1^3B_{2u}$ in naphthalene	-0.95
Lowest states of pyridine	0.5-0.8	$1^1A_1 (C_{2v}) - 1^1A_{1g} (D_{2h})$ in hexatriene	1.45
$3^1A_1$ state of azulene	0.63		
$1^1B_{3u}$ state of naphthalene	0.70		

Improvements: KSDFT/MRCI (Grimme) L. Serrano-Andrés and M. Merchán, *Theochem*, 729, 109-118, 2005.



## Other failures of Time-Dependent DFT methods



Collapse of the excitation energies upon extending the  $\pi$  space: *deviations from experiment (eV)*

	Exp(eV)	TD-DFT
$1^1A_g - 1^3B_u$ gap in polyacetylene	1.3-1.7	<0 (B3LYP, n=100)

$1^1B_u$  ( $L_a$ ) ionic states in polyenes

	SVWN	BP96	B3LYP
butadiene	0.40	0.50	0.33
hexatriene	0.48	0.55	0.31
octatetraene	0.60	0.68	0.43
decapentaene	0.70	0.78	0.50

( $L_a$ ) ionic states in linear acenes (naphthalene,...)

number of rings	BP96	B3LYP	number of rings	BP96	B3LYP
2	0.55	0.28	5	0.74	0.48
3	0.65	0.35	6	0.80	0.53
4	0.71	0.45	8	0.90	0.64

Charge-transfer (CT) situations:

	HCTH	BP96	B3LYP	
CT ( $n\pi^*$ ) in polypeptides	-3.25	-3.39	-1.70	eV with CASPT2
CT ( $\pi\pi^*$ ) in polypeptides	-1.76	-1.87	-0.86	eV with CASPT2
CT $2^1T_{1u}$ state of $Cr(CO)_6$			-0.66	eV from experiment



## Quantum Chemistry for excited states (2006)



The selection of the method and the basis set requires to decide the goal of the calculation and the degree of precision needed to solve the problem:

*Qualitative problems in large systems, trends, low precision in general:*

Calibrated **TD-DFT** (DFT/MRCI [Grimme]).

Known deficiencies:

*underestimation* of charge transfers, zwitterionic states in  $\pi$  delocalized systems, triplet states

*overestimation* of multiconfigurational states, singlet states in general

Expected precision: 0.3-0.5 eV, although the error can reach several eV. (fast methods)

*Quantitative problems in small systems, high precision:*

**Coupled-cluster methods including triples** (CCSD(T): EOM-CC ó CC3). (MRCI for small systems)

Known deficiencies:

*overestimation* of multiconfigurational states

*collapse* in dissociations and low precision in many open-shell systems

Expected precision: 0.1-0.2 eV, except in the mentioned cases. (expensive methods)

*Quantitative problems in small to medium systems, enough precision in photochemistry:*

**Multiconfigurational methods, essentially perturbative** (CASPT2, MR-MP2, MS-CASPT2)

Known deficiencies:

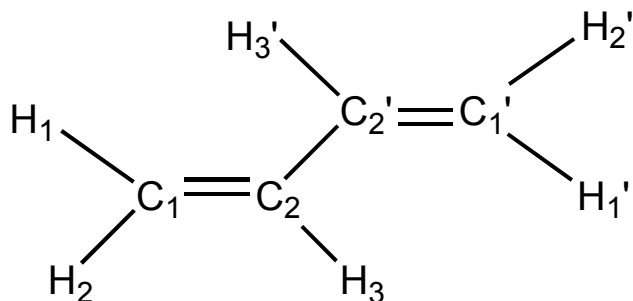
existence of intruder states because of a poor reference (small active spaces)

require more expertise, although they are the only general methods, dealing with degeneracies.

Expected precision: 0.2-0.3 eV. (difficult methods)



# Structure of molecular orbitals of *trans*-1,3-butadiene



$$4 \text{ C x } 6e^- = 24 e^-$$

$$6 \text{ H x } 1e^- = 6 e^-$$

---


$$30 e^-$$

15 MO occupied<sup>2</sup>

$$4 \text{ C x } 5 \text{ AO} = 20 \text{ AO}$$

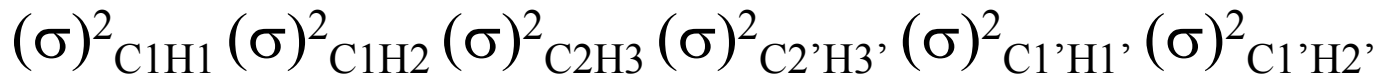
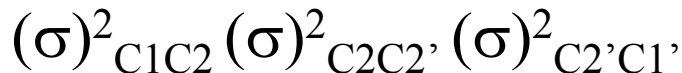
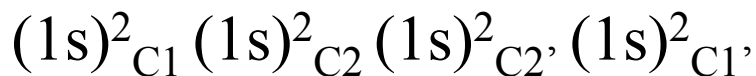
$$6 \text{ H x } 1 \text{ AO} = 6 \text{ AO}$$

---

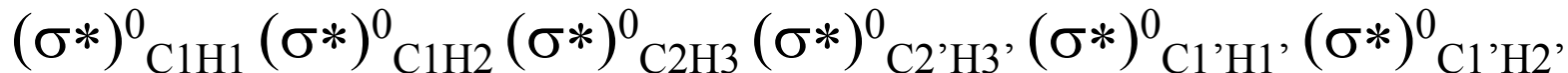
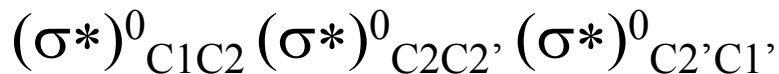
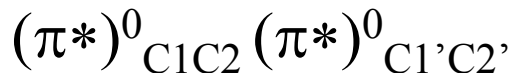
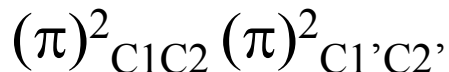

$$26 \text{ AO}$$

26 MO valence

core



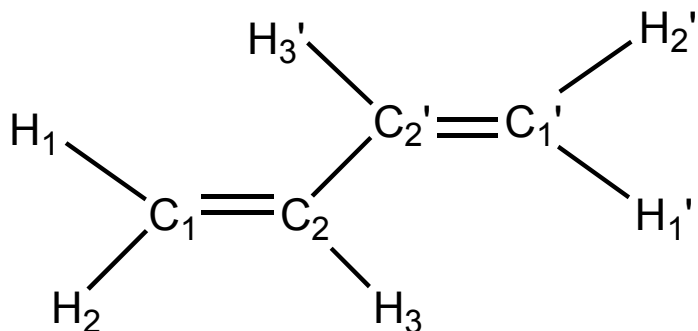
valence







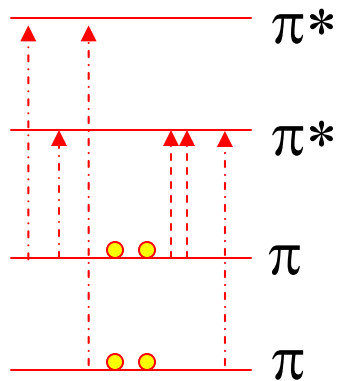
# Classification of molecular orbitals of *trans*-1,3-butadiene within $C_{2h}$ point group



- Using group theory
- Using character table

Use SCF program  
in MOLCAS

		$a_g$	$b_u$	$b_g$	$a_u$	
core	$(1s)_C$	2	2	0	0	
	$(\sigma)_{CC}$	2	1	0	0	
valence	$(\sigma)_{CH}$	3	3	0	0	
	$(\pi)_{CC}$	0	0	1	1	CAS $\pi\pi^*$
	$(\pi^*)_{CC}$	0	0	1	1	
	$(\sigma^*)_{CC}$	2	1	0	0	
	$(\sigma^*)_{CH}$	3	3	0	0	





# Electronic transitions: neutral or cationic systems



Core-Valence: from core orbitals to valence ( $1s \rightarrow \pi^*$ ,  $1s \rightarrow \sigma^*$ )

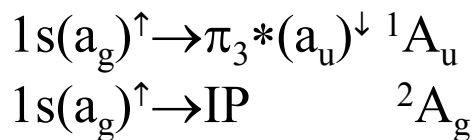
Valence: among valence orbitals ( $\pi \rightarrow \pi^*$ ,  $\sigma \rightarrow \sigma^*$ ,  $\pi \rightarrow \sigma^*$ ,  $\sigma \rightarrow \pi^*$ )

Rydberg: from core or valence orbitals to diffuse Rydberg-type orbitals (spdf..)

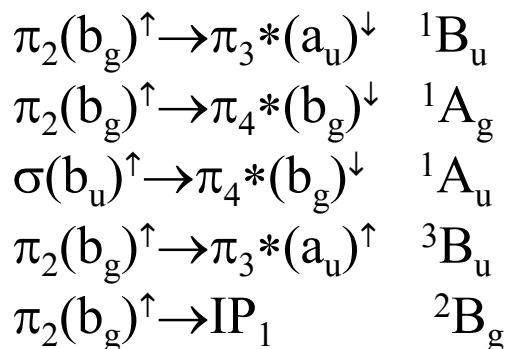
$$(1s)^2 \dots (\sigma)^2 (\pi_1)^2 (\pi_2)^2 \equiv 1^1 A_g \text{ ground state}$$

## Core

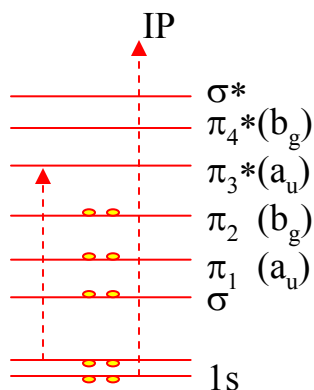
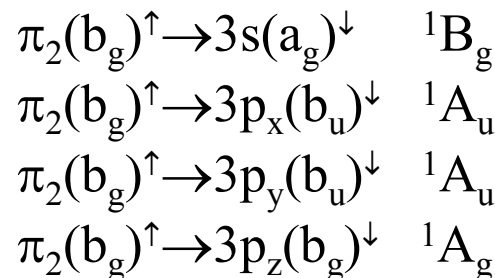
(inner-shell valence)



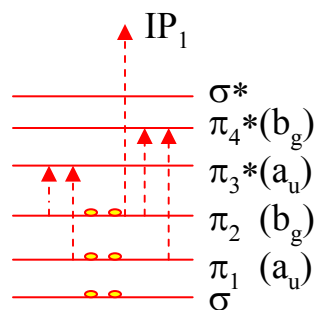
## Valence



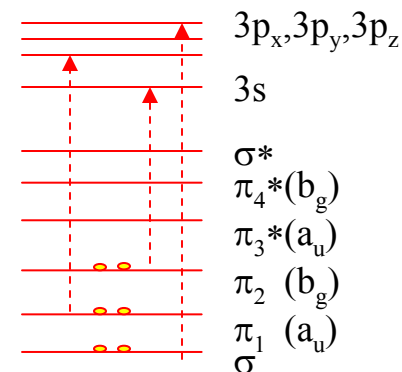
## Rydberg



Auger, X-Ray: 8-10000 eV  
Excited States



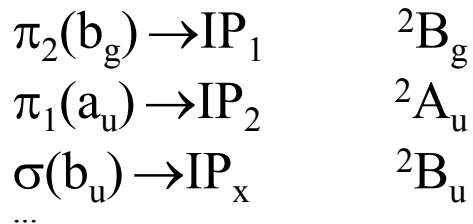
Visible/UV: 0.5-8 eV



UV: 5-IPs eV



IP = Ionization  
Potential



## Rydberg states and orbitals



$$(1s)^2 \dots (\sigma)^2 (\pi_1)^2 (\pi_2)^2 \equiv 1^1 A_g \text{ ground state}$$

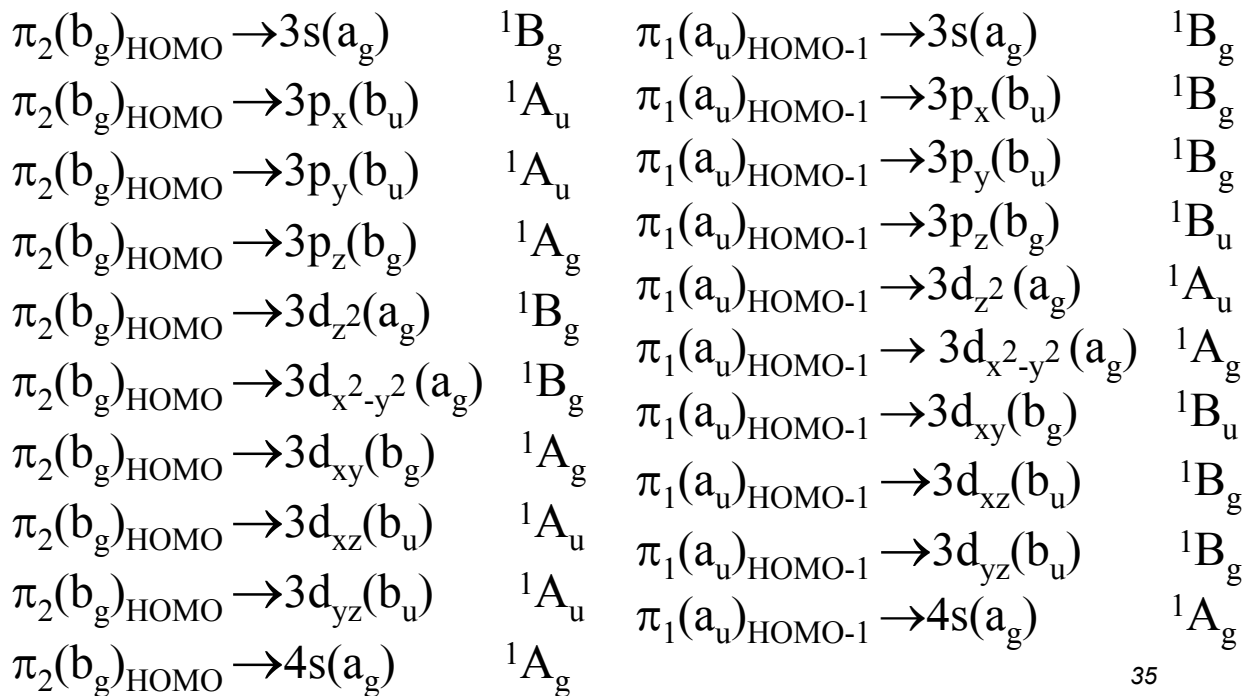
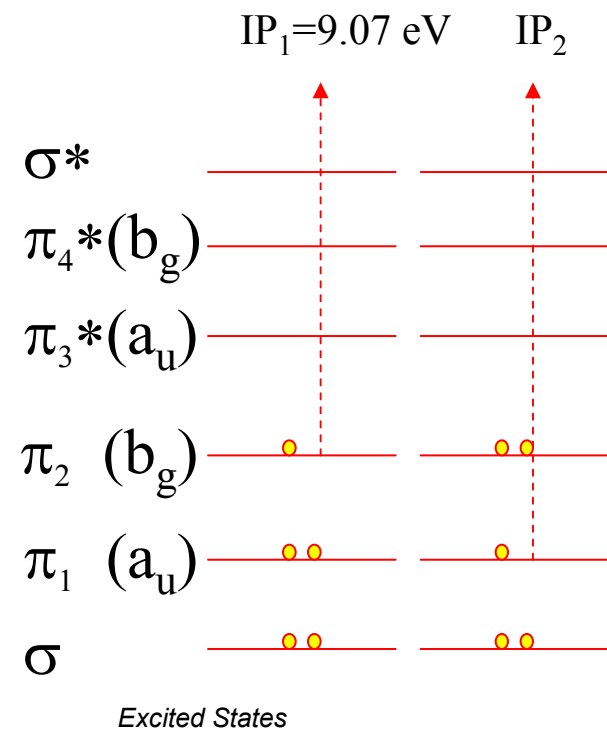
Each one-electron promotion from a molecular orbital generates a convergent series fitting more or less to the equation of the hydrogenoid term:

$$h\nu = IP_i - \frac{R}{(n - \delta)^2}$$

R = Rydberg constant

n = main quantum number for the  
Rydberg orbital (valence+1)

$\delta$  = quantum defect

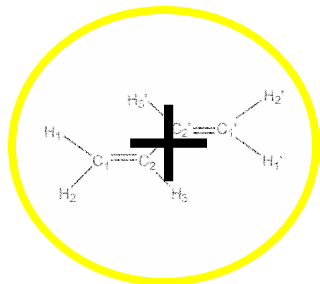




# Rydberg states and orbitals



## What are the Rydberg states? Where they come from?



- When ionizing the molecule (IP) it becomes positively charged
- There are series of excited states in which the electron is bound by cation-electron electrostatic long-distance interactions
- The series start at an energy corresponding to the state  $MO \rightarrow ns$  and converge to each of the ionization potentials

## Which are the properties of Rydberg orbitals and states compared to valence?

- Diffuse orbitals and states, able to represent the electron far from the molecule ( $N e^{-\alpha r^2}$ ,  $\alpha \ll 1$ )

First cartesian moment (dipole moment):  $\langle \phi_1 | x, y, z | \phi_1 \rangle \rightarrow$  charge distribution

Second cartesian moment:  $\sum \langle \phi_1 | x^2, y^2, z^2, xy, xz, yz | \phi_1 \rangle = \langle r^2 \rangle \rightarrow$  spatial extension

$$\langle r^2 \rangle_{\text{Rydberg}} \gg \langle r^2 \rangle_{\text{valence}}$$

Ex. Rydberg 300 au vs valence 50 au

Orbital: much larger than the molecule

- Quantum defect  $\delta$  measures the deviation with the ideal hydrogenoid behavior ( $\delta=0$ ) and represents the degree of penetrability: ns (0.95-1.1), np (0.6-0.8), nd (0.15-(-0.05))

- Are degenerated 3p, 3d, 4p, 4d, 4f, etc?

$$h\nu = IP_i - \frac{R}{(n - \delta)^2}$$

No, because of the molecular asymmetry and the different penetrability

- Low intensity transitions as compared to valence. Decreases when n increases
- Highly perturbed by external effects: solvent, fields, etc.

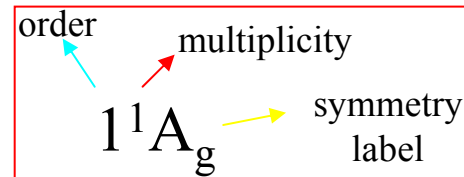


# Nomenclature of electronic states



There is no consensus to name the states. All have advantages, inconvenients, and may be useful

Group theory	Kasha	Mulliken	Platt	Enumerative
$1^1A_g$	-	N	-	$S_0$
$1^1B_u$	$1(\pi\pi^*)$	$V_1$	$1L_a, 1B_b$	$S_1$
$2^1A_u$	$1(n\pi^*)$	W	-	$S_2$
$2^3B_g$	$1(n\pi^*)$	T	-	$T_2$



S: singlet  
T: triplet  
D: doblet

Group theory: The state is described by the behavior of its wave function under the symmetry operations of its point group. It is the most systematic approach

Enumerative: Useful in low-symmetry systems or far from equilibrium situations

Kasha: Traditional. Useful to unsaturated organic molecules

Mulliken: Traditional. Developed to polyienes and hidrocarbons

Platt: Traditional. Developed for acenes. Useful for low-lying states

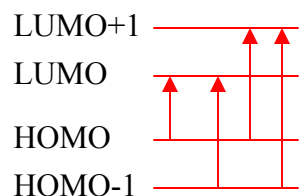
Excitation	State	Properties
$H \rightarrow L$	$L_a$	high $\mu$ , large Stokes
$H-1 \rightarrow L$	$- L_b$	low $\mu$ , weak trans.
$H \rightarrow L+1$	$+ B_b$	intense transition
$H-1 \rightarrow L+1$	$B_a$	medium trans.

How a transition is represented?

As it is an excitation, an arrow is used:

Traditional: State 2  $\leftarrow$  State 1

Nowadays: State 1  $\rightarrow$  State 2



Excited States



## Selection rules: electronic transition moments



Ex. Electronic Transition Moment (TDM o M): transition  $1^1A_g(\phi_1) \rightarrow 1^1B_u(\phi_2)$

$$\langle \phi_1 | \mu_x | \phi_2 \rangle \equiv 1^1A_g \otimes x(b_u) \otimes 1^1B_u \equiv a_g \neq 0 \text{ allowed}$$

$$\langle \phi_1 | \mu_y | \phi_2 \rangle \equiv 1^1A_g \otimes y(b_u) \otimes 1^1B_u \equiv a_g \neq 0 \text{ allowed}$$

$$\langle \phi_1 | \mu_z | \phi_2 \rangle \equiv 1^1A_g \otimes z(b_g) \otimes 1^1B_u \equiv a_u = 0 \text{ forbidden}$$



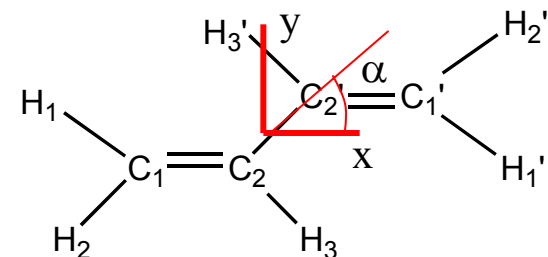
Integral vanishes if does not belong to the totally symmetric representation

Ex. Electronic Transition Moment (TDM o M): transition  $1^1A_g(\phi_1) \rightarrow 2^1A_g(\phi_3)$

$$\langle \phi_1 | \mu_x | \phi_3 \rangle \equiv 1^1A_g \otimes x(b_u) \otimes 2^1A_g \equiv b_u = 0 \text{ forbidden}$$

$$\langle \phi_1 | \mu_y | \phi_3 \rangle \equiv 1^1A_g \otimes y(b_u) \otimes 2^1A_g \equiv b_u = 0 \text{ forbidden}$$

$$\langle \phi_1 | \mu_z | \phi_3 \rangle \equiv 1^1A_g \otimes z(b_g) \otimes 2^1A_g \equiv b_g = 0 \text{ forbidden}$$



*RASSI program in MOLCAS computes states interactions: TDM, etc.*



# *Excited States*

## **1.- Excited States. Spectroscopy, Photophysics and Photochemistry:**

*Processes and magnitudes: what to compute*

## **2.- Quantum-Chemical Methods for Excited States:**

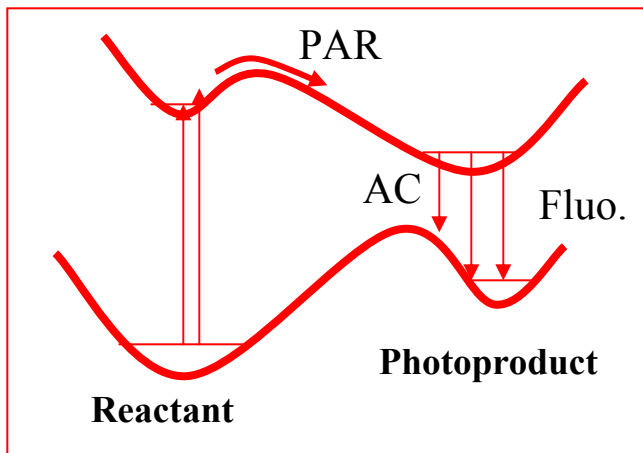
*Potential energy surfaces (PES) and transition probabilities:  
how to compute them. CASSCF, CASPT2, CASSI*

## **3.- Towards a Nonadiabatic Photochemistry:**

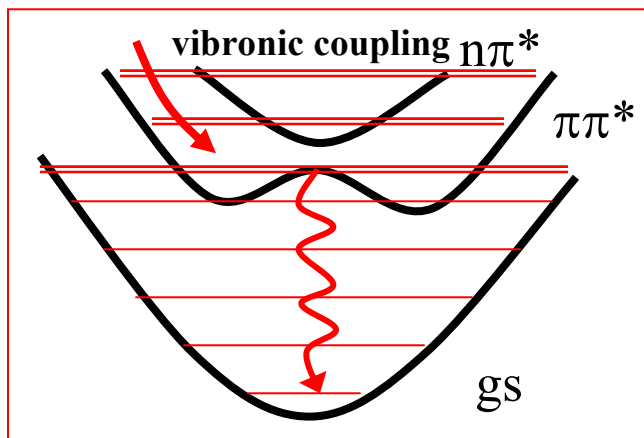
*PES MEPs, crossings, and conical intersections*



# Classical Photochemistry



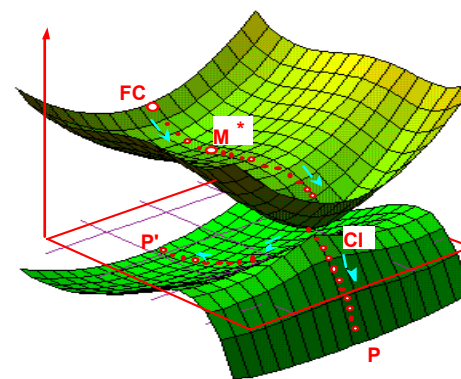
Slow photoreactivity  
(Van der Lugt & Oosterhof, 1969)



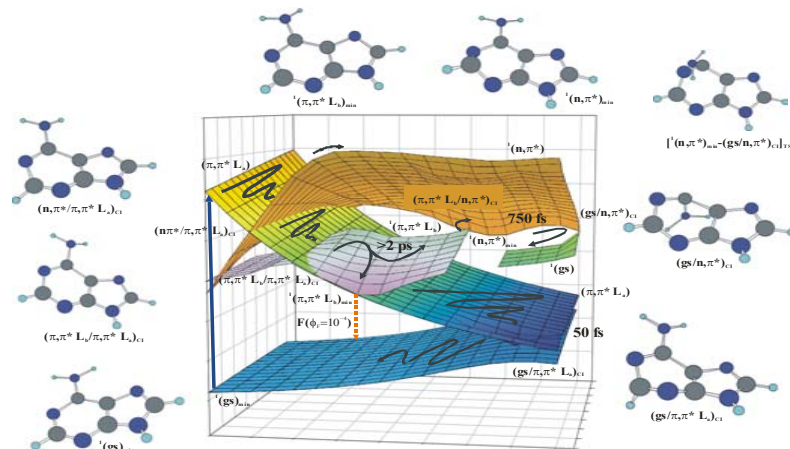
Emission quenching  
“Proximity effect” (Lim, 1977)

# Modern Photochemistry

Quantum-chemical calculation  
Subpicosecond experiments



Conical Intersection concept  
(Teller (1969), Zimmerman, Michl,  
Robb, Olivucci, Bernardi, Domcke, Yarkony, ('90s)...)



Ultrafast photoreactivity

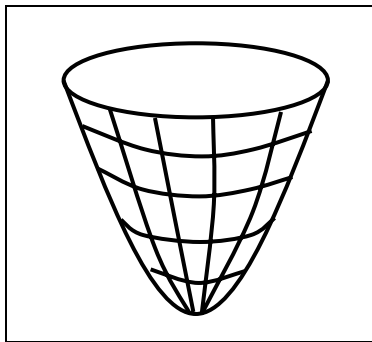




# PES and critical points



## Energy minima:



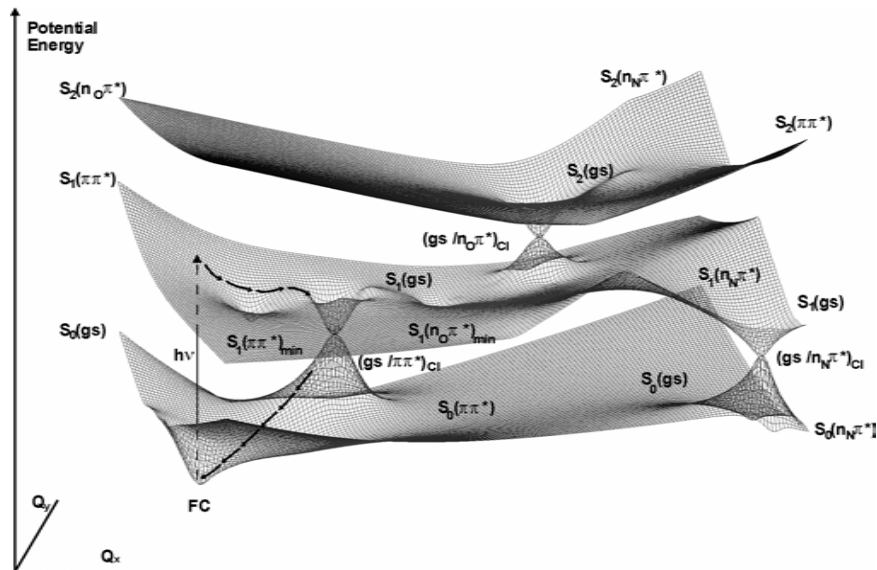
$$g_i(R) = \frac{dU(R)}{dR_i} = 0 \quad \forall dR_i \quad \text{All}$$

$$h_{ij}(R) = \frac{d^2U(R)}{dR_i dR_j} > 0 \quad \forall dR_i dR_j \quad \text{All}$$

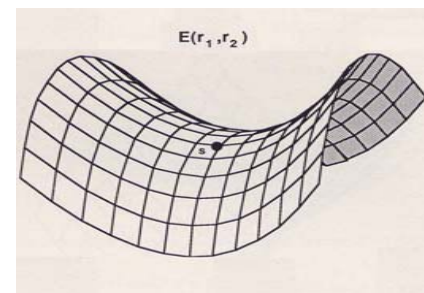
$R_i$ : degrees of freedom

$g_i$ : gradient

$h_i$ : hessian

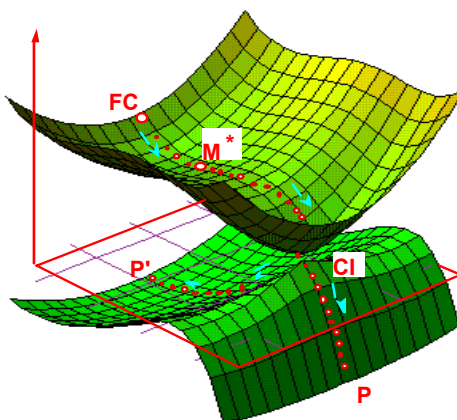


## Saddle points (TS):



$$g_i(R) = \frac{dU(R)}{dR_i} = 0 \quad \forall dR_i \quad \text{All}$$

$$h_{ij}(R) = \frac{d^2U(R)}{dR_i dR_j} \quad \text{at least one} < 0$$



## Conical Intersection:

$$x_1 = \frac{d(E_1 - E_2)}{dQ}$$

$$x_2 = \left\langle \Psi_1 \left| \frac{\partial \Psi_2}{\partial Q} \right. \right\rangle$$



# Breaking the Born-Oppenheimer approach



$$[\hat{T}_e + \hat{T}_N + \hat{T}_N' - V(R_N) - E_{rv,m}] \chi_{rv,n'}^m(R_N) = - \sum_{n' \neq n} C_{nn'} \chi_{rv,n'}^m(R_N)$$

$$V(R_N) = E_{e,n}(R_N) + C_{nn}$$

**Adiabatic approximations:** neglecting NACME (Non-adiabatic coupling matrix elements)

Born-Oppenheimer:  $C_{nn} = C_{nn'} = 0$

Born-Huang:  $C_{nn} \neq 0, C_{nn'} = 0$

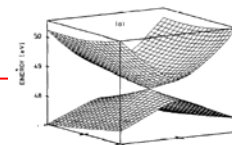
$$C_{12} = \left\langle \Psi_1 \left| \frac{\partial}{\partial Q} \right| \Psi_2 \right\rangle$$

Essentially, what means to neglect NACMEs?

$$\psi_{rve,m}(r_e, R_N) = \sum_{n'} \chi_{rv,n'}^m(R_N) \phi_{e,n'}(r_e; R_N)$$

Representing the total wave function for a single rovibronic states requires the linear combination of ALL (infinite basis) states. Neglecting the contribution of the other states to each state we ignore the coupling among them

**When this approach will fail? When states are close enough:  
avoided crossing and conical intersections**



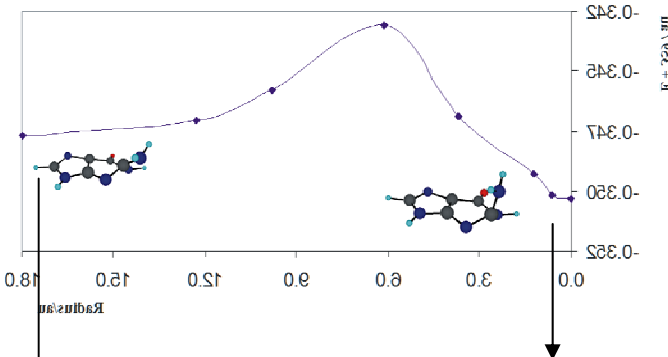
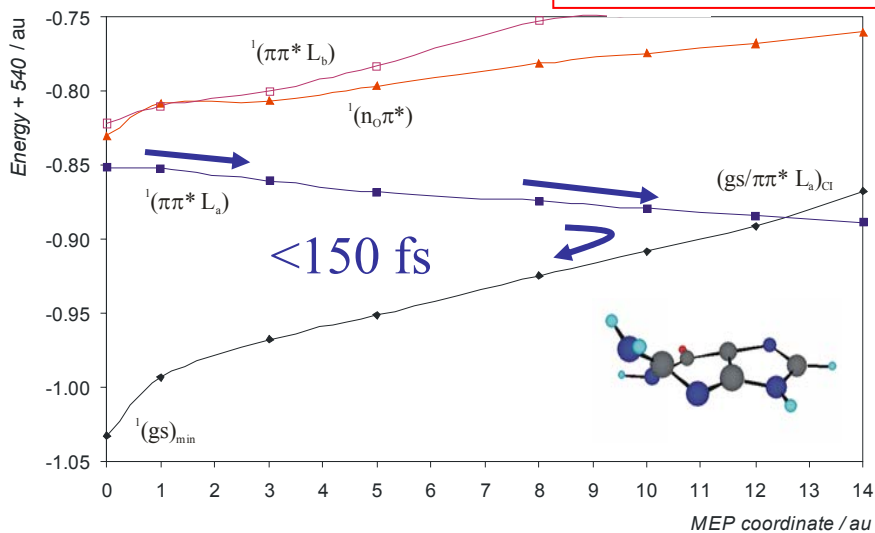


# Mapping PES



**Minimal Energy Reaction Paths (MEP)**  
**Minimal Energy Crossing Point (MECP)**  
**Conical Intersection (CI)**  
**Singlet Triplet Crossing (STC)**

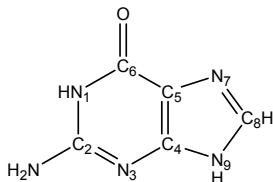
**See Lecture 5**



**CI at the end of the MEP**

**Minimum Energy CI (MECI)**

**9H-Guanine**





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