

# Electronically Excited States

Absorption of light (photon) by molecule

Wavelength range – visible and UV (ca. 800 – 200 nm)

Molecule accepts the energy from the electromagnetic field

→ **promoted to an electronically excited state**

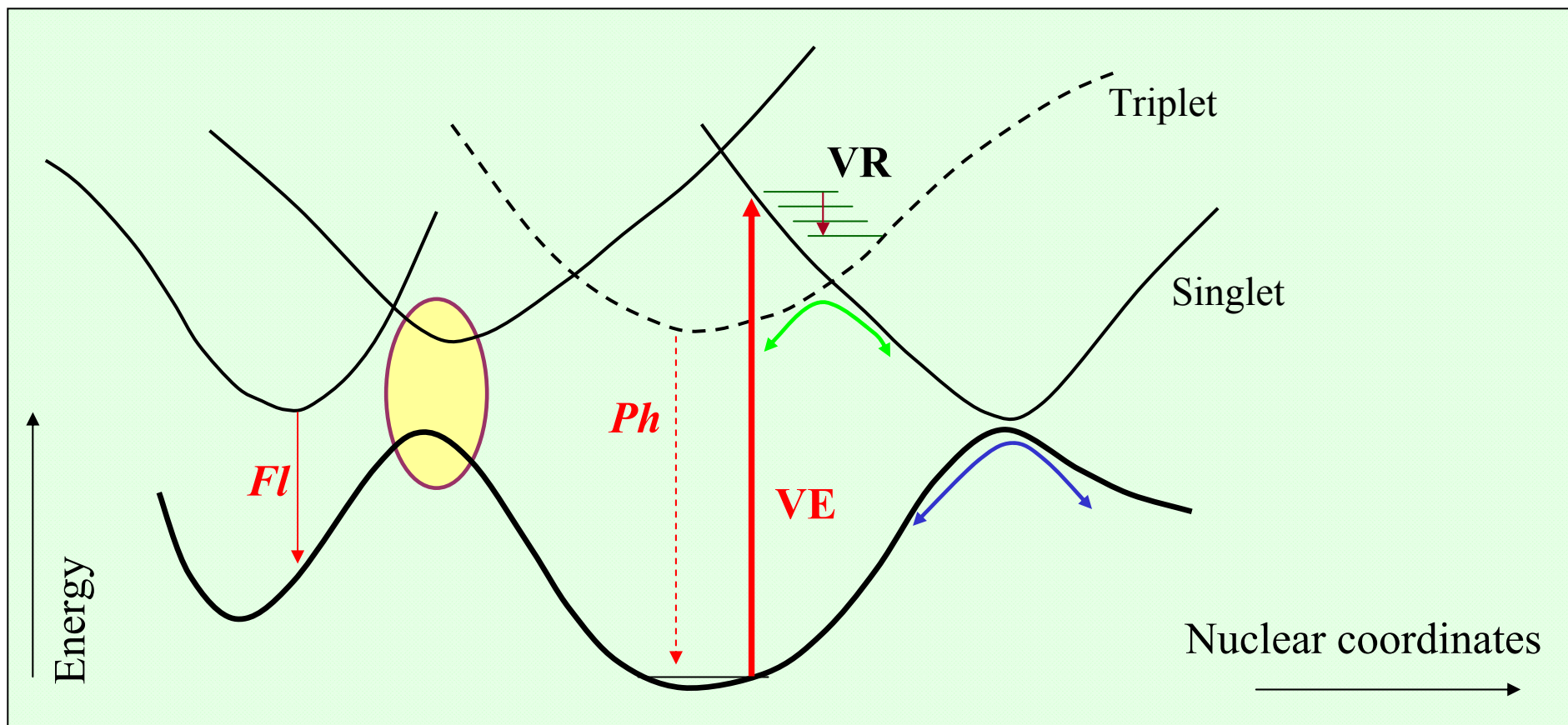
➤ **Spectroscopy**

➤ **Photophysical Processes** – to states of the same species

➤ **Photochemical Processes** – to different chemical species

## *What problems do we have to solve*

- ✓ What is the character of excited states in the vertical region. Are these states accessible via absorption of light (optically allowed)?
- ✓ What is the character of PES?
- ✓ How does the system relax and get rid of the energy excess?
- ✓ Are new products formed?
- ✓ How fast is the relaxation proces?
- ✓ How does the environment influence the excited state behavior
- ✓ How does the excitation interact with other chromophores in the system?

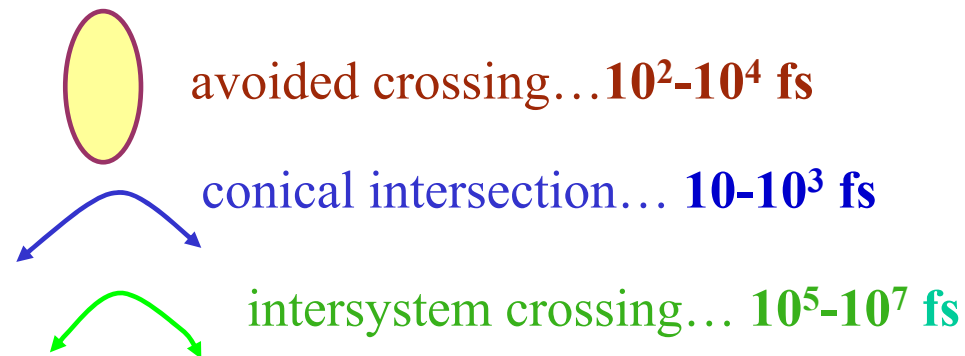


**VE** vertical excitation...1 fs

**VR** vibrational relaxation...  $10^2$ - $10^5$  fs

**Fl** fluorescence ...  $10^6$ - $10^8$  fs

**Ph** phosphorescence ...  $10^{12}$ - $10^{17}$  fs



## What do we have to calculate?

- Calculate excitation energies in the vertical region
- Characterize excited state minima
- Characterize conical intersections
- Calculate the reaction paths between the critical points

Ab initio orbital methods for determining the wave functions and energies of molecules in their ground states are well characterized - large systems can be treated in standard calculation

A comparable situation does not exist for molecules in their electronically excited states

# Description of the system:

## Atomic Orbitals $\rightarrow$ Molecular Orbitals

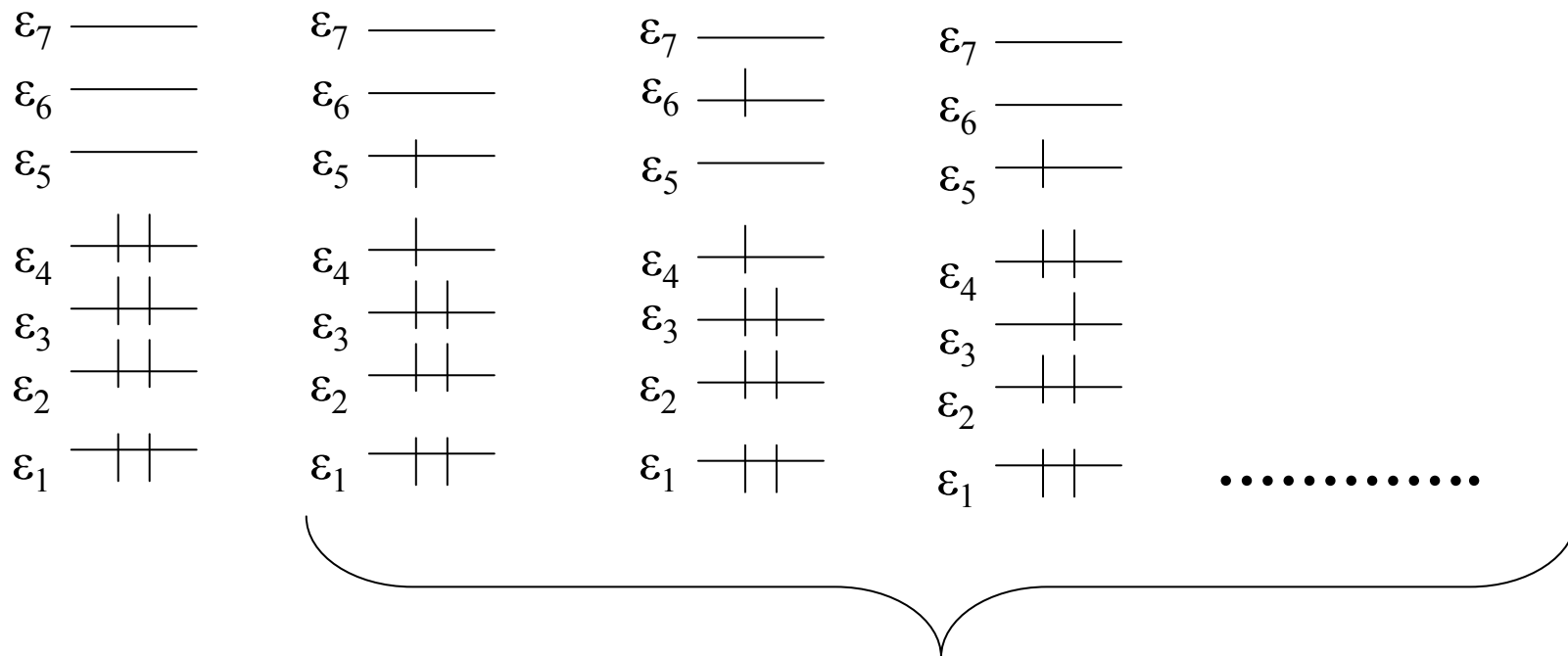
- all electrons assigned to MO's to satisfy Pauli principle (max. 2 electrons per MO)  $\Rightarrow$  occupied and virtual orbitals
- requirement of antisymmetry with respect to interchange  $\Rightarrow$  configuration in the form of Slater determinant

## To represent a state of interest - reference configuration

$\varepsilon_7$  ———  
 $\varepsilon_6$  ———  
 $\varepsilon_5$  ———

$\Psi_0$  – ground state – according to Aufbau principle  
orbitals occupied according to their energy

HF - not exact solution, electron does not move in the averaged field of other electrons, it moves in the instantaneous field of other electrons  $\Rightarrow$  dynamic correlations



Depending on the character of the state all of these configurations can contribute => they need to be included in order to describe the state of the interested: multiconfigurational description => nondynamic correlation

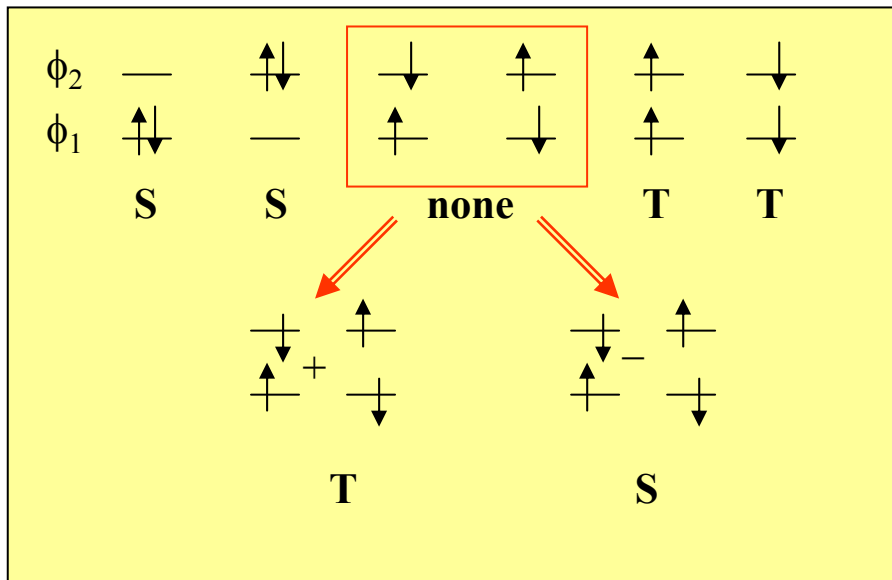
# 1. Solving of the problem of correlation energy - essential in calculations of excited states

Static electron correlation - the wavefunction is composed of strongly interacting electronic configurations

Dynamic electron correlation - necessary in order to obtain accurate qualitative results and correct ordering of states

# 2. Using more flexible basis set than for the ground state - especially true for Rydberg and ionic states

## 2 electrons in two orbitals



=> three singlet states and one triplet state  
(three-fold degenerate)

Relative energies of states:

- depends on orbital separation
  - triplet below singlet (exchange integral)
- Each electron configuration described with Slater determinant:

(notation: subscript -  $\alpha$  el., superscript -  $\beta$  el.)

$$\Psi_1^1 = \det |\phi_1(1)\alpha(1)\phi_1(2)\beta(2)|$$

$$\Psi_2^2 = \det |\phi_2(1)\alpha(1)\phi_2(2)\beta(2)|$$

$$\left. \begin{aligned} \Psi_1^2 &= \det |\phi_1(1)\alpha(1)\phi_2(2)\beta(2)| \\ \Psi_2^1 &= \det |\phi_1(1)\beta(1)\phi_2(2)\alpha(2)| \end{aligned} \right\} \text{“-” combination}$$

Example ethylene, “twisted” ethylene: modeling the orbital separation

two orbitals have different symmetry - first two states can mix together but not with OSS

$$\Phi_{cov}^S = C_1\Psi_1^1 - C_2\Psi_2^2$$

$$\Phi_{ion}^S = C_1\Psi_1^1 + C_2\Psi_2^2$$

$$\Phi_{oss}^S = \frac{1}{\sqrt{2}}(\Psi_1^2 - \Psi_2^1)$$

$$\Phi_{Ms=1}^T = \Psi_{12}$$

For large orbital separation  $C_2$  vanishes  
in first eq. and  $C_1$  vanishes in second eq.

$$\begin{aligned} \phi_2 &\equiv \pi^* = \frac{1}{\sqrt{2}}(L - R) \\ \phi_1 &\equiv \pi = \frac{1}{\sqrt{2}}(L + R) \end{aligned}$$

Individual states can be characterized with respect to “covalent” and “ionic” configurations.



In ethylene  $\pi$  orbitals are combinations of “L” and “R” atomic orbitals.  
Individual states can be characterized with respect to “covalent” and “ionic” configurations.

$$\phi_2 \equiv \pi^* = \frac{1}{\sqrt{2}}(L - R)$$

$$\phi_1 \equiv \pi = \frac{1}{\sqrt{2}}(L + R)$$

$$\begin{aligned} \Phi_{\text{cov}}^S &= C_1\Psi_1^1 - C_2\Psi_2^2 = \frac{1}{\sqrt{2}}[C_1|\pi\alpha\pi\beta\rangle - C_2|\pi^*\alpha\pi^*\beta\rangle] \\ &= \frac{1}{2\sqrt{2}}[C_1(|L\alpha L\beta\rangle + |L\alpha R\beta\rangle + |R\alpha L\beta\rangle + |R\alpha R\beta\rangle) - C_2(|L\alpha L\beta\rangle - |L\alpha R\beta\rangle - |R\alpha L\beta\rangle + |R\alpha R\beta\rangle)] = \dots \text{deg} \dots \\ &= \frac{1}{\sqrt{2}}[|L\alpha R\beta\rangle + |R\alpha L\beta\rangle] \end{aligned}$$

$$\Phi_{\text{ion}}^S = C_1\Psi_1^1 + C_2\Psi_2^2 = \dots = \frac{1}{\sqrt{2}}[|L\alpha L\beta\rangle + |R\alpha R\beta\rangle]$$

$$\begin{aligned} \Phi_{\text{oss}}^S &= \frac{1}{\sqrt{2}}(\Psi_1^2 - \Psi_2^1) = \frac{1}{\sqrt{2}}[|\pi\alpha\pi^*\beta\rangle - |\pi\beta\pi^*\alpha\rangle] \\ &= \frac{1}{2\sqrt{2}}[|L\alpha L\beta\rangle - |R\alpha R\beta\rangle + |R\alpha L\beta\rangle - |L\alpha R\beta\rangle - |L\beta L\alpha\rangle + |R\beta R\alpha\rangle - |R\beta L\alpha\rangle + |L\beta R\alpha\rangle] = \dots \text{deg} \dots \\ &= \frac{1}{\sqrt{2}}[|L\alpha L\beta\rangle - |R\beta R\alpha\rangle] \end{aligned}$$

$$\Phi_{M_S=1}^T = \Psi_{12} = |\pi\alpha\pi^*\alpha\rangle = \frac{1}{2}[|L\alpha L\alpha\rangle - |R\alpha R\alpha\rangle + |R\alpha L\alpha\rangle - |L\alpha R\alpha\rangle] = |R\alpha L\alpha\rangle$$

## Comparison of MCSCF and HF

- HF:
1. guess for density matrix  $P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^*$
  2. construction of  $v^{\text{HF}}(r_i)$  and Fock operator
  3. solve one-electron equation to determine MO
  3. MO used to construct a new density matrix

Process iterated until the density matrix is below a certain threshold

MCSCF:

Before the actual MCSCF calculations a set of trial molecular orbitals is necessary – taken from the previous SCF calculations or MCSCF orbitals from a previous calculations (in case of calculations of energy on PES)

Two sets of iterations  $\Psi_{\text{MCSCF}} = \sum_I C_I \Psi_I$

$$\Psi_I \dots SD \dots \psi_i(r) = \sum_{\mu} C_{\mu i} \phi_{\mu}(r)$$

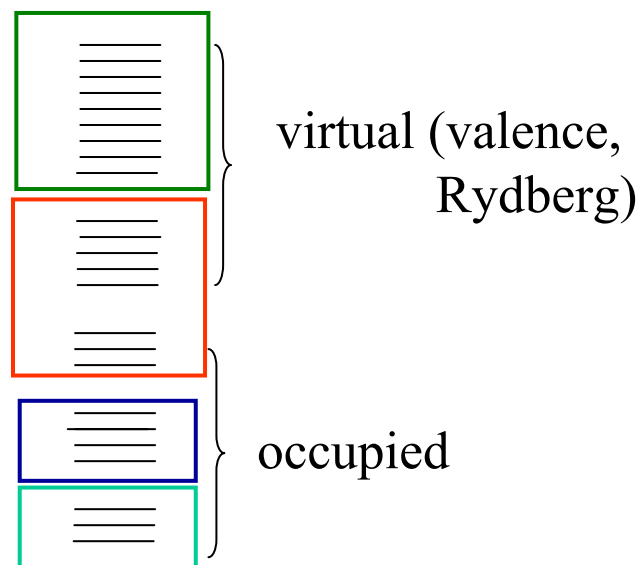
For each set of  $C_I$  solve LCAO  $C_{\mu i}$  (micro-iteration)

# MCSCF - “Multi-configurational self-consistent field”

## Define:

- A set of electronic configurations (Slater determinants)  $\Rightarrow$  **active space**
- The selection of an active space is crucial
- Due to the lack of the dynamical correlation, MCSCF method does not always give the correct ordering of the states – Rydberg states bellow the valence state – more states for MCSCF calculations in the calculations of spectra both, valence and Rydberg orbitals have to be included in the active space
- Near degeneracy of the states of the same symmetry – optimization of the wavefunction for a particular state can result in root flipping **state averaging** – several states with chosen weight on each state

# Defining the wavefunction in MCSCF



**Secondary** kept virtual

**Active** all possible occupation respecting the symmetry and spin

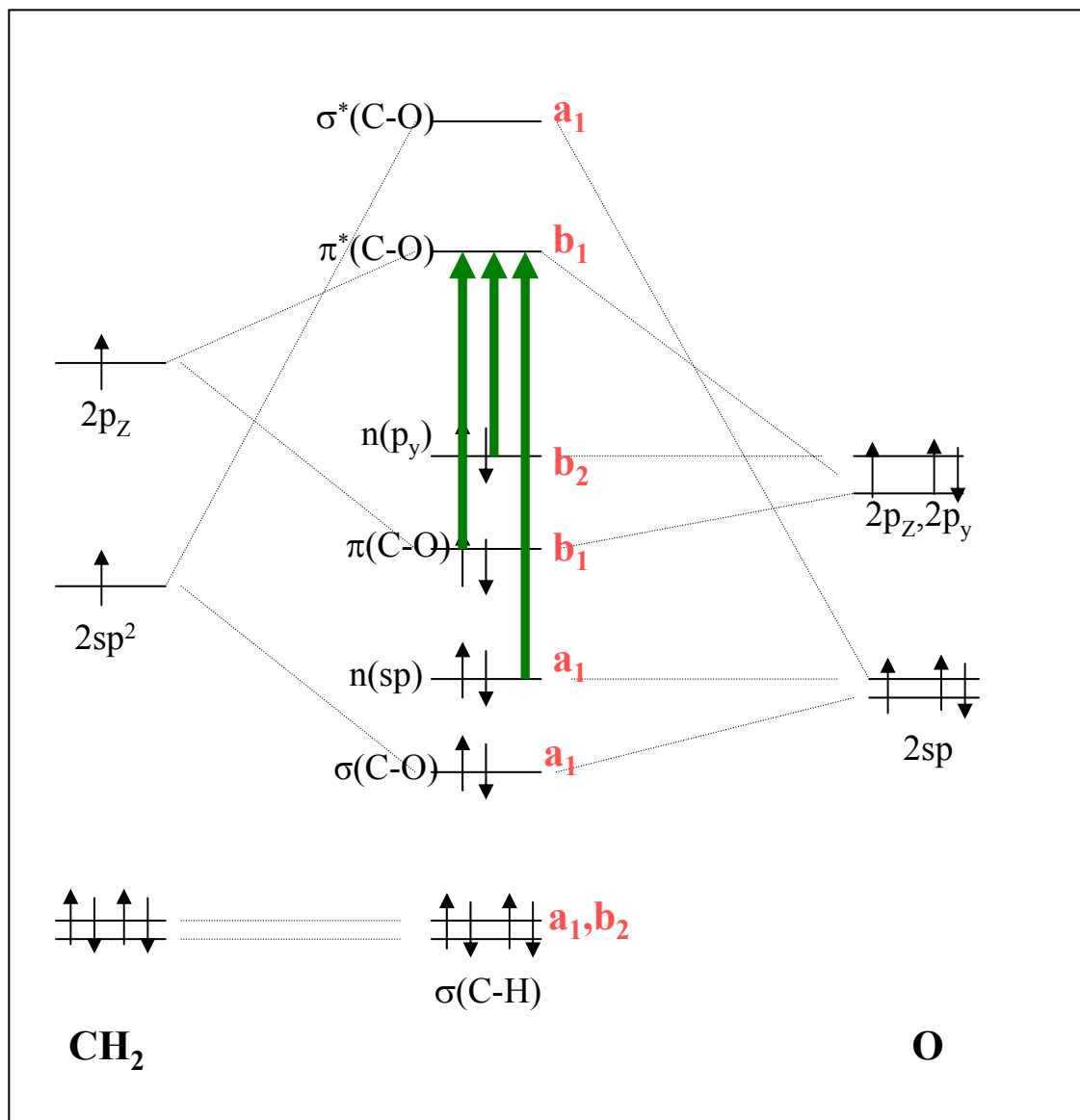
**Valence space - always correct**

**Inactive** doubly occupied

**Core**

taken from previous SCF calculations, not optimized

# Formaldehyde (C<sub>2v</sub>)



The symmetry of the state:  
direct product of the symmetry of orbitals

## Active space (a<sub>1</sub> b<sub>1</sub> b<sub>2</sub> a<sub>2</sub>)

### A<sub>1</sub>(π→π\*)

- minimal space (0,2,0,0) (2el)  
(2,2,0,0) (4el)

### A<sub>2</sub>(n→π\*)

- minimal space (0,1,1,0) (2el)

### B<sub>1</sub>(n→π\*)

- minimal space (1,1,0,0) (2el)  
(2,2,0,0)

- arbitrary space - n electrons in m orbitals

Distorsion of the geometry =>  
lowering of the symmetry, the active space has to be adjust appropriately

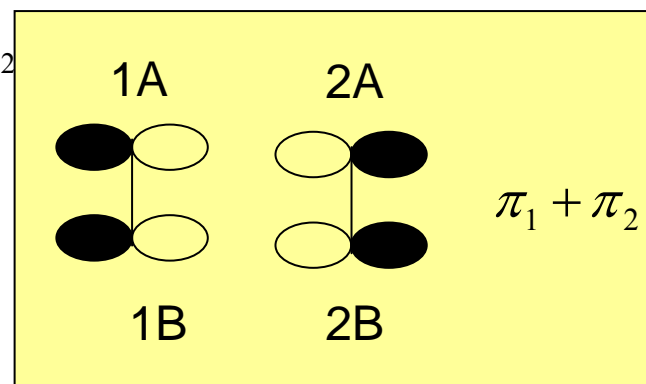
# Selection of the active space – $C_2H_4 + C_2H_4 \rightarrow C_4H_8$ reaction

At separated limit

$$\Psi = \dots(\pi_1)^2(\pi_2)^2 \cong \dots(\pi_+)^2(\pi_-)^2$$

$$\pi_+ = \sqrt{\frac{1}{2}}(\pi_1 + \pi_2) = \frac{1}{2}(\pi_{1A} + \pi_{1B} + \pi_{2A} + \pi_{2B})$$

$$\pi_- = \sqrt{\frac{1}{2}}(\pi_1 - \pi_2) = \frac{1}{2}(\pi_{1A} + \pi_{1B} - \pi_{2A} - \pi_{2B})$$



Small limit... $\pi$  orbitals between A and B broken and replaced by  $\sigma$  between 1 and 2

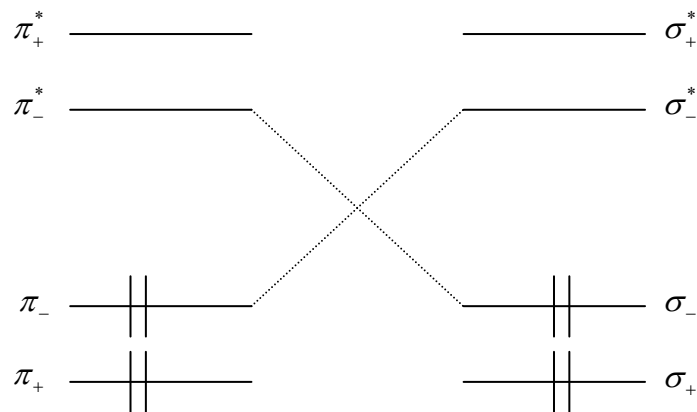
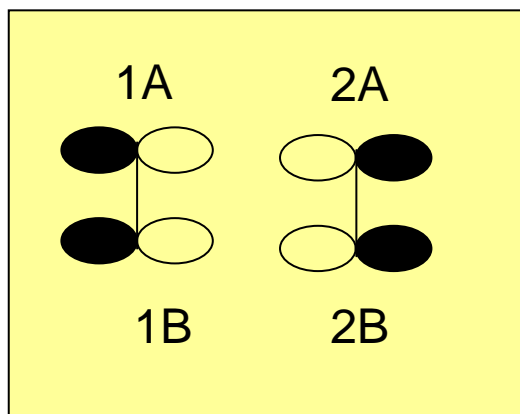
$$\sigma_A \propto (\pi_{1A} + \pi_{2A})$$

$$\sigma_B \propto (\pi_{1B} + \pi_{2B})$$

$$\Psi = \dots(\sigma_A)^2(\sigma_B)^2 \cong \dots(\sigma_+)^2(\sigma_-)^2$$

$$\sigma_+ = \sqrt{\frac{1}{2}}(\sigma_A + \sigma_B) = \frac{1}{2}(\pi_{1A} + \pi_{1B} + \pi_{2A} + \pi_{2B}) = \pi_+$$

$$\sigma_- = \sqrt{\frac{1}{2}}(\sigma_A - \sigma_B) = \frac{1}{2}(\pi_{1A} - \pi_{1B} + \pi_{2A} - \pi_{2B}) = \pi_-^*$$



The reaction can be described using 4 electrons and 4 active orbitals  
 In cyclobutane: all 4 C-C bonds equal, but in the MCSCF (4,4) wavefunction these are not treated at the same level.  $C_A-C_B$  using closed shells,  $C_1-C_2$  include occupations of anti-bonding orbitals  $\Rightarrow$  to have minimum as a square  $\Rightarrow$  (8,8)

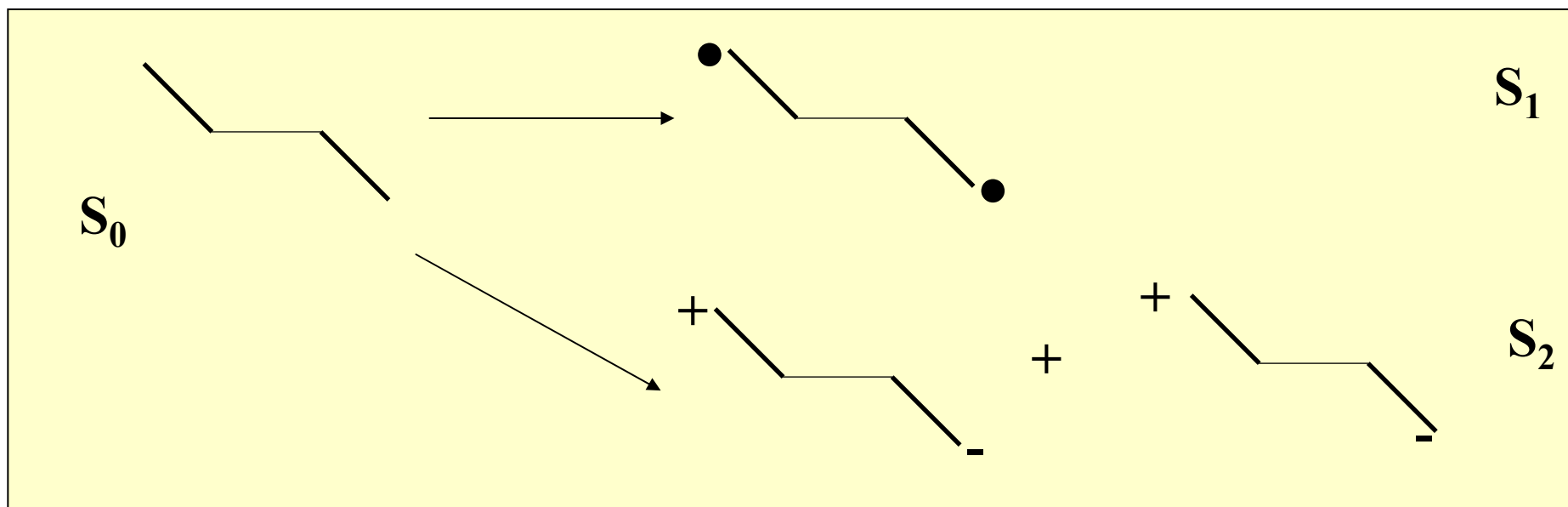
## Cases with one-configurational description problematic

1. Dissociation of covalent chemical bond
2. Virtual orbitals have low energy (Be) and  $O_3$
3. Transition states
4. Transition metals
5. Excited states

# Polyenes

Active space –  $\pi$  electrons

Valence  $\pi$  excited states are of two types – covalent (dot-dot) or ionic (hole-pair)



$S_1$  – 4 electrons in 4 (2p) orbitals

$S_2$  – 4 electrons in 8 (2p + 3p) orbitals



# Classification of the Excited States

*Valence states* – singlet and triplet excited states due to the  $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \sigma^*$ ,  $\pi \rightarrow \sigma^*$ ,  $\sigma \rightarrow \pi^*$

Breaking of the symmetry of the chromophore – label of states only approximate, mixing of the states of different symmetry, in limiting case mixing becomes so strong that the labels lose their utility

*Rydberg states* - one electron is excited to an atomic-like orbital with  $n$  higher than  $n_{valence}$

- For the systems with closed shell configuration - can be viewed as *positively charged core and electron in orbital with  $n_{val}+1, 2, \dots \rightarrow$*

**diffuse character**

- In the gas-phase spectra, very sharp bands

# Assignment of the Rydberg states

Two limiting cases of the coupling of the Rydberg electron with the core

- **L-S coupling scheme** - strong coupling  $\rightarrow$  singlet and triplet states
- **$(\Omega, \omega)$  coupling scheme** - weak coupling  $\rightarrow$  doublet with splitting due to the spin-orbit splitting in the core

$\text{CH}_3\text{Cl}$  -  $n \rightarrow 4s$ ,  $n \rightarrow 4p$  - it is possible to distinguish between predominantly triplet and singlet states

$n \rightarrow 4d$ ,  $n \rightarrow 5s$  - intermediate of these two types of coupling

## Rydberg/valence mixing

Important in the interpretation of spectra of molecules

- effective only when the states are nearly degenerate in energy

(for ethylene observed only in the singlet manifold)

Some molecules - the valence state is completely “dissolved in the sea” of Rydberg states.

$\text{CH}_3\text{F}$ ,  $(\text{CH}_3)_2\text{O}$ ,  $(\text{CH}_3)_3\text{N}$  - little or no evidence of singlet valence excited states

$\text{CH}_3\text{Cl}$ ,  $(\text{CH}_3)_2\text{S}$ ,  $(\text{CH}_3)_3\text{P}$  - all display valence transition, below Rydberg (lower lying  $\sigma^*$ )

## Description of the Rydberg States

- they have to be included in the active space => increase the size of the active space
- the use of diffuse basis set on atoms - mixing of Rydberg orbitals into valence => sometimes makes impossible to define whether the state is of the valence or Rydberg character
- construction of diffuse basis set which is placed in the center of the charge of the cation of the molecule - making the set of atomic-like s, p, and d functions

# Formamide – excitation spectrum

## Experimental:

W band

**5.65 eV** ( $n\pi^*$ )

R<sub>1</sub> band

**6.7 eV**

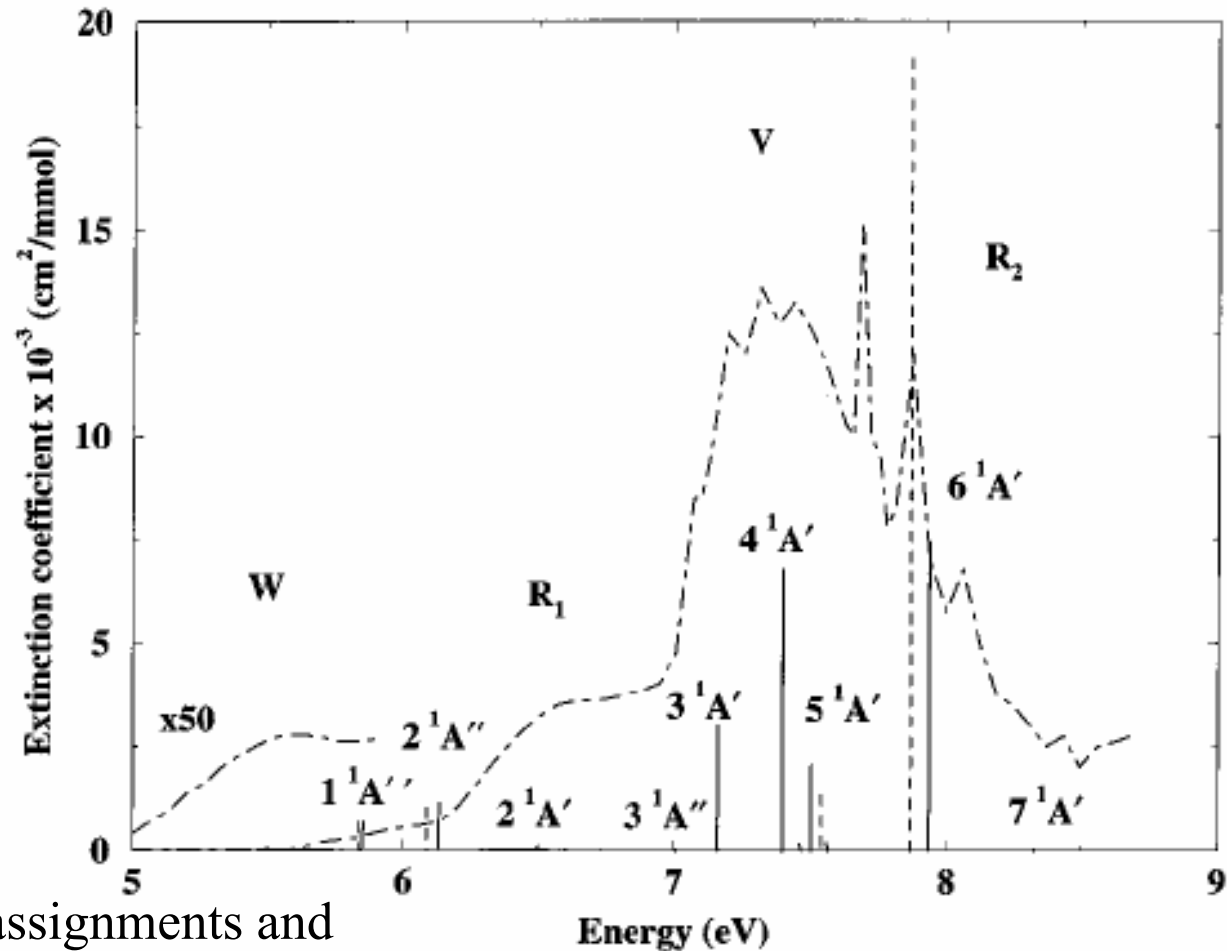
V<sub>1</sub> band

**7.32 eV** ( $\pi\pi^*$ )

$\mu(\pi\pi^*) = 3.7$  D, along NO

R<sub>2</sub> band

**7.8 eV**



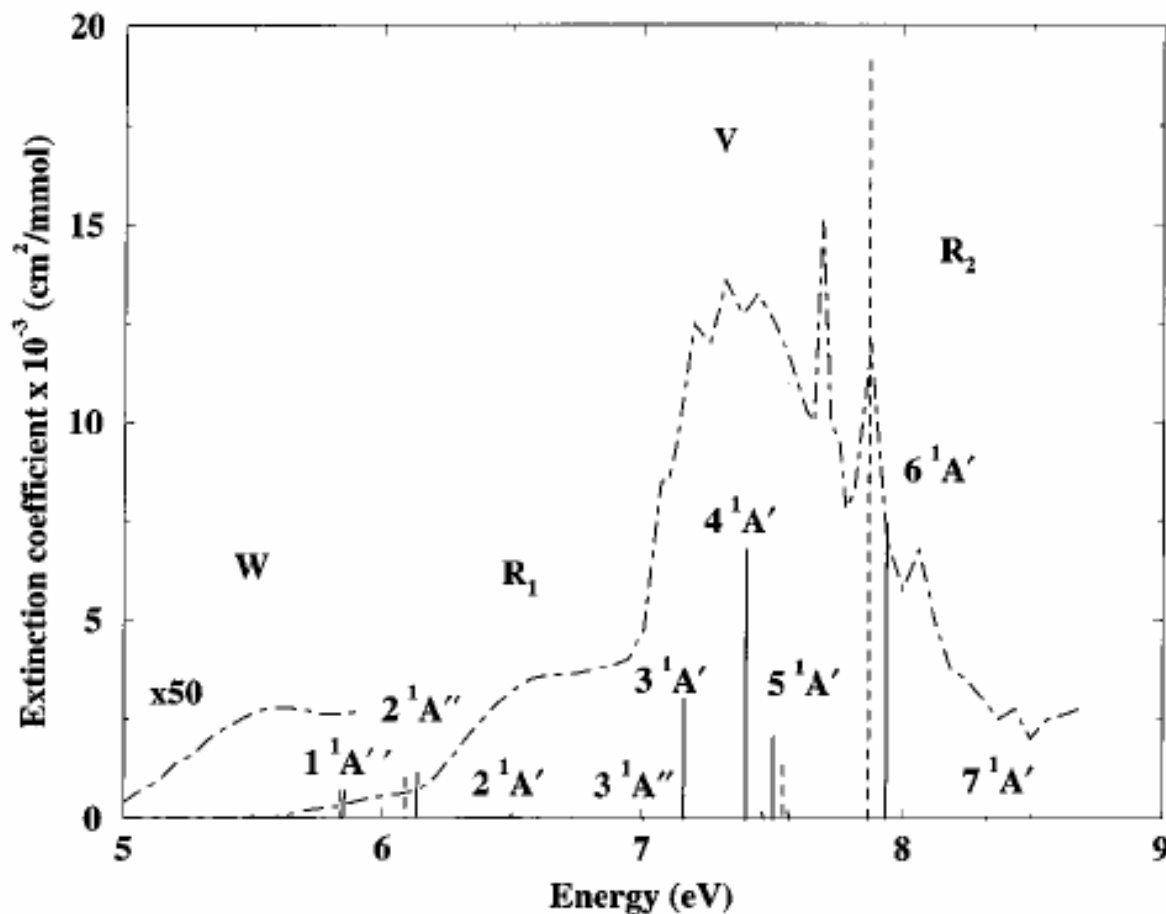
The bands are broad and the assignments and precise locations of the vertical transitions are by no means definitive, e.g. V and R<sub>2</sub> consist of a broad band (1 eV) with several sharp peaks

*J. Chem. Phys.* 49, 5007, 1968

# Formamide – excitation spectrum

*J. Phys. Chem. 100, 13487, 1996*

	VE	State	band
$2^1A'$	6.46	$n3s$	$R_1$
$3^1A'$	7.14	$n3p_y$	$V_1$
$4^1A'$	7.37	$\pi3p_z$	$V_1$
$5^1A'$	7.48	$n3p_x$	$V_1$
$6^1A'$	7.90	$\pi\pi^*$	$R_2$
$1^1A''$	5.82	$n\pi^*$	$W$
$2^1A''$	6.10	$\pi3s$	
$3^1A''$	6.97	$\pi3p_y$	$V_1$
$4^1A''$	7.43	$n3p_z$	
$5^1A''$	7.53	$\pi3p_x$	



$\mu(\pi\pi^*)$  calculated as 3.70 D (exp.: 3.71 D), with increased active new Rydberg state appears and the transition moment drops to 2.4 D.

# H<sub>2</sub>O...HCN

HCN	H <sub>2</sub> O	H <sub>2</sub> O...HCN
$\pi \rightarrow \pi^*$	8.01 (8.23)	7.92 (8.02)
	$n(\text{O}) \rightarrow \sigma^* + \text{Ry}$	8.18 (8.33)
		7.6 (8.10)

CASPT2/aug-cc-pVTZ (cc-pVTZ)

In the complex, the excitation energy of H<sub>2</sub>O is blue-shifted

- observed in bulk water and ice
- calculated for water clusters
- 'boxing-in' effect on a diffuse Rydberg-like state and a Coulombic repulsion between the reversed dipole of the water molecule in its excited state and the positively charged H atom of the surrounding molecule.
- red shift of  $\pi \rightarrow \pi^*$  (generally more polar than in GS) in complex with respect to HCN caused by the stabilization by polar molecule

## Ethylene: xample of a strong valence/Rydberg mixing

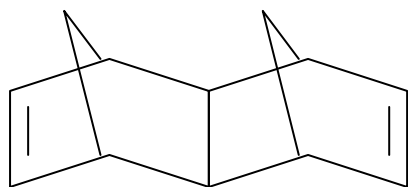
TABLE II. CASSCF and CASPT2 excitation energies (in eV), and CASSI oscillator strengths for ethene.

	CASSCF	PT2D	PT2F	Exp	Error <sup>a</sup>	$\omega^b$	$\langle z^2 \rangle^c$	Osc. str. Calc.	Other calculations <sup>d</sup>		
									CIS	MRCI	CI1
Ground state ( $1^1A_g$ )	...	...	...	...		0.92	11.8	...			
Singlet states											
$1^1B_{1u}(V)$	8.20	7.97	8.40	$\approx 8.0^e$	+0.4	0.91	44.1	0.16	7.78	7.96	7.96
$1^1B_{3u}(3s)$	6.82	6.62	7.17	$7.11^{f,i}$	+0.06	0.92	24.3	0.067	7.10	7.13	7.26
$1^1B_{1g}(3p\sigma)$	7.43	7.27	7.85	$7.80^{j,k}$	+0.05	0.92	17.2		7.68	7.86	7.93
$1^1B_{2g}(3p\sigma)$	7.51	7.37	7.95	$7.90^k$	+0.05	0.92	18.0		7.83	7.89	8.01
$2^1A_g(3p\pi)$	7.92	8.05	8.40	$8.28^k$	+0.12	0.91	36.3		8.10	8.21	8.36
$2^1B_{3u}(3d\sigma)$	8.24	8.11	8.66	$8.62^{f-h,l}$	+0.04	0.92	27.9	0.000 94	8.71	8.73	8.80
$2^1B_{1u}(3d\pi)$	8.94	8.88	9.31	$9.33^m$	-0.02	0.92	175.3	0.078	...	...	8.99
$1^1A_u(3d\pi)$	8.40	8.44	8.94	...	...	0.91	17.8		8.83	9.04	...
$3^1B_{3u}(3d\delta)$	8.51	8.49	9.03	$8.90^{f-h,n}$	+0.13	0.92	102.4	0.000 57	8.92	9.31	...
$1^1B_{2u}(3d\delta)$	8.69	8.73	9.18	$9.05^{f,l}$	+0.13	0.91	17.7	0.077	8.88	8.99	...
Triplet states											
$1^3B_{1u}(T)$	4.65	3.97	4.39	$4.36^m$	+0.03	0.91	11.9		3.54	4.35	...
$1^3B_{3u}(3s)$	6.74	6.49	7.05	$6.98^g$	+0.07	0.92	23.8		6.88	...	...
$1^3B_{1g}(3p\sigma)$	7.41	7.25	7.80	$7.79^g$	+0.01	0.92	17.0		7.60	...	...
$1^3B_{2g}(3p\sigma)$	7.47	7.31	7.90	...	...	0.92	17.7		7.72	...	...
$2^3A_g(3p\pi)$	7.73	7.84	8.26	$8.15^g$	+0.11	0.92	34.9		7.75	...	...
$2^3B_{3u}(3d\sigma)$	8.21	8.01	8.57	$8.57^g$	+0.00	0.91	28.3		8.63	...	...
$2^3B_{1u}(3d\pi)$	8.71	8.77	9.07	...	...	0.92	84.1		...	...	...
$1^3A_u(3d\pi)$	8.40	8.46	8.94	...	...	0.92	17.7		...	...	...
$1^3B_{2u}(3d\delta)$	8.61	8.66	9.09	...	...	0.91	17.5		...	...	...
$3^3B_{3u}(3d\delta)$	8.47	8.42	8.97	...	...	0.92	85.1		...	...	...

J. Chem Phys. 98, 1993, on page 3155



# 1,4:5,8-Bismethano-1,4,4a,8,8a-hexahydronaphthalene



$$A_1 \quad \pi_+ = \pi + \pi$$

$$B_2 \quad \pi_- = \pi - \pi$$

$$B_1 \quad \pi_+^* = \pi^* + \pi^*$$

$$A_2 \quad \pi_-^* = \pi^* - \pi^*$$

	CASPT2	CIS
$1^1B_2$ (R)	5.75	5.72
$1^1A_2$	<b>5.84</b>	<b>6.35</b>
$2^1A_1$ (R)	6.06	5.89
$2^1B_2$ (R)	6.25	6.33
$2^1A_2$ (R)	6.27	6.22
$1^1B_1$	<b>6.60</b>	<b>6.85</b>

	CASPT2	CIS
$1^3A_2$	<b>3.83</b>	<b>4.17</b>
$1^3B_1$	<b>3.93</b>	<b>4.27</b>
$1^3B_2$ (R)	5.72	5.64
$1^3A_1$ (R)	6.02	5.78
$2^3B_2$ (R)	6.24	6.24
$2^3A_2$ (R)	6.34	6.24

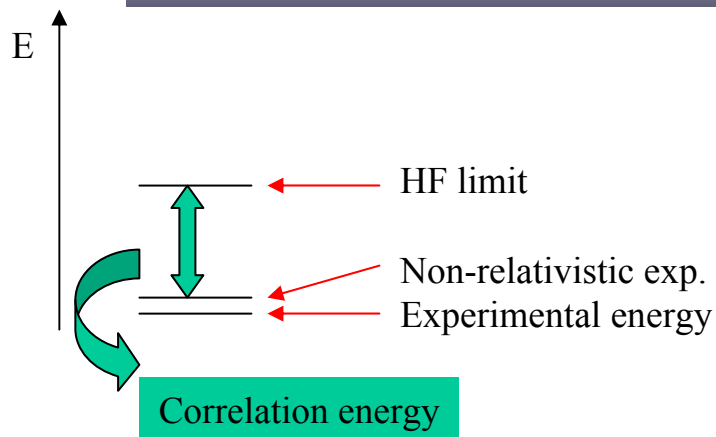
## Solving of the problem of correlation energy - essential in calculations of excited states

“Static” electron correlation: the wavefunction is composed of strongly interacting electronic configurations, treated using the MCSCF approach

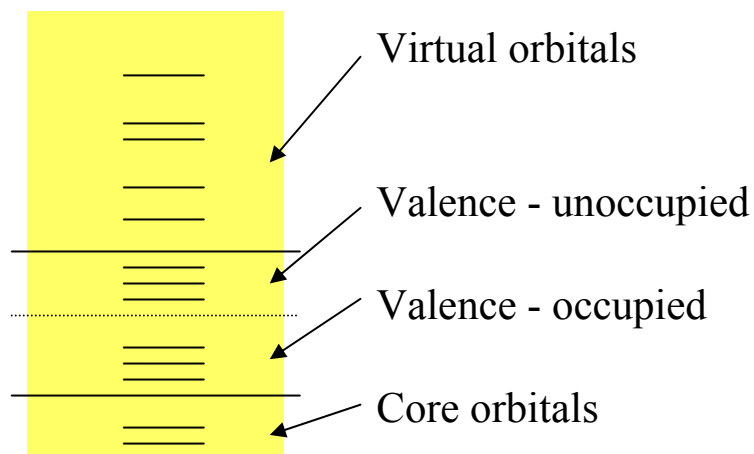
“Dynamic” electron correlation: additional treatment is necessary, since the states of different characters have different amount of this type of correlation, order to obtain accurate qualitative results and correct ordering of states

- For the ground-state calculations: correlation energy using CI or PT approaches, the reference state usually described by a single determinant
- For the excited state calculations: MCSCF energy describes the reference state

# Correlation energy



- Electron correlation results from a close proximity of electrons.
- To include electron correlation electrons must have a chance to escape away from other electrons.
- More Slater determinants in the wavefunction of the system.
- Various methods differ in the specification of Slater determinants in linear expansion and in the criteria used in search for optimal coefficients CI



Mono-, di-, tri-, ... excited determinant from "reference" Slater determinant

Monoexcited determinants: 
$$\Psi^S = \sum_i^{occ} \sum_a^{unocc} c_i^a \Psi_i^a$$

Biexcited determinants: 
$$\Psi^D = \sum_i^{occ} \sum_{\substack{a \\ j \neq i}}^{unocc} \sum_{\substack{b \\ b \neq a}} c_{ij}^{ab} \Psi_{ij}^{ab}$$

$$\Psi_0 = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \varphi_i(1) & \dots & \varphi_n(1) \\ \varphi_1(2) & \varphi_i(2) & \dots & \varphi_n(2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(n) & \varphi_i(n) & \dots & \varphi_n(n) \end{vmatrix} \longrightarrow \Psi_i^a = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \varphi_a(1) & \dots & \varphi_n(1) \\ \varphi_1(2) & \varphi_a(2) & \dots & \varphi_n(2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(n) & \varphi_a(n) & \dots & \varphi_n(n) \end{vmatrix}$$

## Configuration iteration method

$$\Phi^{CI} = c_0 \Psi_0 + \Psi^S + \Psi^D + \Psi^T + \Psi^Q + \dots$$

Variational method

Only coefficients of CI expansion optimized

MO are not optimized (this is different from MCSCF method)

Not size consistent,

Davidson correction for size consistency:  $(1-c_0)^2 \cdot E_{\text{correl}}$

Modern variant of CI method: AQCC, ACPF

# Multireference CI method

## Specification of the wavefunction:

frozen core orbitals

kept doubly occupied always, electrons in frozen core orbitals are not correlated

doubly occupied orbitals

doubly occupied in all reference configurations excitations out of these orbitals are taken into account in the final CSF expansion

active orbitals

variable occupation numbers in the reference configuration

auxiliary orbitals

occupied by at most  $n$  electrons in any of the references

external orbitals

not occupied in any of the references

frozen virtual orbitals

external orbitals into which excitations are not allowed

## Reference system: MCSCF wavefunction

Functional for the correlation energy is made stationary with respect to the expansion coefficients

$$F_{\alpha}(c^{\alpha}) = \frac{\left\langle \sum_i c_i^{\alpha} \Phi_i \left| \hat{H} - E_0^{\alpha} \right| \sum_i c_i^{\alpha} \Phi_i \right\rangle}{\sum_{i \in \text{int}} (c_i^{\alpha})^2 + G \sum_{i \notin \text{int}} (c_i^{\alpha})^2}$$

$G = 2/n_e$	ACPF
$= 1 - (n_e - 3)(n_e - 2)/[n_e(n_e - 1)]$	AQCC
$= 1$	CISD

$n_e$ .....Number of electrons of the system

int.....Set of conf's: reference conf's and all excitations within internal space

$E_0^{\alpha}$ .....Reference energy of the state  $\alpha$

# Second Order Perturbation Theory

System of interest:  $\hat{H}\Psi = E\Psi$   
 "Reference" (known) system:  $\hat{H}_0\Psi_0 = E_0\Psi_0$   
 Perturbation (small !):  $\hat{H} = \hat{H}_0 + \lambda H'$

Introducing a variable ordering parameter  $\lambda$  and determining the strength of the perturbation expand eigenfunctions and eigenvalues in Taylor series:

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}'$$

$$W = W_0 + \lambda W_1 + \lambda^2 W_2 + \dots$$

$$\Psi = \Psi_0 + \lambda\Psi_1 + \lambda^2\Psi_2 + \dots$$

$$\lambda^0 : H_0\Psi_0 = W_0\Psi_0$$

$$\lambda^1 : H_0\Psi_1 + H'\Psi_0 = W_0\Psi_1 + W_1\Psi_0$$

$$\lambda^2 : H_0\Psi_2 + H'\Psi_1 = W_0\Psi_2 + W_1\Psi_1 + W_2\Psi_0$$

$$E_n = W_0 + W_1 + W_2 + \dots$$

$$W_1 = \langle \Psi_0 | \hat{H}' | \Psi_0 \rangle$$

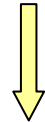
$$W_2 = \sum_{i \neq 0} \frac{|\langle \Psi_0 | \hat{H}' | \Psi_i \rangle|^2}{E_0 - E_i}$$

Using "intermediate no  
with the same power of

ation, the terms can be collected

## PT for electron correlation - Moller-Plesset formulation

Perturbation  $\hat{H}' = \sum_{i<j} r_{ij}^{-1} - \sum_i v^{HF}(i)$



$$E^{MP0} = \sum_{i=1}^n e_i$$

$$E^{MP1} = E^{(0)} + E^{(1)} = E^{HF}$$

$$E^{MP2} = \underbrace{E^{(0)} + E^{(1)}}_{=E^{HF}} + E^{(2)} = E^{HF} + \sum_a \sum_b \sum_r \sum_s \frac{\rho_{cc}^{ab} \rho_{cc}^{ba} \gamma_{virt}^{rs} \gamma_{virt}^{sr}}{e_a + e_b - e_r - e_s} \frac{|\langle \hat{a}ab | rs \rangle - \langle \hat{a}ab | sr \rangle|^2}{e_a + e_b - e_r - e_s}$$

The problem of dynamical correlation for excited states:  
multireference perturbation theory (CASPT2), MCSCF wavefunction  
is zeroth order wavefunction



# Examples on the importance of description of dynamic correlation effects

TABLE IV. CASSCF and CASPT2 excitation energies (in eV), and CASSI oscillat

butadiene

J. Chem. Phys. 98 (4), 3151, 1993,

	CASSCF	PT2D	PT2F	Exp	Error <sup>a</sup>	$\omega^b$	$\langle z^2 \rangle^c$
Ground state ( $1^1A_g$ )	...	...	...	...		0.85	21.9
Singlet states							
$1^1B_u(V)$	8.54	6.12	6.23	5.92 <sup>c,g</sup>	+0.31	0.76	40.9
$1^1B_g(3s)$	6.30	6.11	6.29	6.27 <sup>f</sup>	+0.02	0.84	40.0
$2^1A_g(V)$	6.64	6.23	6.27	?	?	0.80	23.2
$1^1A_u(3p\sigma)$	6.49	6.38	6.56	6.66 <sup>c,g</sup>	-0.10	0.84	36.2
$2^1A_u(3p\sigma)$	6.58	6.51	6.69	6.80 <sup>c,g</sup>	-0.11	0.84	40.1
$2^1B_u(3p\pi)$	6.88	6.75	6.70	7.07 <sup>c,f</sup>	-0.37	0.82	88.9
$2^1B_g(3d\delta)$	7.20	7.14	7.30	7.28 <sup>e</sup>	+0.02	0.84	50.6
$3^1A_g(3d\pi)$	7.55	7.44	7.47	7.48 <sup>f,g</sup>	-0.01	0.84	94.8
$3^1B_u(4p\pi)$	7.85	7.76	7.79	8.00 <sup>c,g</sup>	-0.21	0.83	284.5
Triplet states							
$1^3B_u$	3.39	3.14	3.20	3.22 <sup>c</sup>	-0.02	0.84	21.8
$1^3A_g$	5.08	4.81	4.89	4.91 <sup>c</sup>	-0.02	0.84	22.0

tor strengths for hexatriene

	CASSCF	PT2D	Exp	Error <sup>a</sup>	$\omega^b$	$\langle z^2 \rangle^c$
Ground state ( $1^1A_g$ )	...	...	...		0.78	31.8
Singlet states						
$1^1B_u(V)$	7.36	5.01	4.95 <sup>h</sup>	+0.06	0.70	40.4
$2^1A_g(V)$	5.65	5.19(5.20) <sup>d</sup>	5.21 <sup>j</sup>	-0.01	0.74	31.8
$1^1A_u(3s)$	5.75	5.84	5.67 <sup>k</sup>	+0.17	0.77	69.4
$2^1B_u(3d\pi)$	6.59	6.11	6.06 <sup>h</sup>	+0.05	0.74	85.0
$1^1B_g(3p\sigma)$	5.87	6.12	6.20 <sup>f</sup>	-0.08	0.78	48.0
$3^1A_g(3p\pi)$	6.27	6.19(6.24) <sup>d</sup>	6.22 <sup>l,h,j</sup>	+0.02	0.77	105.6
Triplet states						
$1^3B_u$	2.70	2.55	2.61 <sup>h</sup>	-0.06	0.78	31.8
$1^3A_g$	4.32	4.12	4.11 <sup>h</sup>	+0.01	0.77	31.7

# Single reference methods

## HF used as reference wave-function

CI based method – Configuration interaction singles (CIS)

Propagation approach – linear response technique (RPA or TDHF) – employing a single replacement operator, many variants of development were applied

CC approach – Symmetry-Adapted-Cluster CI (SAC-CI), linear response CC (HF  $\ll$  CC2  $\ll$  CCSD  $\ll$  CC3  $\ll$  CCSDT)

Up to date the most accurate methods to compute excited states in small to medium size molecules

## Time-Dependent Density Functional Theory

# Configuration Interaction Singles

The computationally and conceptually simplest wave-function-based method

HF ground state  $\Phi_0(r)$

$$\Phi_0(r) = |\phi_1(r)\phi_2(r)\dots\phi_n(r)|$$

CIS wave function - replacing occupied  $i$  by virtual  $a$

$$\Psi_{CIS} = \sum_{ia} c_i^a \Phi_i^a(r)$$

$n \times v$  dimension

$$\hat{H}(r)\Psi(r) = \left[ \hat{T}(r) + \hat{V}_{el-nuc}(r) + \hat{V}_{el-el}(r) \right] \Psi(r) = E\Psi(r)$$

projection onto the space of singly excited determinants

$$\sum_{ia} \langle \Phi_j^b | \hat{H} | \Phi_i^a \rangle c_i^a = E_{CIS} \sum_{ia} c_i^a \delta_{ij} \delta_{ab}$$

$$\sum_{ia} \{(\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + (ia \parallel jb)\} c_i^a = \omega_{CIS} \sum_{ia} c_i^a \delta_{ij}\delta_{ab}$$

Written in the matrix notation as an eigenvalue problem

$$\mathbf{A}\mathbf{X} = \omega\mathbf{X}$$

$\mathbf{A}$  matrix representation of Hamiltonian in the spaces of the singly occupied determinants

$\omega$  diagonal matrix of the excitation energies

$\mathbf{X}$  matrix of CIS expansion coefficients

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + (ia \parallel jb)$$

Excitation energies obtained by solving secular equation

$$(\mathbf{A} - \omega)\mathbf{X} = 0$$

Eigenvalues correspond to excitation energies, eigenvectors to CI expansion coefficients

$$E_{CIS} = E_{HF} + \sum_{ia} (c_i^a)^2 (\varepsilon_a - \varepsilon_i) + \sum_{ia,jb} c_i^a c_j^b (ia \parallel jb)$$

# Time dependent Density Functional Theory

Ground-state DFT in the Kohn-Sham formulation relies on the Hohenberg-Kohn theorems

1. Hohenberg-Kohn theorem: one-to-one mapping between the exact electron density  $\rho(\mathbf{r})$  and the exact external potential  $V_{\text{ext}}(\mathbf{r})$

$V_{\text{ext}}(\mathbf{r})$  determines exact ground-state  $\Psi(\mathbf{r}) \Rightarrow \Psi(\mathbf{r})$  is a functional of the electron density

2. Hohenberg-Kohn theorem: existence of a variational principle

**Limited to time-independent systems, i.e. ground states**

**The Runge-Gross theorem: time-dependent analogue of the first HK theorem:**

Time-dependent electron density  $\rho(\mathbf{r},t)$  determines time-dependent  $V_{\text{ext}}(\mathbf{r},t)$  and time-dependent function  $C(t)$  and thus time-dependent  $\Psi(\mathbf{r},t)$ , up to a time-dependent phase factor.

$$H(t) = T + V_{\text{ext}}(t) + W$$

*T...kinetic energy operator*

*W...electron-electron interaction*

*$V_{\text{ext}}(t)$  ...external potential*

$$H(t) = T + V_{ext}(t) + W$$

Hamiltonian determines the wavefunction

$$H(t) |\Phi(t)\rangle = i \frac{\partial}{\partial t} |\Phi(t)\rangle$$

Constructed in terms of a set of orbitals obeying the equation  $(-\frac{1}{2}\nabla^2 + v_s(r,t))\phi_i(r,t) = i \frac{\partial}{\partial t} \phi_i(r,t)$

and generating time-dependent density  $\rho_s(r,t) = \sum_{i=1}^N |\phi_i(r,t)|^2$

$$v_s(r,t) = v_{ext}(r,t) + v_J(r,t) + v_{xc}(r,t)$$

## Linear response TDDFT

Considering small time-dependent external perturbation

$$H'(t) = H + \partial V^{ext}(t), \quad H'_{KS[\rho](t)} = H_{KS[\rho]} + \partial V_{H[\rho](t)} + \partial V_{xc[\rho](t)} + \partial V^{ext}(t)$$

The variation of Hartree and exchange-correlation potentials to the can be expanded

$$\partial V_H[\rho](r) = \frac{\partial V_H[\rho]}{\partial \rho} \partial \rho = \frac{1}{|r-r'|} \partial \rho(r'), \quad \partial V_{xc}[\rho](r) = \frac{\partial V_{xc}[\rho]}{\partial \rho} \partial \rho = f_{xc}(rt, r't') \partial \rho(r')$$

# Limitations

B3LYP and PBE – most widely used xc functionals.

Although developed with respect to the electronic ground state, they are used in TDDFT calculations

Reliability of TDDFT should always be checked by comparison with either benchmark calculations or experimental data and by sensitivity to the choices of xc functionals.

**Typical error for valence excited states which are well below IP – 0.1 -0.5 eV**  
(almost comparable with EOM-CCSD or CASPT2).

Requires to include large sets of virtual orbitals

**Accuracy reached at very favorable computational cost – TDDFT applicable for large molecules**

## Accuracy of TDDFT:

The difference of KS orbital energies (leading terms of the diagonal elements of  $A$ ) are excellent approximations for excitation energies => orbital energy differences are much better estimates of valence-excited states in KS-DFT than in HF theories

## Severe problems:

Rydberg states and valence states of extended  $\pi$  systems – wrong long-range behavior of current standard xc functionals - decay faster than  $1/r$  ( $r$ - electron-nuclear distance)

Charge-transfer excited states

# Methods to be used

Problem	Approach	Methods
Vertical excitation spectra and stationary points in excited states	Adiabatic quantum chemistry	CC2, TDDFT CASPT2, MR-CISD
Conical intersections	Nonadiabatic quantum chemistry	MCSCF, MR-CISD
Reaction paths	Adiabatic quantum chemistry	MCSCF, CASPT2 MR-CISD
Lifetimes	Dynamics methods	MCSCF, MR-CISD



## Intensity of the band

### Lambert-Beer law:

$$A = \log(I_0/I) = \log(1/T) = \varepsilon(\lambda)cd$$

Rough measure of the intensity of an electronic transition -  $\varepsilon_{max}$

A – absorbance

T - transmittance

c – concentration

d – thickness of the sample

$\varepsilon(\lambda)$  – molar extinction coefficient

Total area under the absorption band – physically more meaningful

$$f \sim \int \varepsilon(\nu) d\nu$$

$f$  – oscillator strength,  
dimensionless quantity

**Theoretical expression for the oscillator strength** – using of perturbation theory to treat the interaction between electromagnetic radiation and the molecule  
 Oscillating field – perturbation that varies in the time

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(l)}(t)$$

Hamiltonian of unperturbed system,  
 in the absence of radiation

describes interaction between light and the molecule

Probability of the transition is proportional to the matrix element:

$$\langle \Psi_t | \hat{H}^{(l)} | \Psi_0 \rangle^2$$

$$f^{(r)} = \text{const} \cdot |e_U \cdot \tilde{M}_{0 \rightarrow f}|^2$$

$$\tilde{M}_{0 \rightarrow f} = \langle \Psi_f^{tot} | \hat{M} | \Psi_0^{tot} \rangle$$

Transition moment

$$\hat{M} = -|e| \sum_j r_j + |e| \sum_A Z_A R_A$$

Dipole moment operator

## **Selection Rules** – can be derived from the expression for the transition moment

$$M_{0 \rightarrow f} = \int \psi_{v'}^* \psi_v d\tau_n \int \psi_{e'}^* \hat{\mu}_e \psi_e d\tau_e \int \psi_{s'}^* \psi_s d\tau_s$$

➤ *spin selection rules* –  $\int \psi_{s'}^* \psi_s d\tau_s$

electronic transition is allowed only if the spin of the two states are the same, but spin-orbit coupling

➤ *orbital selection rules* –  $\int \psi_{e'}^* \hat{\mu}_e \psi_e d\tau_e$

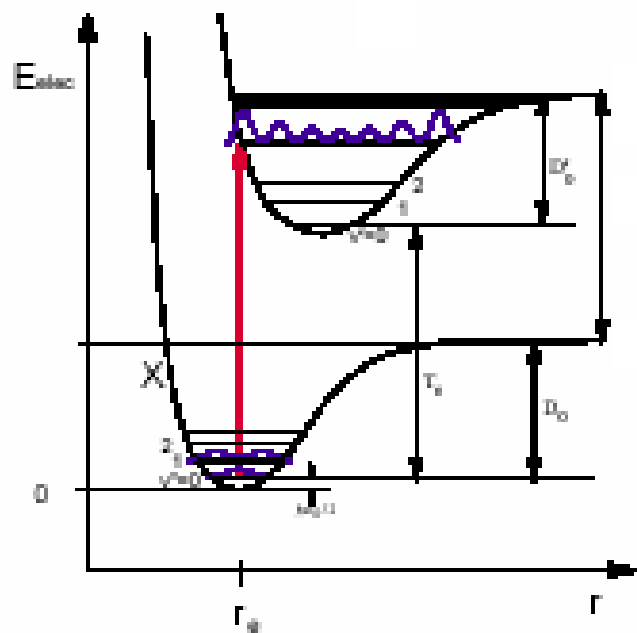
integral nonzero if the direct product of irreducible representations of the ground and excited states and of the transition moment operator is totally symmetric, may be broken due to a symmetry-lowering vibrational motions

➤ *selection rules based on a small value of  $M_{0 \rightarrow f}$*  - small orbital overlap –  $n \rightarrow \pi^*$  and charge transfer transitions

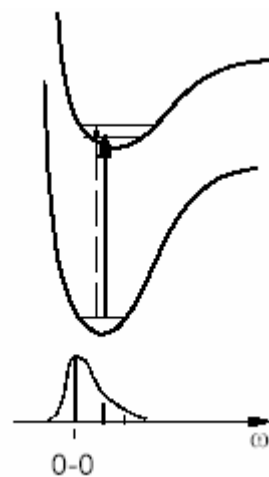
# Franck-Condon principle -

The electronic transition much faster than vibrations of nuclei – **vertical transition**.

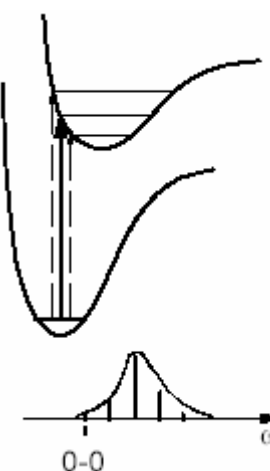
**Quantum chemical explanation** - the overlap of vibrational wavefunctions – the most intense transition between vibrational states with the largest overlap – Franck-Condon transition



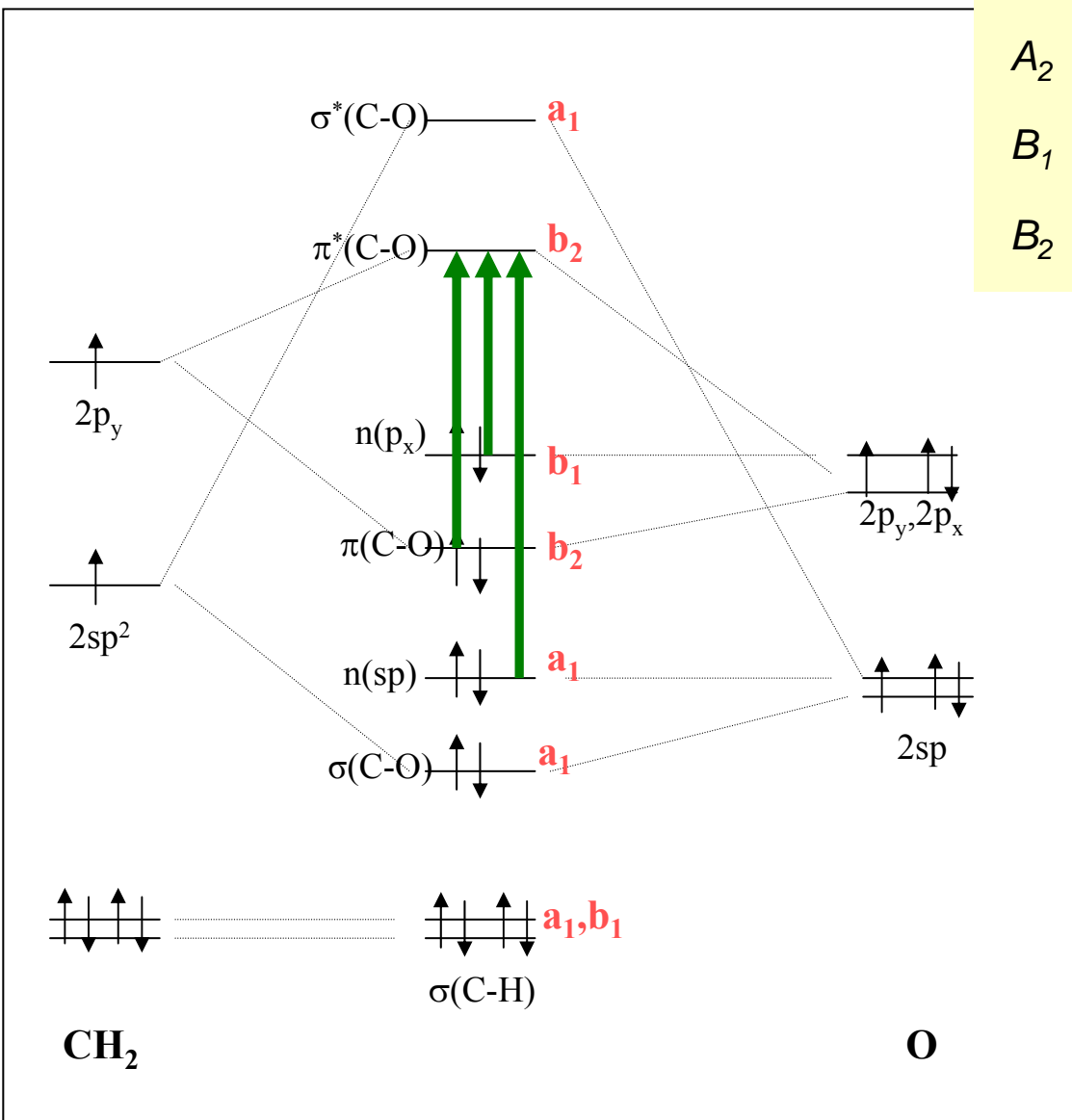
Smaller displacement



Larger displacement



# Formaldehyde



$C_{2v}$	E	$C_2(z)$	$\sigma(xz)$	$\sigma(yz)$	
$A_1$	1	1	1	1	z
$A_2$	1	1	-1	-1	
$B_1$	1	-1	1	-1	x
$B_2$	1	-1	-1	1	y

$n \rightarrow \pi^*$  ( $b_1 \rightarrow b_2$ )

<del>x</del>	<del><math>b_1 \times B_1 \times b_2</math></del>	<del><math>B_2</math></del>
<del>y</del>	<del><math>b_1 \times B_2 \times b_2</math></del>	<del><math>B_1</math></del>
<del>z</del>	<del><math>b_1 \times A_1 \times b_2</math></del>	<del><math>A_2</math></del>

$n \rightarrow \pi^*$  ( $a_1 \rightarrow b_2$ )

x	$a_1 \times B_1 \times b_2$	$A_2$
<b>y</b>	<b><math>a_1 \times B_2 \times b_2</math></b>	<b><math>A_1</math></b>
z	$a_1 \times A_1 \times b_2$	$B_2$

# Nonadiabatic processes

Nonadiabatic processes facilitated by a close proximity of potential energy surfaces . When the energy gap between the surfaces is small the adiabatic (Born-Oppenheimer) approximation breaks down.

# Born-Oppenheimer approximation

$$H(r, R)\Psi(r, R) = E\Psi(r, R)$$

$$H(r, R) = T^{nuc} + H^{el}(r; R) \quad \text{Depends parametrically on } R$$

BO (adiabatic) approximation: the coupling between the nuclear and electronic degree of freedom is ignored.

$$\Psi(r, R) = \psi(r; R)\chi(R)$$

Solving the electronic SE provides the electronic wavefunction

$$H^{el}(r; R)\Psi_I(r; R) = E_I^{el}(R)\Psi_I(r; R) \quad \longrightarrow \quad \text{Back to SE} \quad \longrightarrow$$

Nuclear wavefunction and total energy

# Beyond BO approximation

$$\Psi(r, R) = \sum \Psi(r, R) \chi_I(R)$$

Total wavefunction is not a product of el. and nuclear wavefunction but rather an expansion in terms of electronic wavefunction

$$\left[ T^{nuc} - \frac{1}{2\mu} K_{II}(R) + E_I^{el}(R) \right] \chi_I(R) - \sum_{J \neq I} \frac{1}{2\mu} \left[ K_{IJ}(R) + 2f_{IJ}(R) \cdot \nabla \right] \chi_J(R) = E \chi_I(R)$$

$\nabla$ ...gradient over the nuclear coordinates,  $\mu$ ...reduced mass

$$K_{IJ}(R) = \langle \psi_I(r; R) | \nabla^2 \psi_J(r; R) \rangle$$

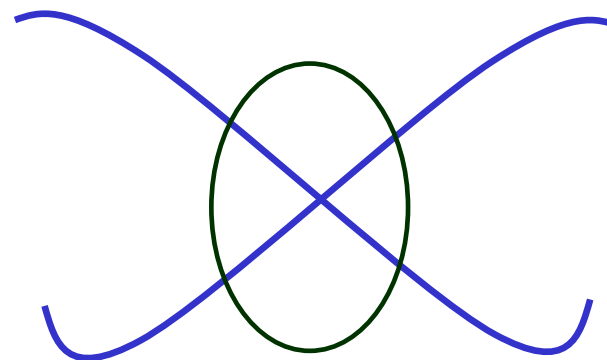
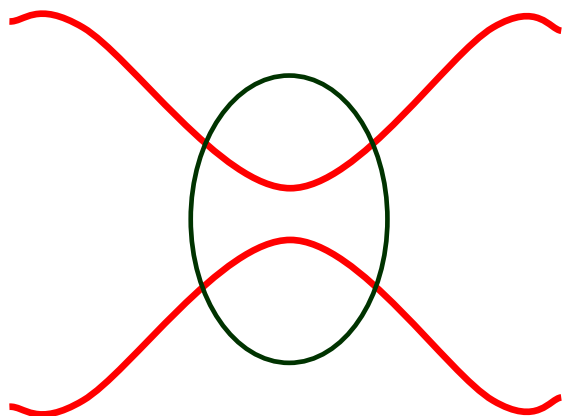
$$f_{IJ}(R) = \langle \psi_I(r; R) | \nabla \psi_J(r; R) \rangle \dots \text{derivative coupling}$$

Coupling terms neglected in BOA, originated from the nuclear kinetic operator operating on the electronic wavefunction

Derivative coupling is a measure of the variation of the electronic wavefunction with nuclear coordinates



# Adiabatic vs. diabatic representation



Adiabatic representation: electronic wavefunctions taken as the eigenfunctions of the electronic Hamiltonian

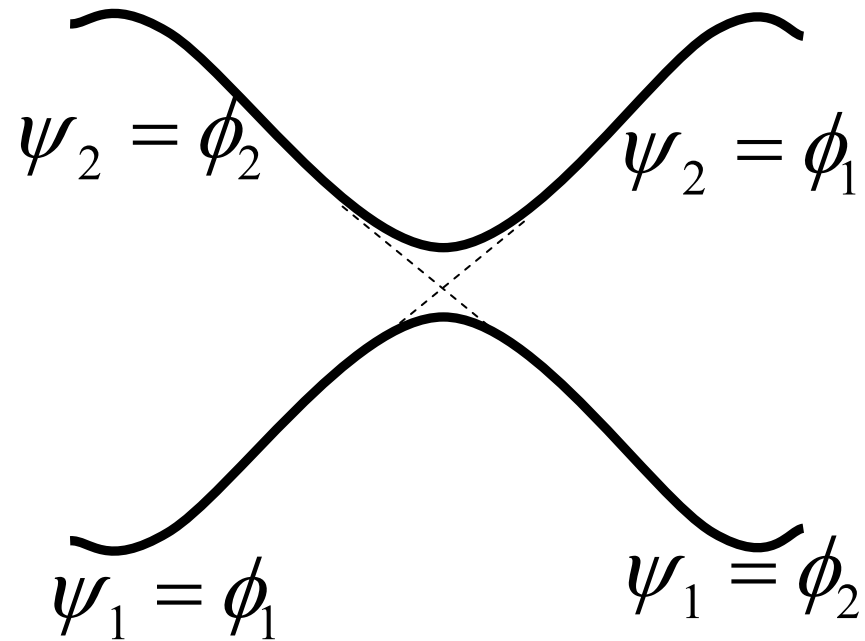
$$H_{IJ} = \langle \psi_I | H^{el} | \psi_J \rangle = 0$$

Coupling between different electronic states occurs through the nuclear kinetic energy terms

Diabatic representation is made by transformation of the adiabatic. The electronic wavefunctions are not the eigenfunctions of the electronic Hamiltonian, they are chosen to eliminate the derivative coupling, coupling terms do not appear in SE

$$H_{IJ} = \langle \phi_I | H^{el} | \phi_J \rangle \neq 0$$

# Adiabatic vs. diabatic representation



Diabatic wavefunctions keeps the character of the states

## The noncrossing rule

$$\psi_1 = c_{11}\phi_1 + c_{21}\phi_2 \quad \phi_1, \phi_2 \dots \text{ diabatic states}$$

$$\psi_2 = c_{12}\phi_1 + c_{22}\phi_2 \quad \psi_1, \psi_2 \dots \text{ adiabatic states}$$

Adiabatic electronic energies are eigenvalues of the Hamiltonian matrix

$$H^e = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \quad E_{1,2} = \bar{H} \pm \sqrt{\Delta H^2 + H_{12}^2}$$

$$\bar{H} = (H_{11} + H_{22}) / 2$$

$$\Delta H = (H_{11} - H_{22}) / 2$$

$$H_{12} = \langle \phi_1 | H(R) | \phi_2 \rangle$$

$$E_1 = E_2 \Rightarrow H_{11} = H_{22}, H_{12} = 0$$

For diatomic molecules – only 1 degree of freedom

Two electronic states cannot become degenerate, unless  $H_{12} = 0$

=> Noncrossing rule

**Systems with 3 and more atoms:** there is  $N^{\text{int}} - 2$  ( $3N-8$ ) dimensional space where the two conditions are satisfied

### Derivation of the conditions for conical intersection:

Taylor expansion around  $R_0$  ( $R_X$ )

$$\left. \begin{aligned} \bar{H}(R) &= \bar{H}(R_0) + \nabla \bar{H}(R_0) \cdot \delta R \\ \Delta H(R) &= 0 + \nabla(\Delta H)(R_0) \cdot \delta R \\ H_{12}(R) &= 0 + \nabla H_{12}(R_0) \cdot \delta R \end{aligned} \right\} \begin{aligned} \nabla(\Delta H) \cdot \delta R &= 0 \\ \nabla H_{12} \cdot \delta R &= 0 \\ &\text{to keep degeneracy} \end{aligned}$$

Vectors along the energy different gradient and the coupling gradient:

$$\mathbf{x} = \mathbf{g}/g = \nabla(\Delta H) / g$$

$$\mathbf{y} = \mathbf{h}/h = \nabla H_{12} / h$$

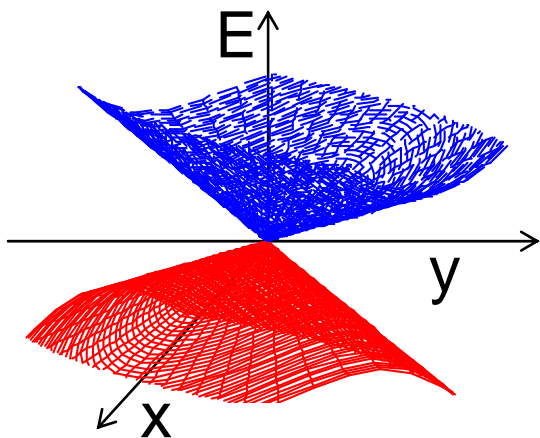
$g, h$ ...the norms of the vectors

$$E_{1,2} = s_x x + s_y y \pm \left[ g^2 x^2 + h^2 y^2 \right]^{1/2}$$

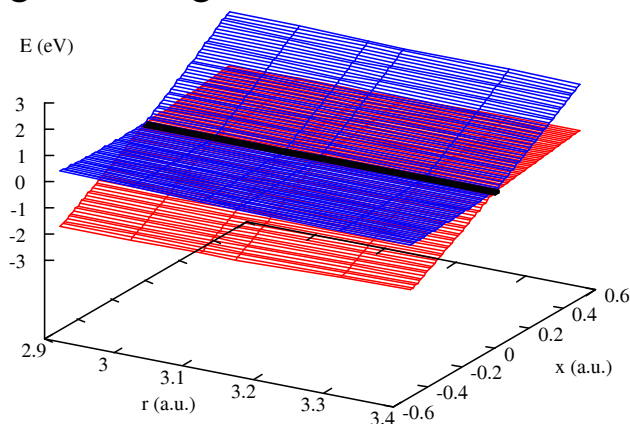
Around the CI along the  $x$ ,  $y$  coordinates: the potentials have a form of **double cone**

- Displacements  $x$  and  $y$  along the  $\mathbf{g}$  and  $\mathbf{h}$  define the **branching space**. Geometrical displacements along these vectors lift the degeneracy.
- Displacements along the other  $3N-8$  internal coordinates keep the degeneracy. This coordinate space is called „**seam**“ or „**intersection**“ space.

Along branching plane



Along branching and seam coordinates



Conical intersections in Molecular Systems, S. Matsika in Rev. Comp. Chem. 23, 83, 2007

## Derivative coupling

By using the gradient operator  $\nabla$  on:  $H^{el}\psi_I = E_I^{el}\psi_I$   
multiplying by  $\psi_J^*$  and integrating over electronic coordinates

$$f_{IJ}(R) = \frac{\langle \psi_I | \nabla H^{el} | \psi_J \rangle}{E_J^0 - E_I^0}$$

At the conical intersection, the energy difference is zero and the derivative coupling becomes infinity

## Locating of conical intersection

- The states must be treated at the same level
- Analytic gradients should be available
- Dynamical and nondynamical correlation should be available

Multireference method



Large computational demands

To locate the conical intersection, the energy of one state is minimized with the constraint to the energy difference between the two states being zero. The coupling is zero.

Using Lagrange-Newton Method

$$L_{IJ} = E_I + \xi_1(E_I - E_J) + \xi_2 H_{IJ} + \sum_{i=1}^M \lambda_i K_i$$

1.term: minimizes energy of state I(J)

2.term: restricts energy difference to 0

3.term: restricts off-diagonal terms to 0

4.term: allows for geometry restrictions

Conical intersection	Structure	Examples
Twisted		Polar substituted ethylenes ( $\text{CH}_2\text{NH}_2^+$ )
Twisted-pyramidalized		Ethylene 6-membered rings (aminopyrimidine)
Stretched-bipyramidalized		Polar substituted ethylenes Formamide 5-membered rings (pyrrole, imidazole)
H-migration/carbene		Ethylidene Cyclohexene
Out-of-plane O		Formamide Rings with carbonyl groups (pyridone, cytosine, thymine)
Bond breaking		Heteroaromatic rings (pyrrole, adenine, thiophene, furan, imidazole)
Proton transfer		Watson-Crick base pairs

M. Barbatti



# Photodynamics

- The investigation of PES – investigation of all possible channels, including dissociative channels
- The optimization of the critical points: minima, transition structures, and surface crossings
- The calculations of the reaction path to connect the critical points
- Performing dynamics simulations -

# Molecular dynamics: Surface hopping

$$\psi(\mathbf{r}, \mathbf{R}, t) = \sum_k c_k(\mathbf{R}, t) e^{-i\gamma_k(t)} \phi_k(\mathbf{R}; \mathbf{r}, t) \quad \Longrightarrow \quad i\hbar \frac{\partial \psi}{\partial t} = H_e \psi$$

$$\dot{c}_k = - \sum_{i \neq k} c_i(t) e^{i(\gamma_k(t) - \gamma_i(t))} d_{ki}(t) \quad \text{where} \quad d_{ki} = \langle \phi_k | \frac{\partial}{\partial t} \phi_i \rangle_r = \mathbf{v} \cdot \langle \phi_k | \nabla_R | \phi_i \rangle_r = \mathbf{v} \cdot \mathbf{h}_{ki}$$

Time derivative Nonadiabatic coupling vector

Tully, JCP **93**, 1061 (1990); Ferretti et al. JCP **104**, 5517 (1996)

**Population:**  $a_{ki} = c_k c_i^*$

$$\dot{a}_{kj} = \sum_i \left( a_{ki} e^{-i\gamma_{kj}} \mathbf{v} \cdot \mathbf{h}_{ij} - a_{ij} e^{i\gamma_{kj}} \mathbf{v} \cdot \mathbf{h}_{ki} \right)$$

- Two electronic states are coupled only by the nonadiabatic coupling vector  $\mathbf{h}_{ij}$  (adiabatic representation).

- Nuclear motion is obtained by integrating the Newton eqs.

$$-\nabla_{\mathbf{R}_I} E_i = M_I \frac{d^2 \mathbf{R}_I}{dt^2}$$

- At each time, the dynamics is performed on one unique adiabatic state,  $E_i = H_{ii}$ .

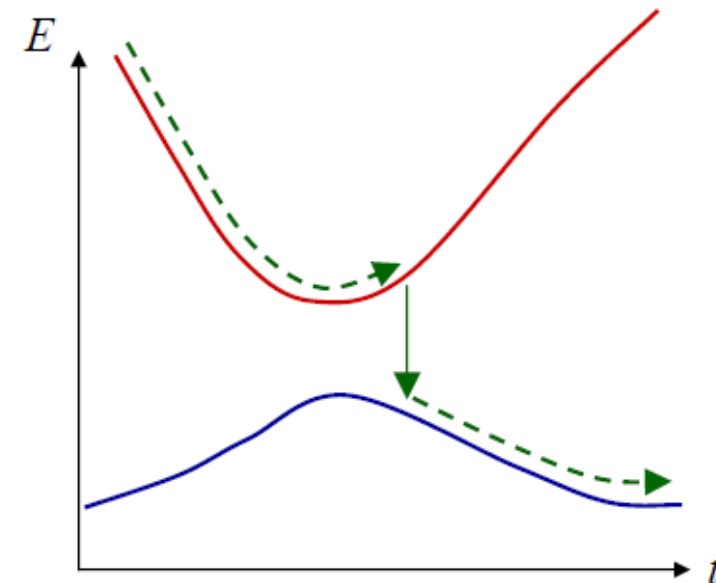
- In the adiabatic representation,  $E_i(\mathbf{R})$ ,  $\nabla E_i$  and  $\mathbf{h}_{ji}$  are obtained with traditional quantum chemistry methods.

- $a_{ji}$  is obtained by integrating

$$\dot{a}_{kj} = \sum_i \left( a_{ki} e^{-i\gamma_{kj}} \mathbf{v} \cdot \mathbf{h}_{ij} - a_{ij} e^{i\gamma_{kj}} \mathbf{v} \cdot \mathbf{h}_{ki} \right)$$

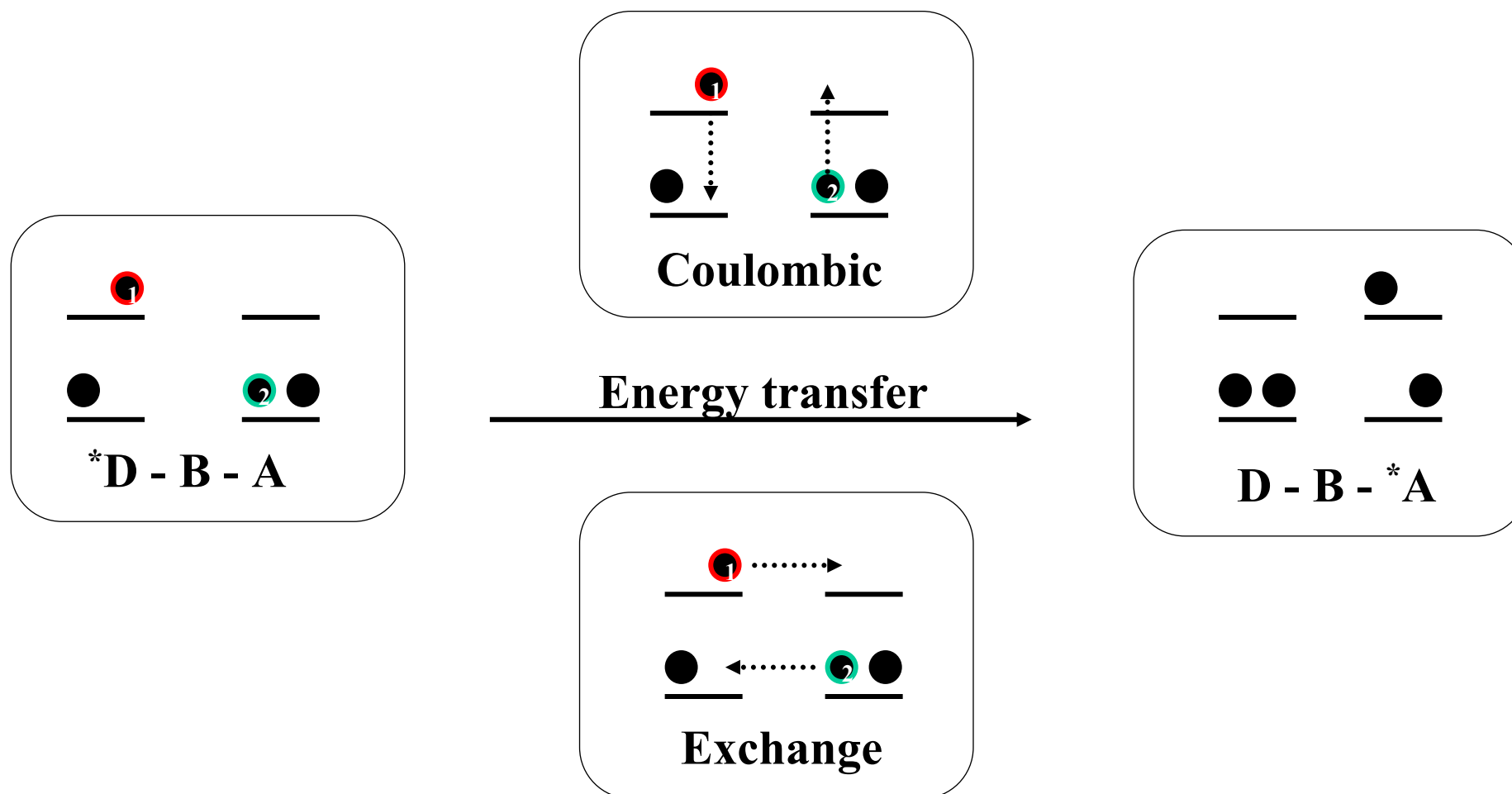
- The transition probability  $g_{kj}$  between two electronic states is calculated at each time step of the classical trajectory.

- A random event decides whether the system hops to other adiabatic state.



# *Energy Transfer*

Radiationless transition between two “localized” electronically excited states.



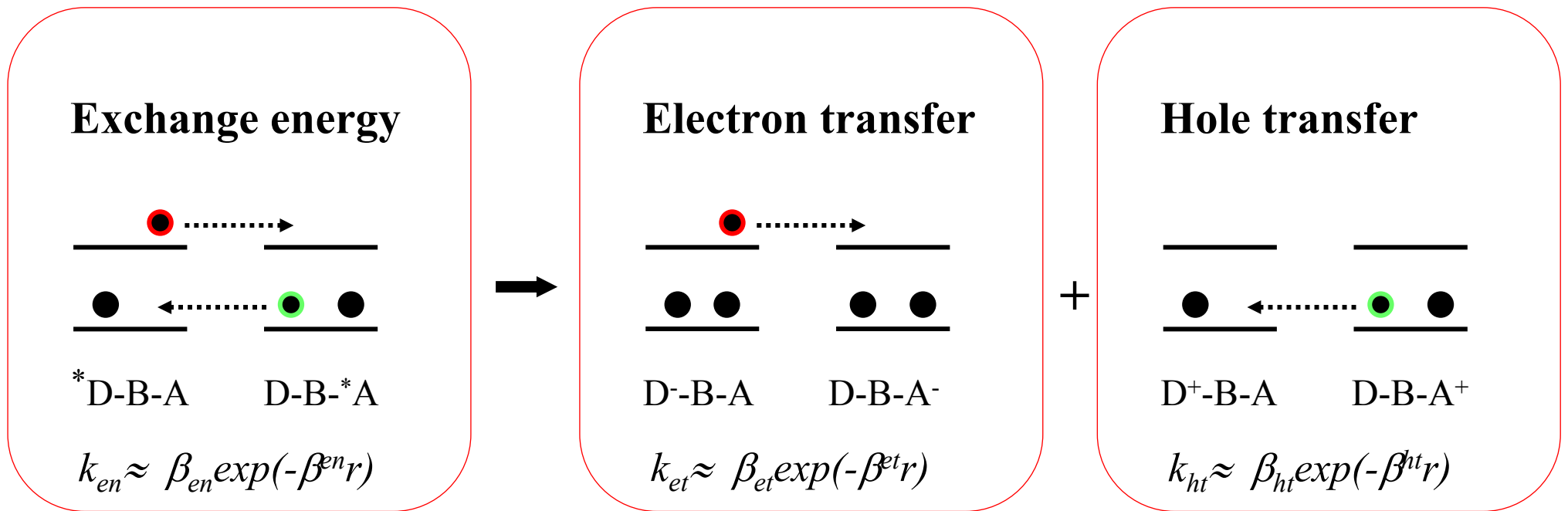
## Coulombic mechanism (resonance, Förster-type, TS)

- long-range mechanism, does not require physical contact between donor and acceptor
- dipole-dipole term -  $1/r_{AB}^3$  distance dependence
- efficient for systems with high oscillator strength - singlet-singlet transitions

## Exchange mechanism (Dexter-type, TB)

- requires orbital overlap between donor and acceptor, directly or via the bridge
- exponential distance dependence
- $\beta^{en}$  sum of  $\beta^{et}$  and  $\beta^{ht}$
- triplet-triplet transitions

# Exchange interaction - double electron transfer process



$$k_{en} \approx C k_{et} k_{ht} \quad \beta^{en} \approx \beta^{et} + \beta^{ht}$$

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