The Configuration Interaction method
Principle and practical examples

The HF wavefunction

HF approximation

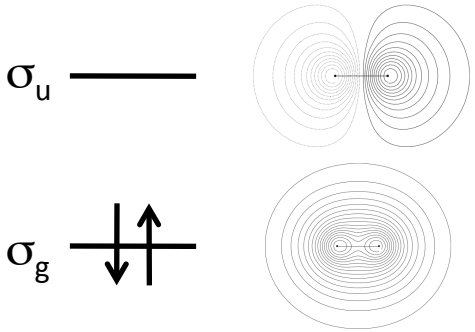
one single Slater determinant is used, corresponding to the occupation of the lowest-energy MOs:

$$\Phi(1,2,3..N) = N\begin{vmatrix} \phi_1(1) & \phi_2(1) & \dots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \dots & \phi_N(2) \\ \dots & \dots & \dots & \dots \\ \phi_1(N) & \phi_2(N) & \dots & \phi_N(N) \end{vmatrix}$$

The one-electron functions ϕ_i are the spin-MOs:

$$\phi_i(i) = \varphi_i(x_i, y_i, z_i) \times \xi_i(\sigma)$$

H_2 molecule in the LCAO approximation



$$\psi(1,2) = \frac{1}{\sqrt{2}}\sigma_g(1)\sigma_g(2) \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$\sigma_g = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B)$$

$$\sigma_u = \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B)$$

$$\psi(1,2) = \frac{1}{2\sqrt{2}(1+S)}(1s_A(1) + 1s_B(1))(1s_A(2) + 1s_B(2)) \times [spin]$$

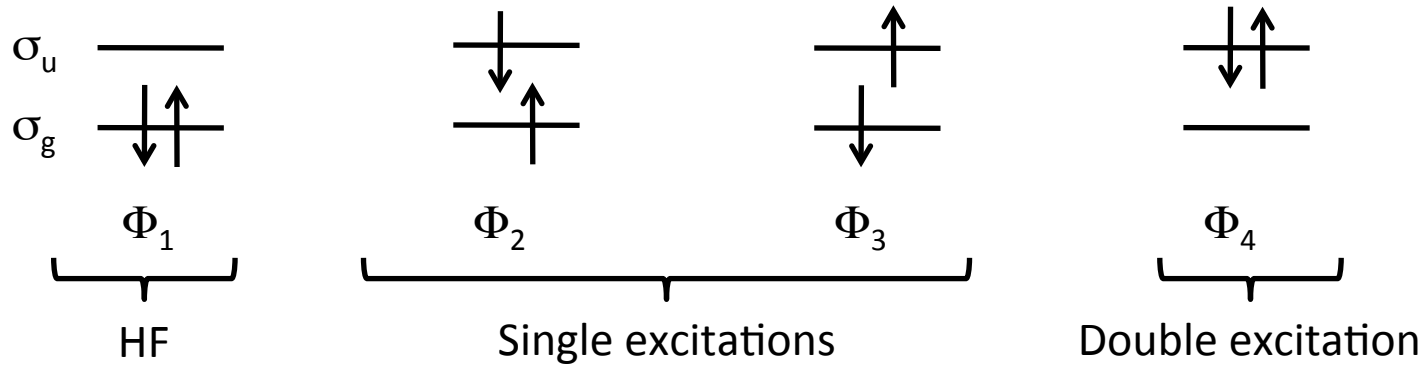
$$= \frac{1}{2\sqrt{2}(1+S)}\left\{\underbrace{1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)}_{\text{ionic configurations}} + \underbrace{1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)}_{\text{covalent configuartions}}\right\} \times [spin]$$

The CI wavefunction

Linear combination of Slater determinants: various occupations of the MOs are allowed

$$\Psi^{IC} = \sum_k C_k \Phi_k$$

Electron configurations for the H_2 molecule in the LCAO approximation



$\Psi^{IC} = C_1\Phi_1 + C_2\Phi_2 + C_3\Phi_3 + C_4\Phi_4$

Combining 4 Slater determinants → 4 CI electronic states
(ground state + 3 excited states)

Calculation of the CI expansion coefficients C_k

$$\Psi^{IC} = \sum_{k=1}^{M} C_k \Phi_k$$

CI coefficients obtained from the diagonalisation of the CI matrix
M Slater determinants → CI matrix **H** of dimension (M×M)

$$\mathbf{H} = \begin{pmatrix} \langle \Phi_1 | \hat{H} | \Phi_1 \rangle & \langle \Phi_2 | \hat{H} | \Phi_1 \rangle & \ldots & \langle \Phi_M | \hat{H} | \Phi_1 \rangle \\ \langle \Phi_1 | \hat{H} | \Phi_2 \rangle & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ \langle \Phi_1 | \hat{H} | \Phi_M \rangle & \ldots & \ldots & \langle \Phi_M | \hat{H} | \Phi_M \rangle \end{pmatrix}$$

Diagonal terms = energies of each electron configuration
Off-diagonal terms = couplings between the various configurations

Slater rules

Only 3 types of non zero $\left\langle \Phi_i \middle| \hat{H} \middle| \Phi_j \right\rangle$ terms in the CI matrix

1) Φ_i and Φ_j are identical (diagonal terms)

$$\langle \Phi | \hat{H} | \Phi \rangle = \sum_m \langle m | \hat{h} | m \rangle + \frac{1}{2} \sum_m \sum_n \left[(mm|nn) - (mn|mn) \right]$$

2) Φ_i and Φ_j differ by 1 spin-MO: Φ_i = |…m…> ; Φ_j = |…p…>

$$\left\langle \Phi_i \middle| \hat{H} \middle| \Phi_j \right\rangle = \langle m | \hat{h} | p \rangle + \sum_n \left[(mp|nn) - (mn|pp) \right]$$

Brillouin's theorem: no coupling between the HF and the single excited configurations

$$\left\langle \Phi_{HF} \middle| \hat{H} \middle| \Phi_{SINGLE} \right\rangle = \langle m | \hat{F} | p \rangle = 0$$

3) Φ_i and Φ_j differ by 2 spin-MOs: Φ_i = |…mn…> ; Φ_j = |…pq…>

$$\left\langle \Phi_i \middle| \hat{H} \middle| \Phi_j \right\rangle = (mp|nq) - (mq|np)$$

General form of the CI matrix

$$\mathbf{H} = \begin{pmatrix} \langle \Phi_{HF} | \hat{H} | \Phi_{HF} \rangle & 0 & \langle \Phi_D | \hat{H} | \Phi_{HF} \rangle & 0 & 0 & 0 \\ 0 & \langle \Phi_S | \hat{H} | \Phi_S \rangle & \langle \Phi_D | \hat{H} | \Phi_S \rangle & \langle \Phi_T | \hat{H} | \Phi_S \rangle & 0 & 0 \\ \langle \Phi_{HF} | \hat{H} | \Phi_D \rangle & \langle \Phi_S | \hat{H} | \Phi_D \rangle & \langle \Phi_D | \hat{H} | \Phi_D \rangle & \langle \Phi_T | \hat{H} | \Phi_D \rangle & \langle \Phi_Q | \hat{H} | \Phi_D \rangle & 0 \\ 0 & \langle \Phi_S | \hat{H} | \Phi_T \rangle & \langle \Phi_D | \hat{H} | \Phi_T \rangle & \langle \Phi_T | \hat{H} | \Phi_T \rangle & \langle \Phi_Q | \hat{H} | \Phi_T \rangle & \ldots \\ 0 & 0 & \langle \Phi_D | \hat{H} | \Phi_Q \rangle & \langle \Phi_T | \hat{H} | \Phi_Q \rangle & \langle \Phi_Q | \hat{H} | \Phi_Q \rangle & \ldots \\ 0 & 0 & 0 & \ldots & \ldots & \ldots \end{pmatrix}$$

CI matrix for the H_2 molecule

4 Slater determinants → CI matrix of dimension (4×4)

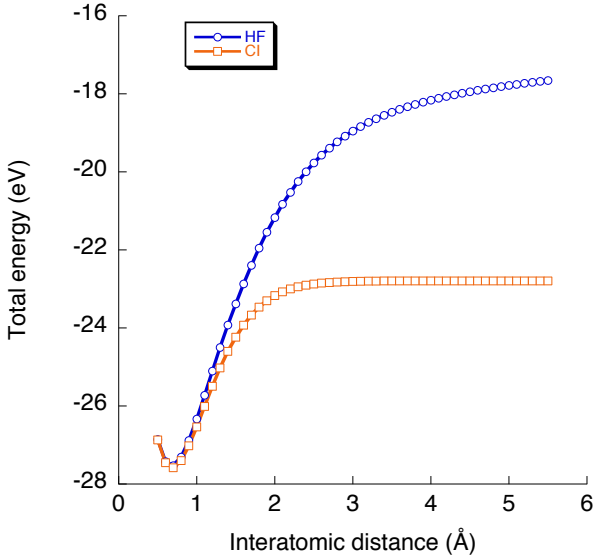
$$\mathbf{H} = \begin{pmatrix} \langle \Phi_1 | \hat{H} | \Phi_1 \rangle & 0 & 0 & \langle \Phi_4 | \hat{H} | \Phi_1 \rangle \\ 0 & \langle \Phi_2 | \hat{H} | \Phi_2 \rangle & \langle \Phi_3 | \hat{H} | \Phi_2 \rangle & \langle \Phi_4 | \hat{H} | \Phi_2 \rangle \\ 0 & \langle \Phi_2 | \hat{H} | \Phi_3 \rangle & \langle \Phi_3 | \hat{H} | \Phi_3 \rangle & \langle \Phi_4 | \hat{H} | \Phi_3 \rangle \\ \langle \Phi_1 | \hat{H} | \Phi_4 \rangle & \langle \Phi_2 | \hat{H} | \Phi_4 \rangle & \langle \Phi_3 | \hat{H} | \Phi_4 \rangle & \langle \Phi_4 | \hat{H} | \Phi_4 \rangle \end{pmatrix}$$

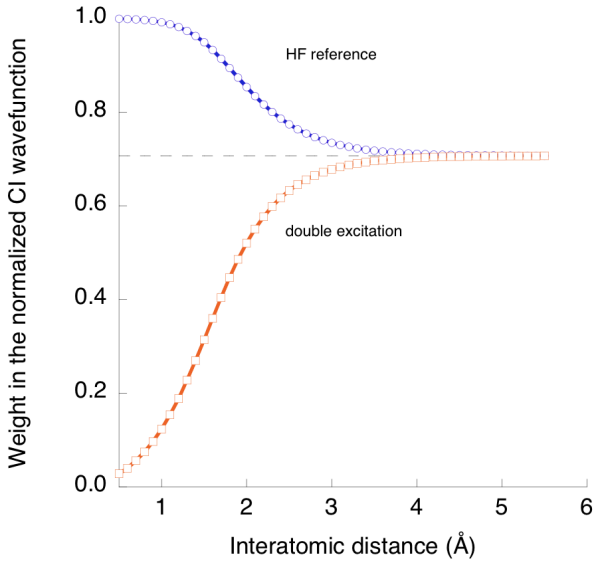
CI/AM1 calculation

```
C.I. MATRIX (eV)
                    1           2           3           4
-------------------------------------------------------
         1 -41.755076
         2   0.000000 -32.867376
         3   0.000000  -0.924620 -32.867376
         4   0.924620   0.000000   0.000000 -23.979294

C.I. MATRIX (eV) – energies relative to the HF configuration
                    1           2           3           4
-------------------------------------------------------
         1   0.000000
         2   0.000000   8.888081
         3   0.000000  -0.924620   8.888081
         4   0.924620   0.000000   0.000000  17.776162
```

Dissociation of the H_2 molecule





HF

$\Psi^{HF} = \Phi_1$

$\Psi^{HF} = 50\%(H^+/^-H) + 50\%(H\bullet/\bullet H)$

CI

$\Psi^{CI} = C\times(\Phi_1) + \sqrt{(1-C^2)}\times(\Phi_4)$

$C = f(R)$

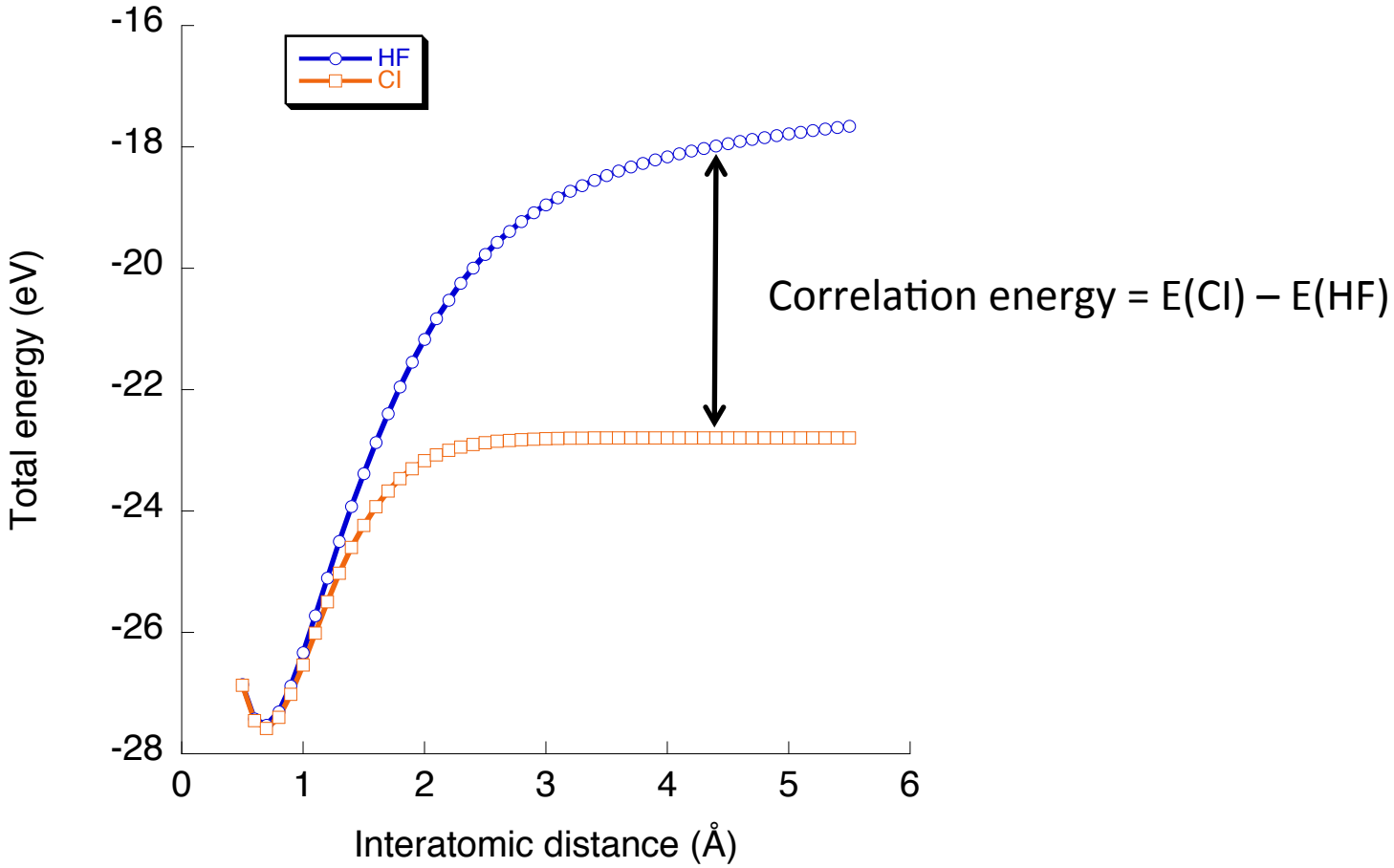
$R \rightarrow R_{eq}$ $C \rightarrow 1$ $\Psi^{CI} \approx \Phi_1$

$50\%(H^+/^-H) + 50\%(H\bullet/\bullet H)$

$R \rightarrow \infty$ $C \rightarrow 1/\sqrt{2}$ $\Psi^{CI} = 1/\sqrt{2}\times\Phi_1 + 1/\sqrt{2}\times\Phi_4$

$100\%(H\bullet/\bullet H)$

Correlation energy



Practical limitation of CI: Large systems

CI expansion over M Slater determinants

$$\Psi^{IC} = \sum_{k=1}^{M} C_k \Phi_k$$

N electrons in K MOs
Number of Slater determinants: combinatorial explosion

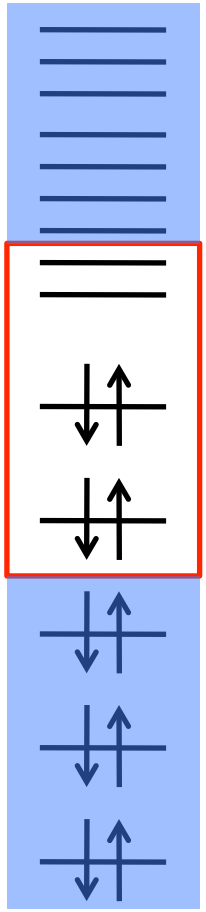
$$M = C_N^{2K} = \frac{2K!}{N!(2K-N)!}$$

Example of benzene:
N = 30 electrons in K = 30 valence MOs → M = $1.18 \times 10^{+17}$

Full CI impossible in most cases

Truncated CI calculation

Selection of a small number of « active » MOs



Always unoccupied

Active MO space

Always occupied

Selection of a few types of electron excitations

Only Singles (SCI)
Singles + Doubles (SDCI)

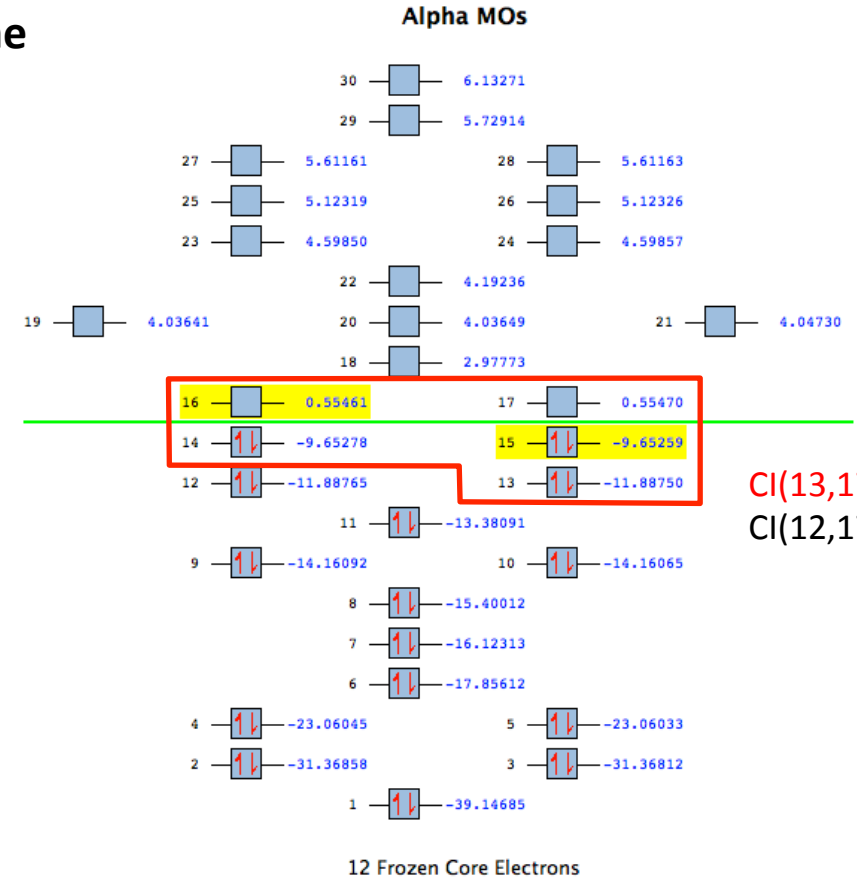
If all possible types of excitation within the active space are included:
→ Complete Active Space (CAS) calculation

Note:
SCI: does not change the total energy of the ground state compared to HF (Brillouin's theorem). Frequently used for simulating absorption spectra.

Active space definition

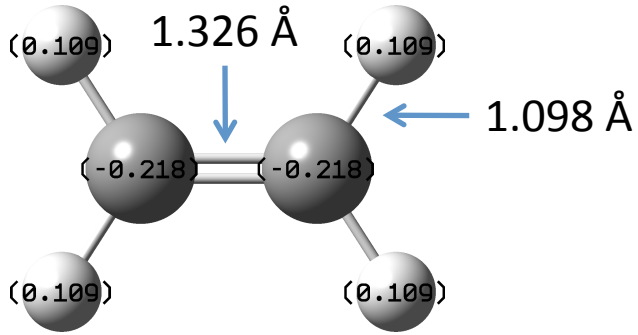
The active space should:
- be « sufficiently large » (tests vs. size)
- respect the symmetry of the molecule (MOs degeneracies)
- (for photo-chemistry) include all the MOs of interest *along all the reaction path*

Example of benzene

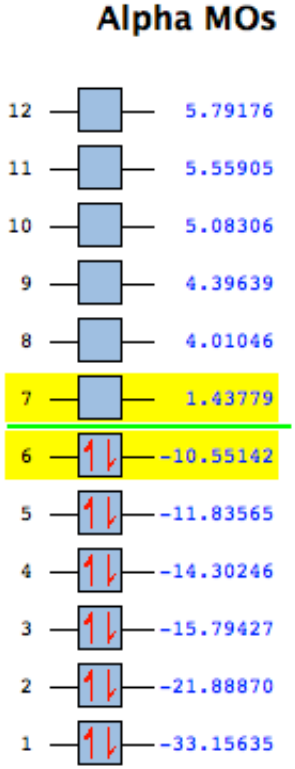


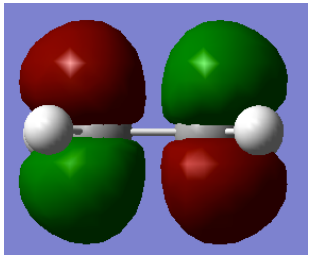
CI(13,17): not correct
CI(12,17) or CI(14,17) are correct

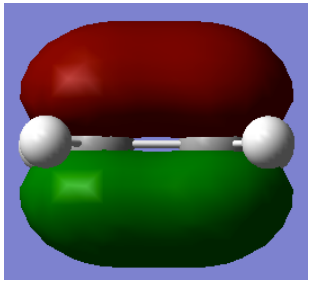
Ethylene molecule
SCF/AM1 calculation



FINAL HEAT OF FORMATION	=	16.471116 kcal
	=	68.931621 kJ
ELECTRONIC ENERGY	=	-737.526966 eV
CORE-CORE REPULSION	=	427.165969 eV
TOTAL ENERGY	=	-310.360997 eV
GRADIENT NORM	=	0.004842
RMS GRADIENT NORM	=	0.001398
IONIZATION POTENTIAL	=	10.551419 eV
HOMO-LUMO GAP	=	11.989210 eV



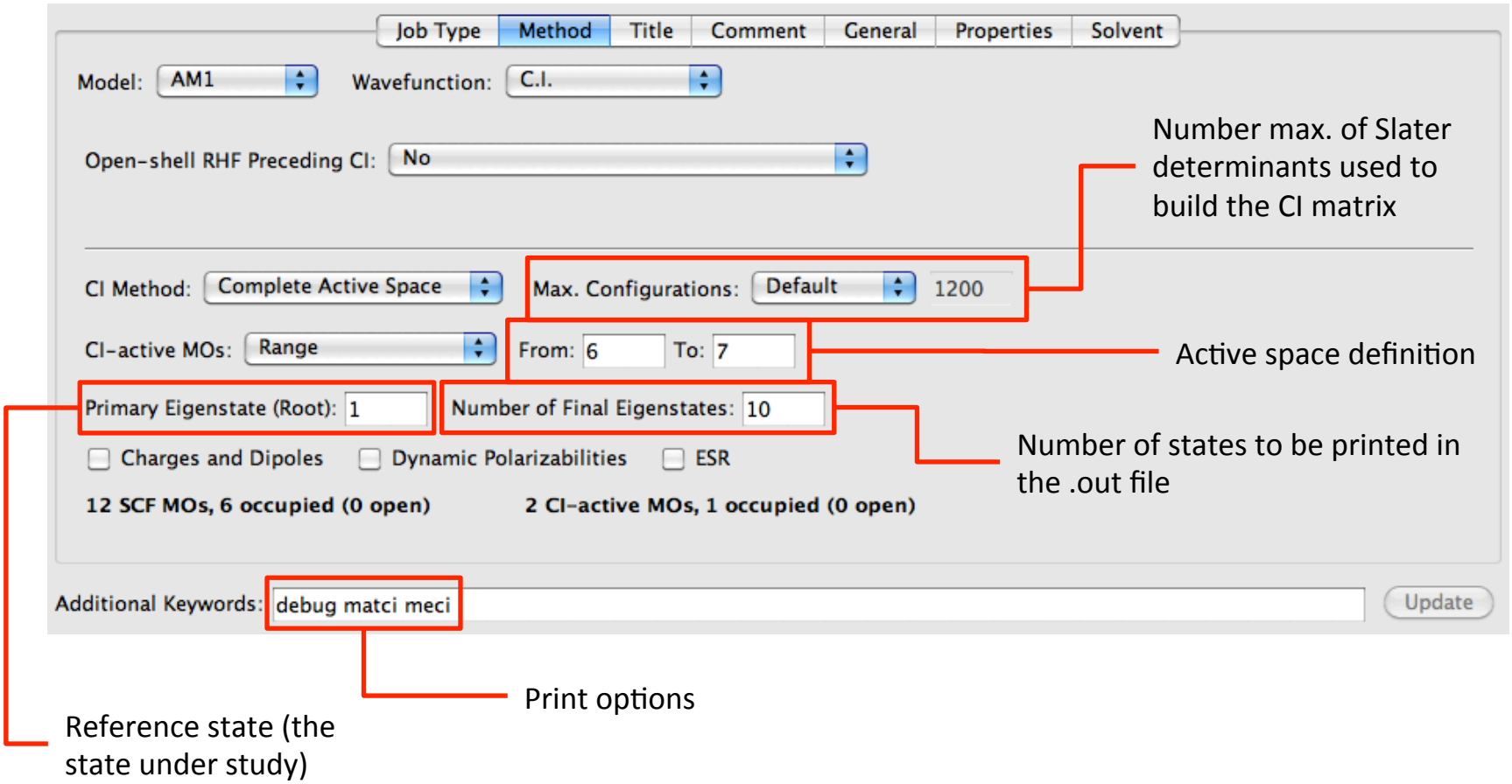




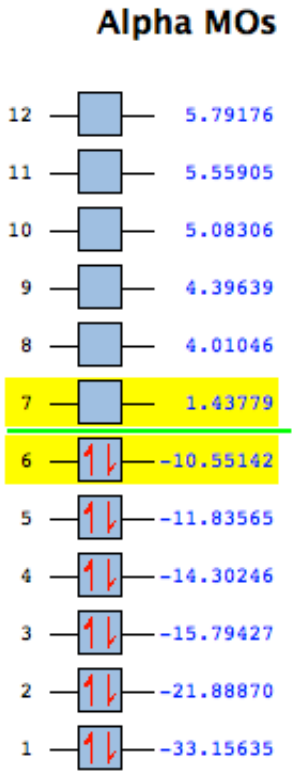
4 Frozen Core Electrons

Ethylene molecule
CI(6,7)/AM1 calculation (frozen geometry)

Start from the geometry optimized at the SCF/AM1 level
Job type = energy



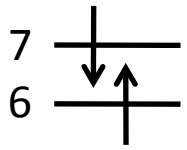
Ethylene molecule
CI(6,7)/AM1 calculation (frozen geometry)

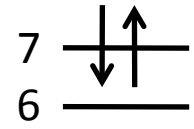


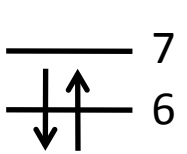
4 Frozen Core Electrons

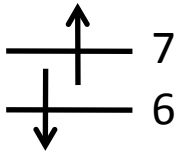
CONFIGURATIONS CONSIDERED IN C.I.

M.O. NUMBER : 6 7









1	1	0	RHF state Φ_1
0.00000 eV	1	0	
2	1	0	Single excitations Φ_2 and Φ_3
4.52813 eV	0	1	
3	0	1	
4.52813 eV	1	0	
4	0	1	Double excitation Φ_4
9.05625 eV	0	1	

C.I. MATRIX (eV)

	1	2	3	4
1	0.000000			
2	0.000000	4.528126		
3	0.000000	-1.809479	4.528126	
4	1.809479	0.000000	0.000000	9.056251

Ethylene molecule
CI(6,7)/AM1 calculation (frozen geometry)

C.I. MATRIX (eV)

	1	2	3	4
1	0.000000			
2	0.000000	4.528126		
3	0.000000	-1.809479	4.528126	
4	1.809479	0.000000	0.000000	9.056251

diagonalisation

MO: 00	1:SINGLET	2:TRIPLET	3:SINGLET	4:SINGLET
: 67	eV: 0.0000	3.0668	6.6858	9.7526
1 20	96%	0%	0%	4%
	(0.9820)	(0.0000)	(0.0000)	(0.1889)
2 +-	0%	50%	50%	0%
	(0.0000)	(0.7071)	(0.7071)	(0.0000)
3 -+	0%	50%	50%	0%
	(0.0000)	(0.7071)	(-0.7071)	(0.0000)
4 02	4%	0%	0%	96%
	(-0.1889)	(0.0000)	(0.0000)	(0.9820)

CI ground state:

$\Psi_1 = 0.9820\Phi_1 - 0.1889\Phi_4$

First excited state (triplet):

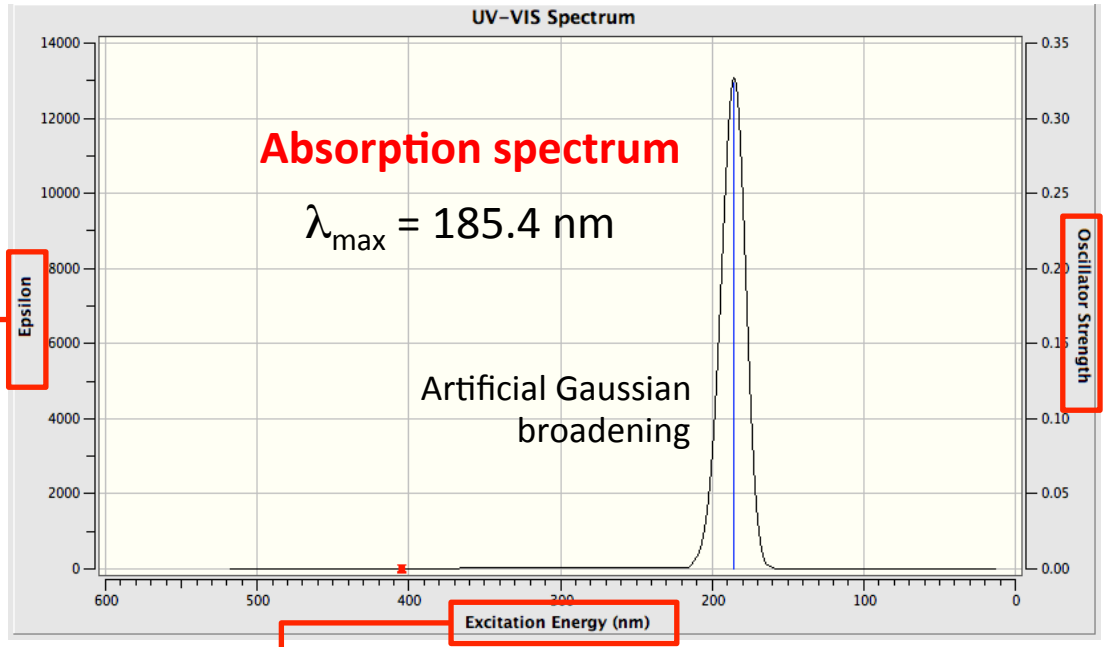
$\Psi_1 = 0.707\Phi_2 + 0.707\Phi_3$

Second excited (singlet):

$\Psi_1 = 0.707\Phi_2 - 0.707\Phi_3$

Ethylene molecule
CI(6,7)/AM1 calculation (frozen geometry)

```
TRANSITION DIPOLE (A.U.) AND OSC. STRENGTHS FROM STATE  1 (SINGLET) TO OTHERS
STATE   eV       nm       X       Y       Z     STRENGTH
  2    3.067    404.3                                  FORBIDDEN TO TRIPLET
  3    6.686    185.4  -1.4051  0.0000  0.0000  0.3234
  4    9.753    127.1   0.0000  0.0000  0.0000  0.0000
```



Transition dipole:

$$\vec{\mu}_{0e} = -|e|\langle \Psi_0 | \vec{r} | \Psi_e \rangle$$

Unit = C.m

1 a.u. of μ = 8.478358 10-30 C.m
= 2.5415 D

Oscillator strength:

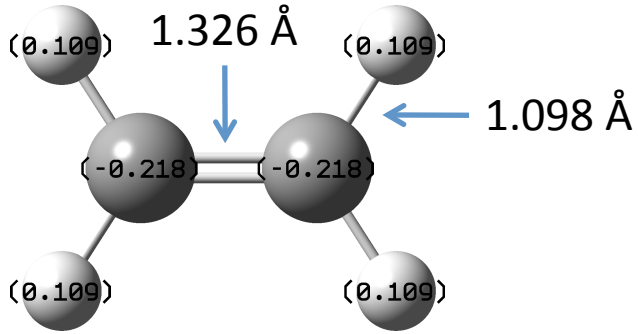
$$f_{0e} = \frac{2}{3}\Delta E |\vec{\mu}_{0e}|^2$$

Dimensionless

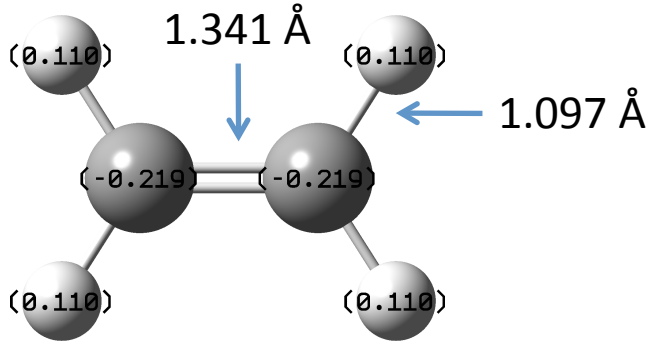
Proportional to the absorption intensity

Exctinction coefficient ε $f_{0e} \propto \int \varepsilon d\nu$; with ε in mol⁻1.cm⁻¹.L and ν in cm⁻¹, $f_{0e} \approx 4.3 \times 10^{-9} \int \varepsilon d\nu$

Ethylene molecule in its ground state
HF/AM1 calculation



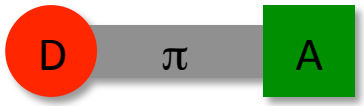
CI(6,7)/AM1 calculation



Change in the geometry:
$d_{C=C}$ increases by 0.015 Å due to the contribution of the double excitation in the ground state WF

Description of the optical properties of push–pull chromophores using essential-state models

Dipolar molecule



2-state model

$$|N\rangle = \text{D}\!-\!\text{A} \qquad E_N = 0$$

$$|Z\rangle = \text{D}^+\!-\!\text{A}^- \qquad E_Z = 2\eta$$

$$\langle N|\hat{H}|Z\rangle = -\sqrt{2}t$$

$$\langle N|Z\rangle = \delta_{NZ}$$

2 parameters: t and η
depend on the strength of the D/A groups
and on the nature of the conjugated bridge

Hamiltonian matrix

$$\mathbf{H} = \begin{pmatrix} 0 & -\sqrt{2}t \\ -\sqrt{2}t & 2\eta \end{pmatrix}$$

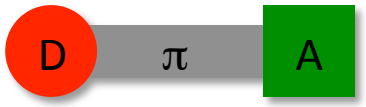
$$|g\rangle = \sqrt{(1-\rho)}\,|N\rangle + \sqrt{\rho}\,|Z\rangle$$

$$|e\rangle = \sqrt{\rho}\,|N\rangle - \sqrt{(1-\rho)}\,|Z\rangle \qquad (0 \le \rho \le 1)$$

ρ = amount of charge transfer
in the ground state (electron conjugation)

$\text{D}^{+\rho}\!-\!\text{A}^{-\rho}$

Dipolar molecule

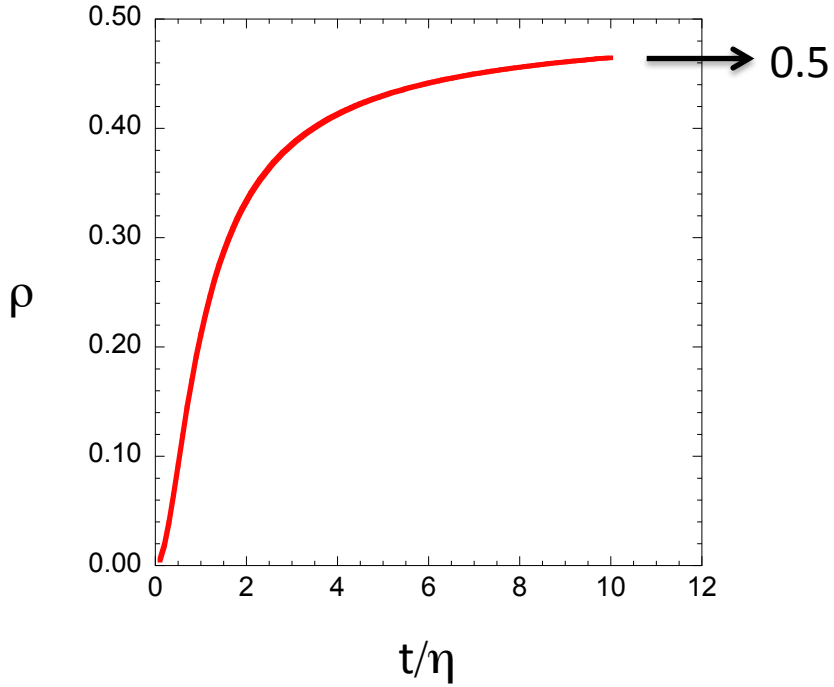


Diagonalization of the H matrix

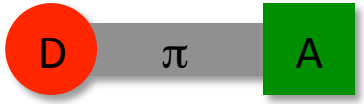
$$\begin{vmatrix} -\varepsilon & -\sqrt{2}t \\ -\sqrt{2}t & 2\eta-\varepsilon \end{vmatrix} = 0 \quad \Rightarrow \quad \begin{cases} \varepsilon_g = \eta\left(1-\sqrt{1+2t^2/\eta^2}\right) \\ \varepsilon_e = \eta\left(1+\sqrt{1+2t^2/\eta^2}\right) \end{cases} \quad \Rightarrow \quad \rho = \frac{t^2/\eta^2+1-\sqrt{1+2t^2/\eta^2}}{2t^2/\eta^2+1-\sqrt{1+2t^2/\eta^2}}$$

$2\eta = E_Z - E_N > 0$

$t > 0$



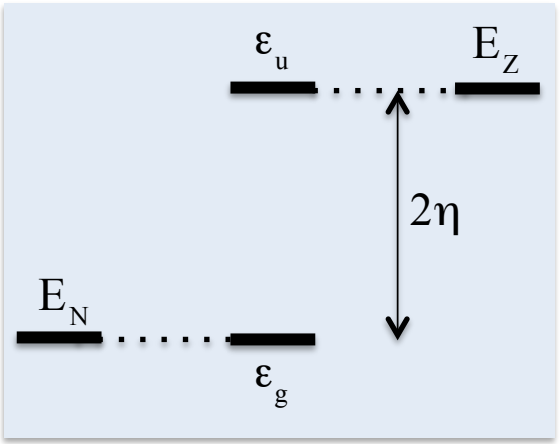
Dipolar molecule



Coupling diagrams

$$\rho = \frac{t^2/\eta^2 + 1 - \sqrt{1 + 2t^2/\eta^2}}{2t^2/\eta^2 + 1 - \sqrt{1 + 2t^2/\eta^2}}$$

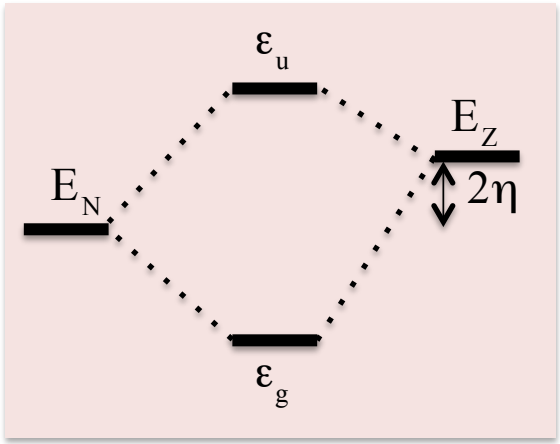
$t/\eta = 0 \Rightarrow \rho = 0$



$|g\rangle = |N\rangle$

D — A

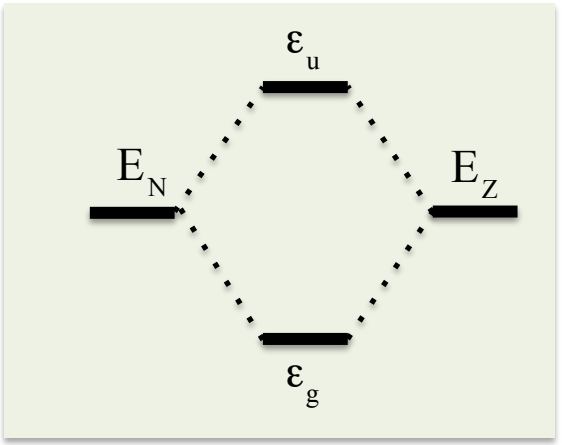
$t/\eta > 0 \Rightarrow 0 < \rho < 0.5$



$|g\rangle = \sqrt{(1-\rho)}|N\rangle + \sqrt{\rho}|Z\rangle$

$D^{+\rho}$ — $A^{-\rho}$

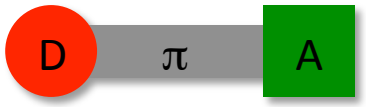
$t/\eta \to \infty \Rightarrow \rho \to 0.5$



$|g\rangle = \frac{1}{\sqrt{2}}|N\rangle + \frac{1}{\sqrt{2}}|Z\rangle$

$D^{+0.5}$ — $A^{-0.5}$

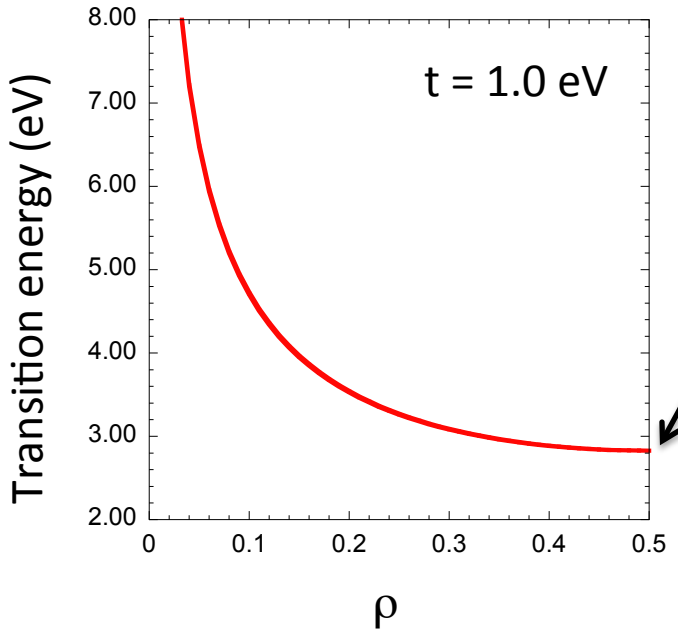
Dipolar molecule



Transition energy

$$\Delta E_{ge} = \varepsilon_e - \varepsilon_g = 2\sqrt{\eta^2 + 2t^2}$$

$$\Delta E_{ge} = \sqrt{2}t\sqrt{\frac{1}{(1-\rho)\rho}}$$

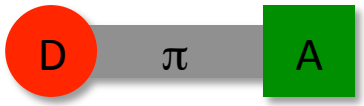


ΔE_{ge} *min for* $\rho = 0.5$

$D^{+0.5}$ — $A^{-0.5}$

The electron conjugation in the ground state lowers the transition energy

Dipolar molecule



Transition dipole

$|N\rangle =$ D — A $\quad \mu_N = \langle N|\hat{\mu}|N\rangle = 0$

$|Z\rangle =$ D$^+$ → A$^-$ $\quad \mu_Z = \langle Z|\hat{\mu}|Z\rangle = \mu_0$

$$\mu_{ge} = \langle g|\hat{\mu}|e\rangle$$

$$\mu_{ge} = \left\langle \sqrt{(1-\rho)}|N\rangle + \sqrt{\rho}|Z\rangle \middle| \hat{\mu} \middle| \sqrt{\rho}|N\rangle - \sqrt{(1-\rho)}|Z\rangle \right\rangle$$

We assume that $\langle N|\hat{\mu}|Z\rangle = \langle Z|\hat{\mu}|N\rangle = 0$

$$\Rightarrow \quad \mu_{ge} = \mu_0\sqrt{(1-\rho)\rho}$$

Oscillator strength

$$\Rightarrow \quad f_{ge} \propto \Delta E_{ge}|\mu_{ge}|^2 = \mu_0^2 t\sqrt{2(1-\rho)\rho}$$