Theoretical Chemistry

Frédéric Castet

frederic.castet@u-bordeaux.fr

université de BORDEAUX

Summary

- The Hartree-Fock-Roothaan method
- Pople and Dunning basis sets
- Semiempirical models
- **Configuration interaction**
- Möller-Plesset perturbation theory
- Density functional theory
- Time-dependent DFT

HARTREE-FOCK METHOD

Single determinant wavefunction

$$\Phi_{HF} = \frac{1}{\sqrt{(2N)!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \dots & \psi_{2N}(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \dots & \psi_{2N}(\mathbf{r}_2) \\ \dots & \dots & \dots & \dots \\ \psi_1(\mathbf{r}_{2N}) & \psi_2(\mathbf{r}_{2N}) & \dots & \psi_{2N}(\mathbf{r}_{2N}) \end{vmatrix}$$

Spin-orbitals

$$\psi_\mu(\mathbf{r}_\mu) = \phi_\mu(\mathbf{r}_\mu) \times \xi_\mu(\sigma_\mu)$$

Spin function α or β

Atomic or molecular orbital

Linear Combination of Atomic Orbitals (Roothan)

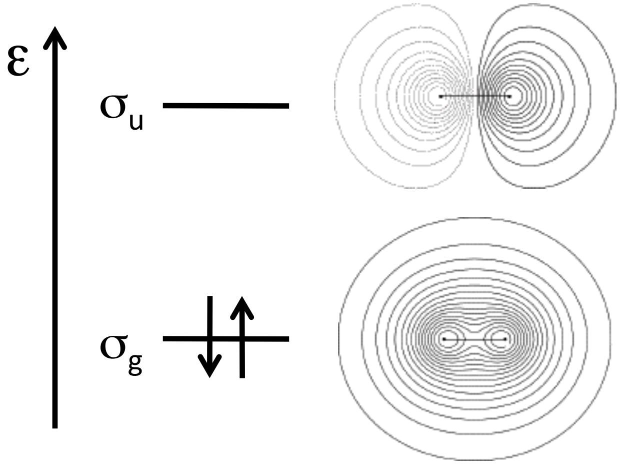
$$\phi_i(\mathbf{r}) = \sum_{p=1}^{M} C_{pi} \chi_p(\mathbf{r})$$

Atomic functions

Expansion coefficients = ***variational parameters***

HARTREE-FOCK METHOD

H_2 molecule in the LCAO approximation



$$\Phi_{\mathrm{HF}}\left(1,2\right)=\frac{1}{\sqrt{2}}\sigma_{\mathrm{g}}(1)\sigma_{\mathrm{g}}(2)\times\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]$$

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

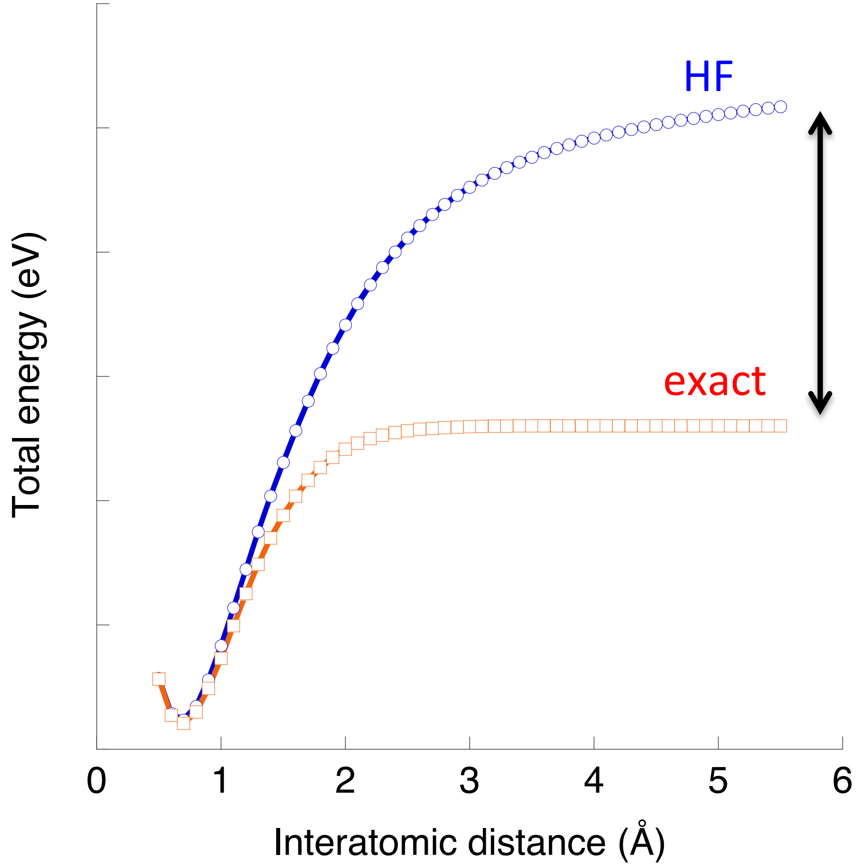
$$\sigma_u=\frac{1}{\sqrt{2(1-S)}}\left(1s_A-1s_B\right)$$

$$\Phi_{\mathrm{HF}}\left(1,2\right)=\frac{1}{4(1+\mathrm{S})}\left(1\mathrm{s}_{\mathrm{A}}(1)+1\mathrm{s}_{\mathrm{B}}(1)\right)\left(1\mathrm{s}_{\mathrm{A}}(2)+1\mathrm{s}_{\mathrm{B}}(2)\right)\times\left[\mathrm{spin}\right]$$

$$=\frac{1}{4(1+\mathrm{S})}\left\{\underbrace{1\mathrm{s}_{\mathrm{A}}(1)1\mathrm{s}_{\mathrm{A}}(2)+1\mathrm{s}_{\mathrm{B}}(1)1\mathrm{s}_{\mathrm{B}}(2)}_{\text{ionic configurations}}+\underbrace{1\mathrm{s}_{\mathrm{A}}(1)1\mathrm{s}_{\mathrm{B}}(2)+1\mathrm{s}_{\mathrm{B}}(1)1\mathrm{s}_{\mathrm{A}}(2)}_{\text{covalent configuartions}}\right\}\times\left[\mathrm{spin}\right]$$

HARTREE-FOCK METHOD

H_2 molecule in the LCAO approximation



Correlation energy

$E_{corr} = E_{exact} - E_{HF}$

CONFIGURATION INTERACTION

CI multi-determinant wavefunction

Linear combination of the reference (HF) configuration and of excited configurations

$$\Psi = a_0 \Phi_{HF} + \sum_{i=1} a_i \Phi_i$$

a_k = *variational parameters*

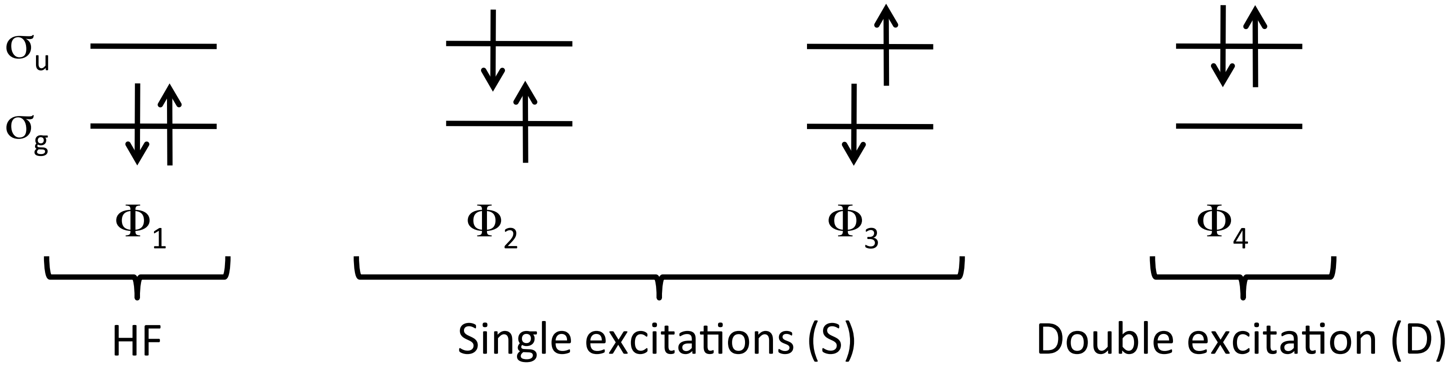
Full CI = includes ***all possible excited configurations***

Provides the exact (non-relativistic) energy of the ground and excited states (within the chosen LCAO model)

CONFIGURATION INTERACTION

CI multi-determinant wavefunction

Electron configurations for the H_2 molecule in the LCAO approximation



$\Psi^{IC} = a_1\Phi_1 + a_2\Phi_2 + a_3\Phi_3 + a_4\Phi_4$

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

CONFIGURATION INTERACTION

Calculation of the CI expansion coefficients a_k

CI coefficients obtained from the diagonalisation of the Hamiltonian matrix in the Slater determinants basis

M Slater determinants → CI matrix **H** of dimension (M×M)

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

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

CONFIGURATION INTERACTION

Slater rules

Only 3 types of non zero 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…>

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

CONFIGURATION INTERACTION

General form of the CI matrix

$$\mathbf{H} = \begin{pmatrix} \langle \Phi_{HF} | \hat{H} | \Phi_{HF} \rangle & 0 & \langle \Phi_{D} | \hat{H} | \Phi_{HF} \rangle & 0 & 0 & 0 \\ 0 & \langle \Phi_{S} | \hat{H} | \Phi_{S} \rangle & \langle \Phi_{D} | \hat{H} | \Phi_{S} \rangle & \langle \Phi_{T} | \hat{H} | \Phi_{S} \rangle & 0 & 0 \\ \langle \Phi_{HF} | \hat{H} | \Phi_{D} \rangle & \langle \Phi_{S} | \hat{H} | \Phi_{D} \rangle & \langle \Phi_{D} | \hat{H} | \Phi_{D} \rangle & \langle \Phi_{T} | \hat{H} | \Phi_{D} \rangle & \langle \Phi_{Q} | \hat{H} | \Phi_{D} \rangle & 0 \\ 0 & \langle \Phi_{S} | \hat{H} | \Phi_{T} \rangle & \langle \Phi_{D} | \hat{H} | \Phi_{T} \rangle & \langle \Phi_{T} | \hat{H} | \Phi_{T} \rangle & \langle \Phi_{Q} | \hat{H} | \Phi_{T} \rangle & \ldots \\ 0 & 0 & \langle \Phi_{D} | \hat{H} | \Phi_{Q} \rangle & \langle \Phi_{T} | \hat{H} | \Phi_{Q} \rangle & \langle \Phi_{Q} | \hat{H} | \Phi_{Q} \rangle & \ldots \\ 0 & 0 & 0 & \ldots & \ldots & \ldots \end{pmatrix}$$

CONFIGURATION INTERACTION

CI matrix for the H_2 molecule

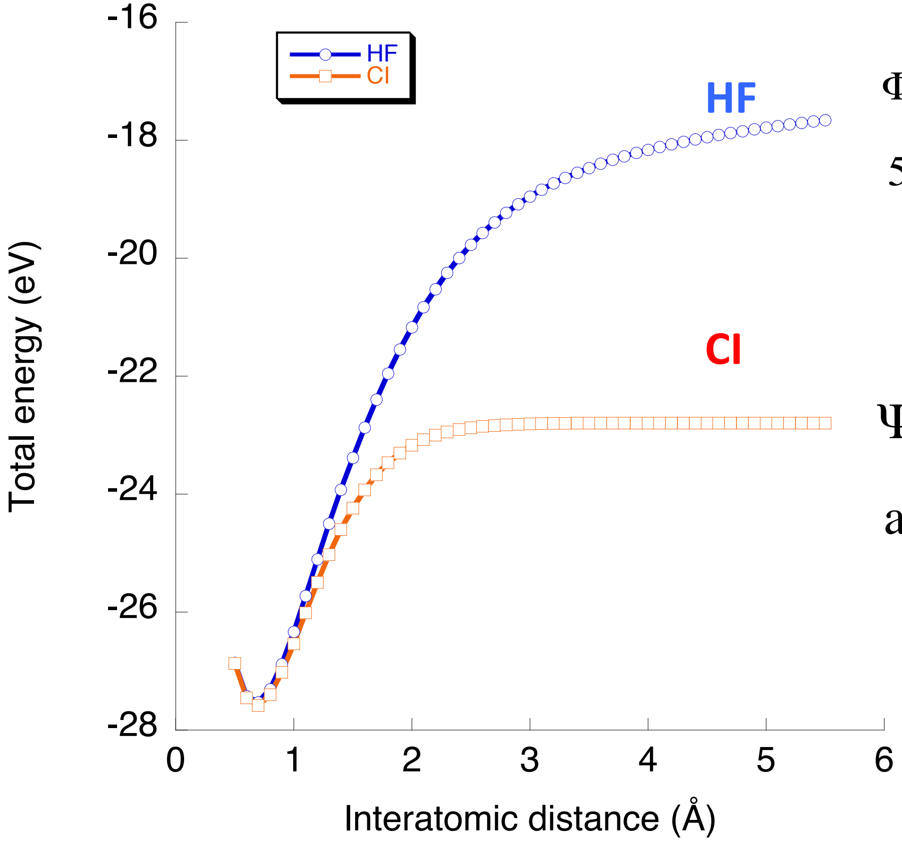
4 Slater determinants → CI matrix of dimension (4×4)

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

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
```

CONFIGURATION INTERACTION



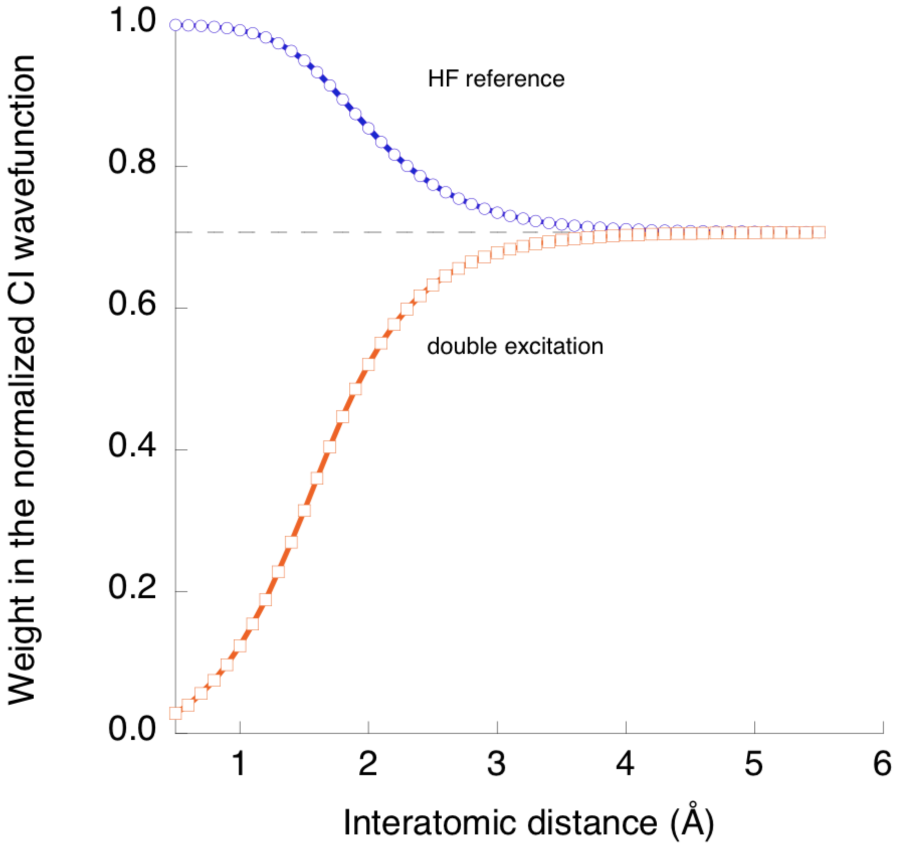
$$\Phi_{HF}(1,2) = \frac{1}{\sqrt{2}}\sigma_g(1)\sigma_g(2)\times\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]$$

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

$$\Psi = a_0\Phi_{HF} + \sqrt{\left(1-a_0^2\right)}\Phi_D$$

$$a_0 = f\left(R\right)$$

CONFIGURATION INTERACTION



$$R \rightarrow R_{eq} \quad \Rightarrow a_0 \rightarrow \approx 1$$

$$\Psi \approx \Phi_{HF}$$

$$R \rightarrow \infty \quad \Rightarrow a_0 \rightarrow \frac{1}{\sqrt{2}}$$

$$\Psi = \frac{1}{\sqrt{2}}\Phi_{HF} + \frac{1}{\sqrt{2}}\Phi_{D}$$

CONFIGURATION INTERACTION

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

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

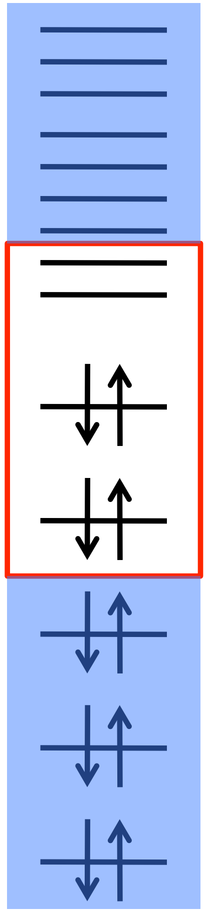
Example of benzene (valence electrons, single-zeta minimal basis set)**:**
N = 30 electrons in K = 30 valence MOs → M = $1.18 \times 10^{+17}$

Full CI impossible in most cases

CONFIGURATION INTERACTION

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)

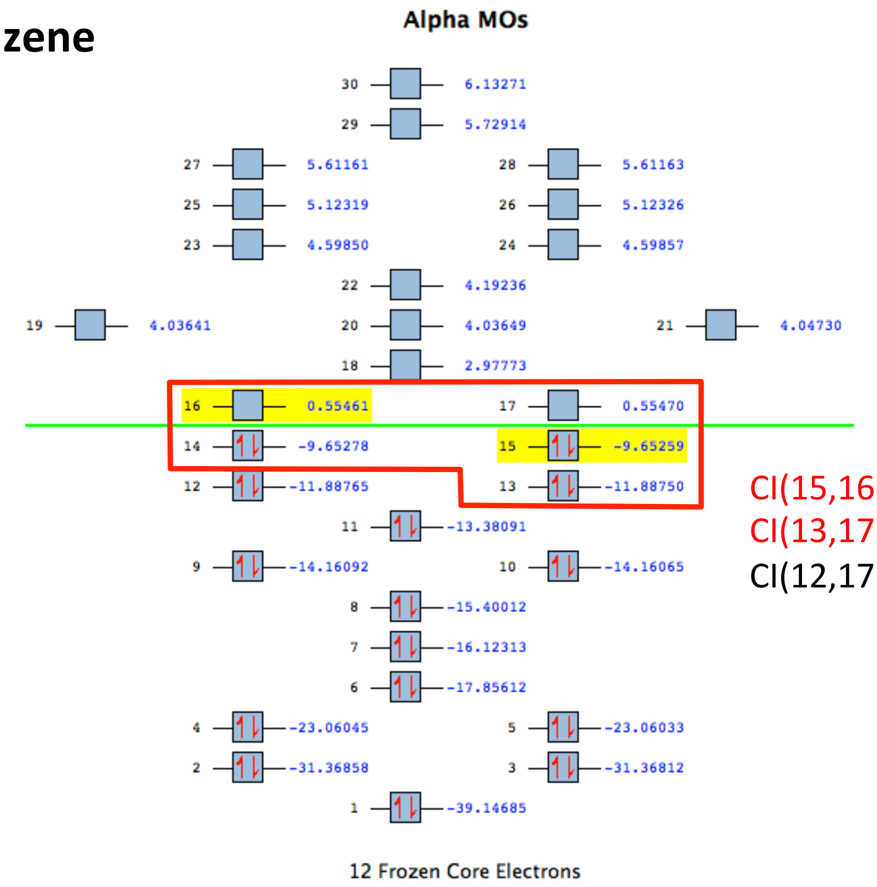
If all possible types of excitation within the active space are included:
→ Complete Active Space (CAS) calculation

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(15,16) = (HOMO,LUMO) not correct

CI(13,17): not correct

CI(12,17) or CI(14,17) are correct

MULTI-CONFIGURATIONAL SCF

Refinements of the CI scheme

$$\Psi = a_0 \Phi_{HF} + \sum_{i=1} a_i \Phi_i$$

MC-SCF: LCAO coefficients re-optimized in each excited configuration

CAS-SCF: *Complete Active Space SCF*
Account for *all possible* multiple excitations within the active MO space

Huge calculations, limited to small systems (<20 atoms)

Accuracy* : HF < IC < CAS-SCF

** for a given basis set and a given active MO space*

APPLICATION TO ABSORPTION SPECTROSCOPY

Accessible quantities from CI calculations

Transition energies and wavelengths

$\Delta\mathrm{E}, \lambda$

Transition dipoles

$$\vec{\mu}_{0\mathrm{e}} = -|e|\left\langle \Psi_0 \middle| \vec{r} \middle| \Psi_\mathrm{e} \right\rangle$$

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

Oscillator strengths

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

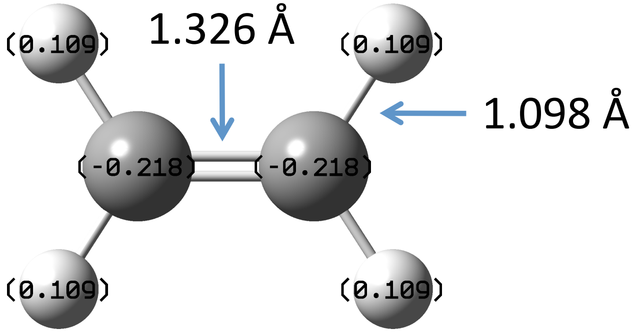
Dimensionless (proportional to the absorption intensity)

Exctinction coefficient ε $f_{0\mathrm{e}} \propto \int \varepsilon d\nu$

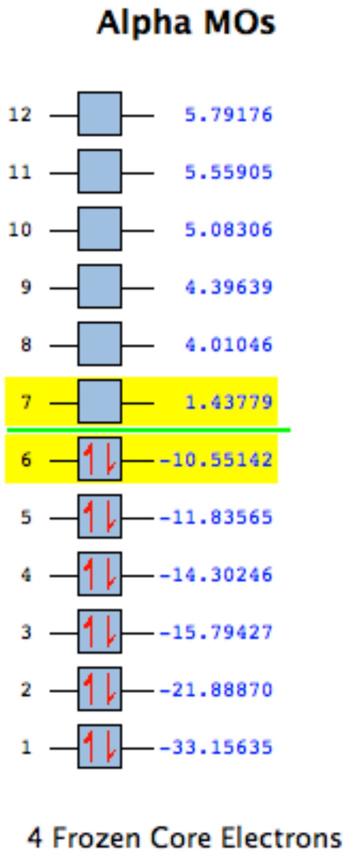
With ε in mol⁻1.cm⁻¹.L and ν in cm⁻¹, $f_{0\mathrm{e}} \approx 4.3 \times 10^{-9} \int \varepsilon d\nu$

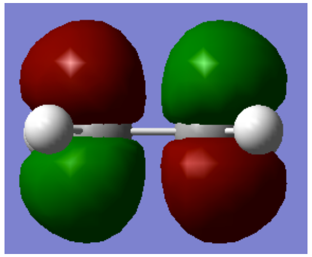
A CASE STUDY: THE ETHYLENE MOLECULE

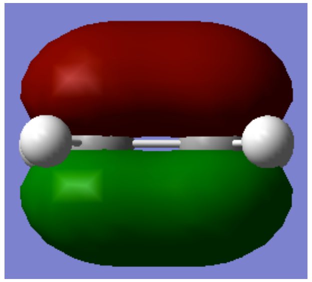
Ethylene molecule
SCF/AM1 calculation



```
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
```

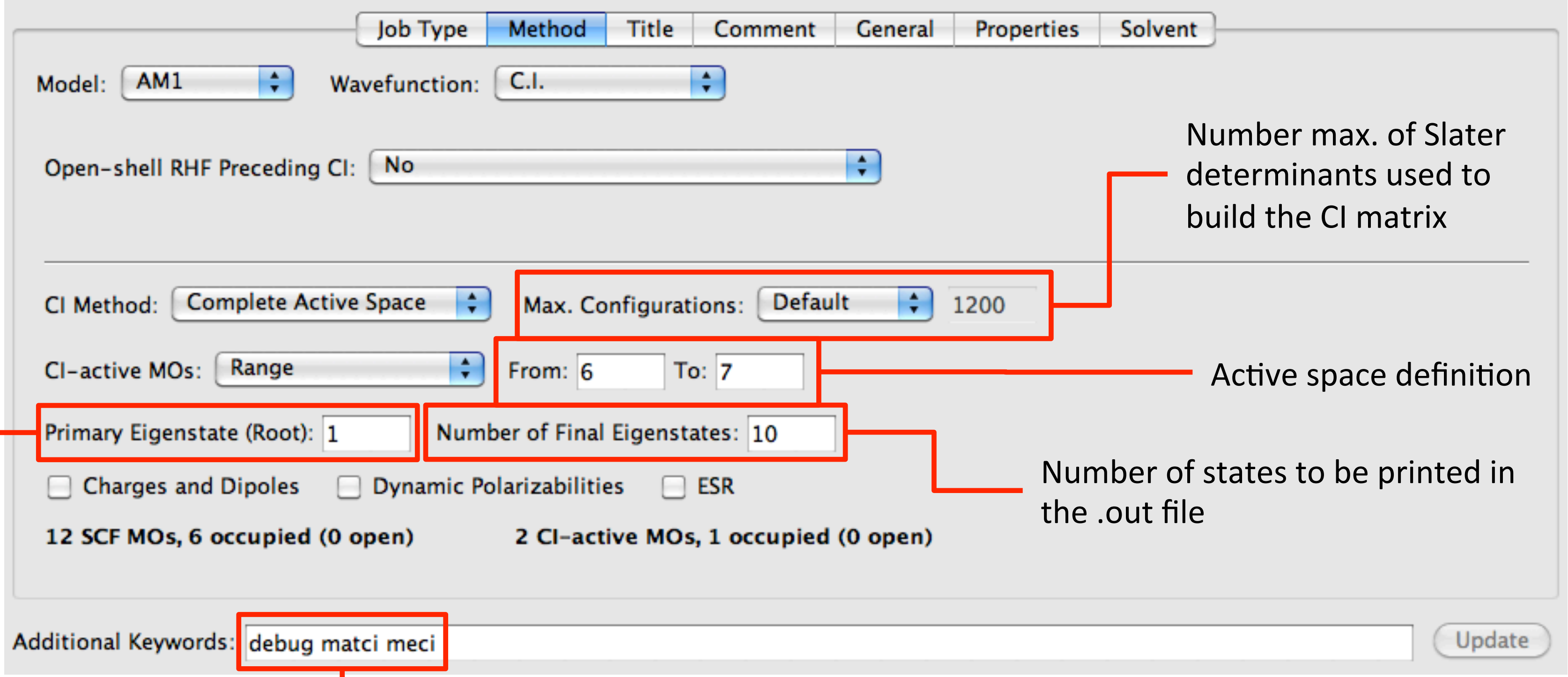






Ethylene molecule
CI(6,7)/AM1 calculation (frozen geometry)

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



Model: AM1
Wavefunction: C.I.
Open-shell RHF Preceding CI: No
CI Method: Complete Active Space
Max. Configurations: Default 1200
CI-active MOs: Range
From: 6 To: 7
Primary Eigenstate (Root): 1
Number of Final Eigenstates: 10
☐ Charges and Dipoles ☐ Dynamic Polarizabilities ☐ ESR
12 SCF MOs, 6 occupied (0 open)
2 CI-active MOs, 1 occupied (0 open)
Additional Keywords: debug matci meci

Number max. of Slater determinants used to build the CI matrix

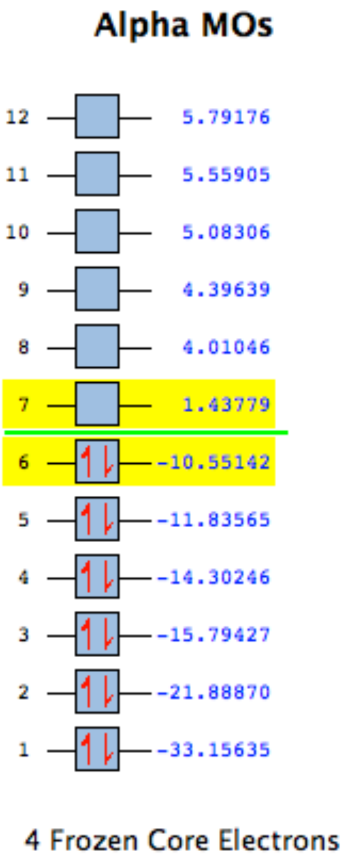
Active space definition

Number of states to be printed in the .out file

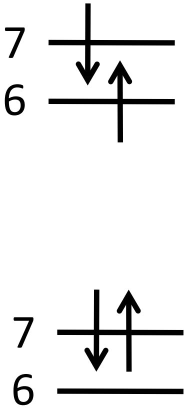
Print options

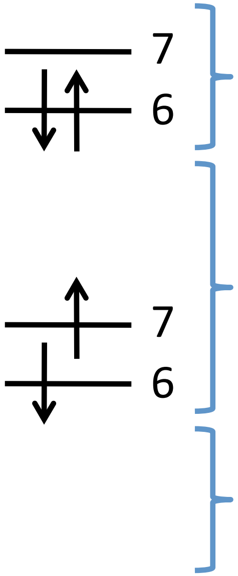
Reference state
(the state under study)

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



```
CONFIGURATIONS CONSIDERED IN C.I.
M.O. NUMBER :   6   7

                  1   1   0
  0.00000 eV      1   0

                  2   1   0
  4.52813 eV      0   1

                  3   0   1
  4.52813 eV      1   0

                  4   0   1
  9.05625 eV      0   1
```





RHF state Φ_1

Single excitations Φ_2 and Φ_3

Double excitation Φ_4

```
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):

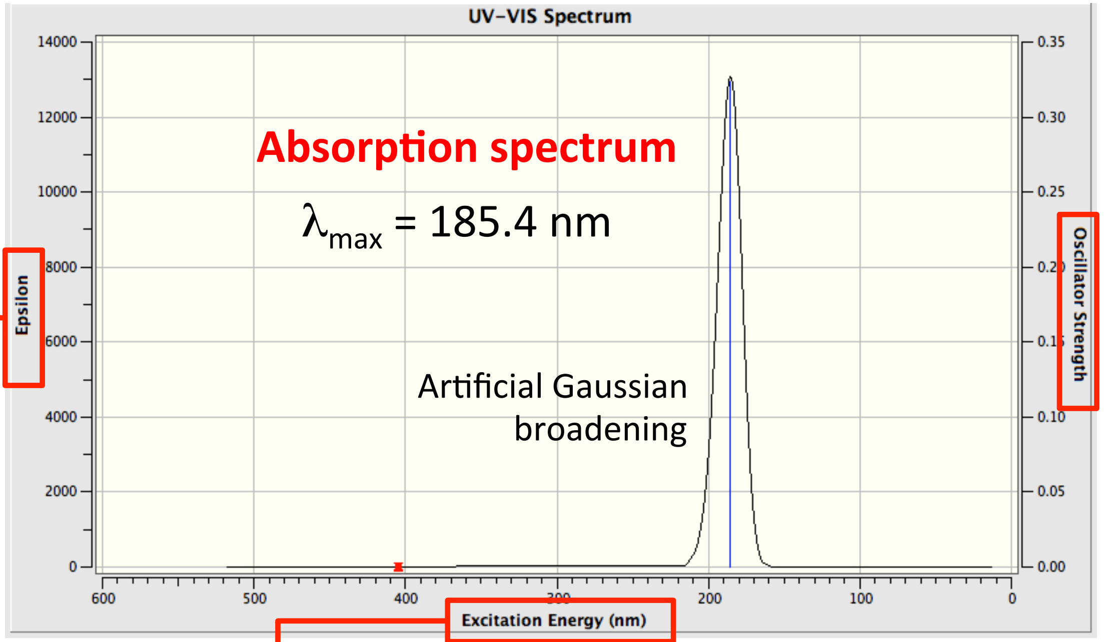
$$\Psi_1 = 0.707\Phi_2 + 0.707\Phi_3$$

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
```



Absorption spectrum

λ_{max} = 185.4 nm

Artificial Gaussian broadening

This is not an energy !

Transition dipole:

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

Unit = C.m

1 a.u. of μ = 8.478358 10-30 C.m

= 2.5415 D

Oscillator strength:

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

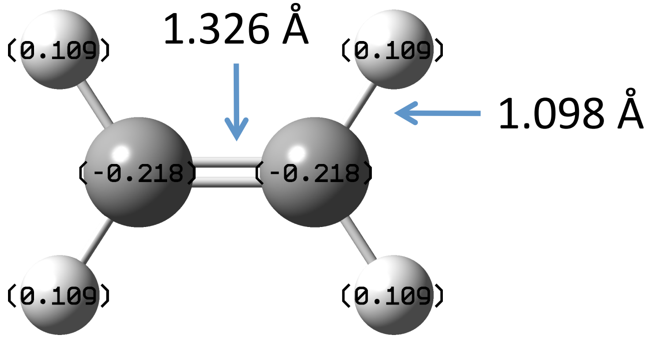
Dimensionless

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}, $f_{0e} \approx 4.3\times 10^{-9}\int \varepsilon d\nu$

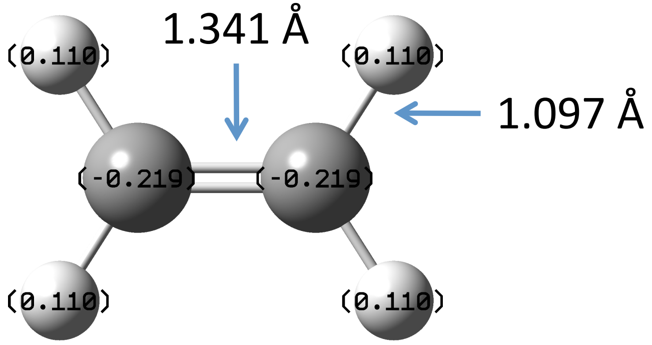
Ethylene molecule in its ground state

CI(6,7)/AM1 calculation (HF geometry)



Electronic structure of the ground state: unchanged from SCF/AM1 (symmetry reasons)

CI(6,7)/AM1 calculation (relaxed geometry)



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

APPLICATION TO EMISSION SPECTROSCOPY

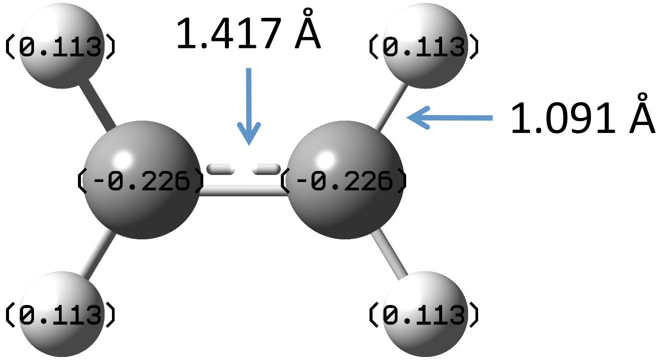
Ethylene molecule
CI(6,7)/AM1 calculation (geometry optimization of the first singlet excited state)

Keywords:

```
AM1 C.I.(6,7) CIDIP ROOT=2 SINGLET CISTATE=10 TRUSTE T=AUTO DEBUG MATCI MECI
```

or:

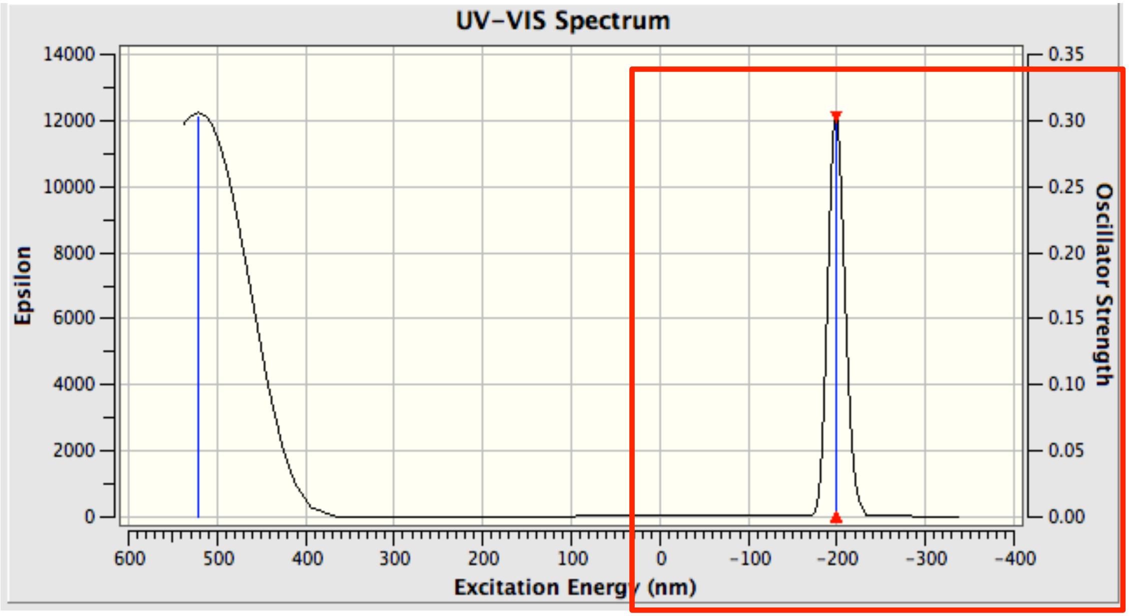
```
AM1 C.I.(6,7) CIDIP ROOT=3 CISTATE=10 TRUSTE T=AUTO DEBUG MATCI MECI
```



Compared to the ground state, $d_{C–C}$ increases by 0.076 Å
Intermediate between single and double bond

Ethylene molecule
CI(6,7)/AM1 calculation (geometry optimization of the first singlet excited state)

```
TRANSITION DIPOLE (A.U.) AND OSC. STRENGTHS FROM STATE  3 (SINGLET) TO OTHERS
 STATE   eV        nm        X        Y        Z      STRENGTH
   1   -6.237    -198.8   1.4070   0.0000   0.0000   0.3025
   2   -3.859    -321.3                                      FORBIDDEN TO TRIPLET
   4    2.378     521.4   2.2786   0.0000   0.0000   0.3025
```



Emission spectrum

λ_{max} = 198.8 nm