Hartree-Fock (HF) Equations

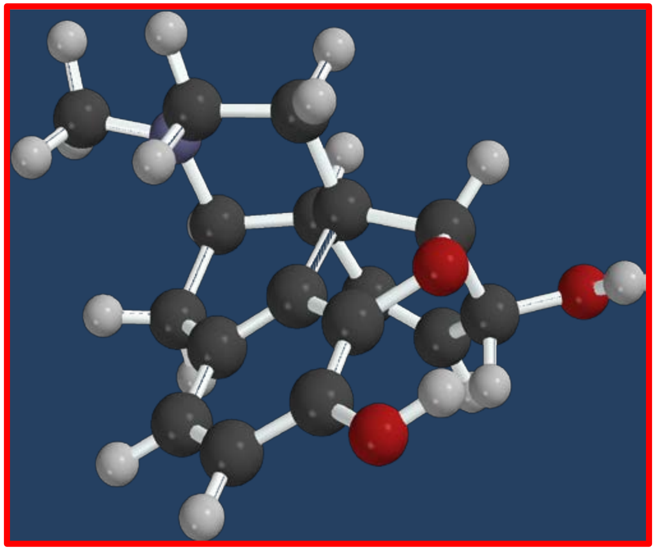
Computational Chemistry
Elective Course
Chemistry Degree
4th Year

Contents

- Molecular Hamiltonian
- Many-electron and one-electron functions
- Molecular energy: core, Coulomb and exchange integrals
- Coulomb and exchange operators
- Optimal spin-orbitals : Brillouin theorem
- Fock operator: HF equations
- Canonical HF Equations

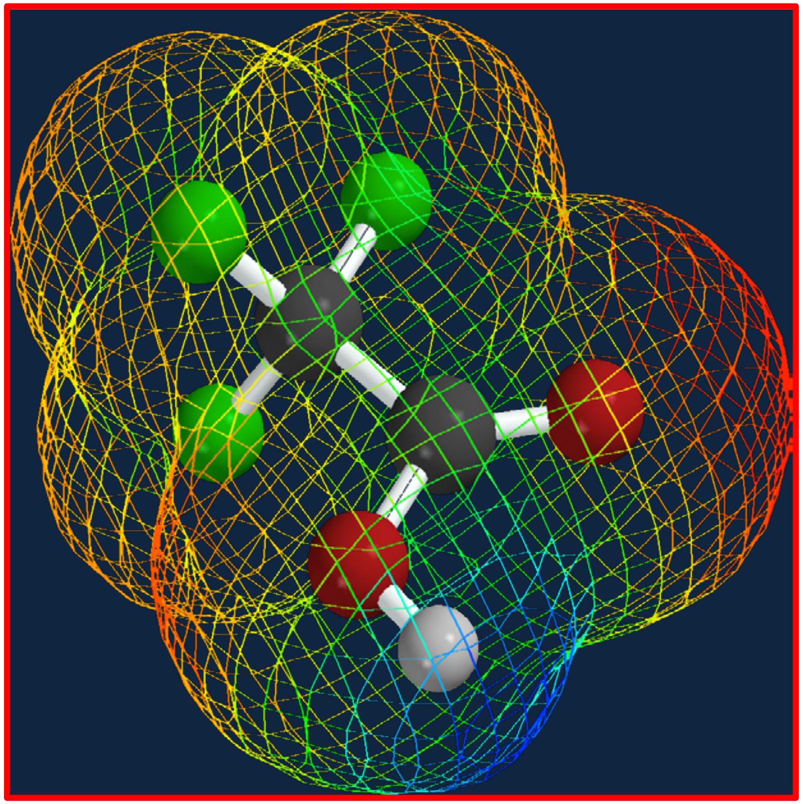
How do we represent a molecule?

- N electrons and M nuclei
- Fixed nuclei in a given position (Born-Oppenheimer approx.)
- Electrostatic interactions between point charges
- → (Differential) Schrödinger equation not resolvable analytically



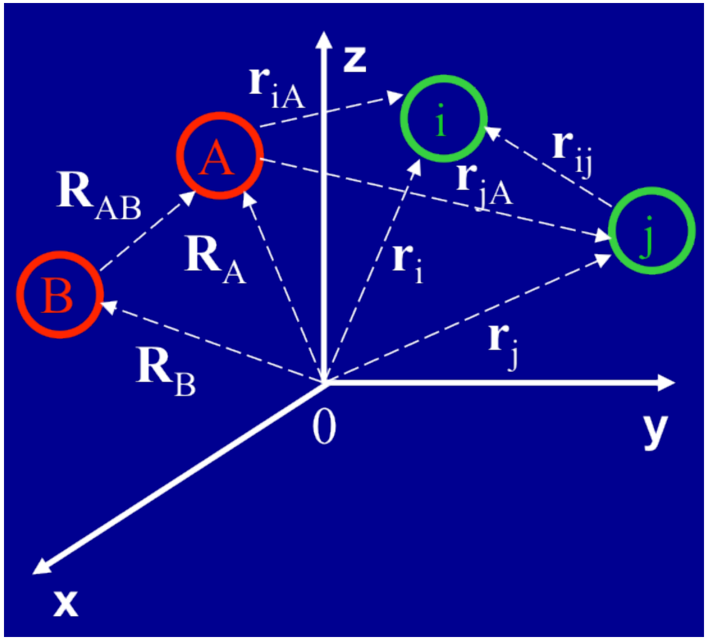
A resolvable model: Hartree-Fock

- Electrostatic interaction between average charge distributions
- → (Differential) Schrödinger equation resolvable
- Electron motion **correlation** is added a posteriori (if needed)



Molecular Hamiltonian

- System → molecule:
  - N electrons
  - M nuclei



$$H\,\Psi = E\,\Psi$$

$$\Psi = \Psi\left(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots \mathbf{x}_N\right) \qquad \mathbf{x}_i = \left(\mathbf{r}_i, \omega_i\right)$$

Spatial coor.

Spin coor.

Electronic Hamiltonian:

$$H = \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} - \overbrace{\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}}}^{h(\mathbf{r}_i)} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}$$

(in atomic units)

One-electron and many-electron wavefunctions

Molecular spin-orbital: $\chi_i(\mathbf{x_i}) = \psi_j(\mathbf{r_i})\eta(\omega_i) \rightarrow \eta(\omega_i)\begin{cases}\alpha(\omega_i)\\ \beta(\omega_i)\end{cases}$

Many-electron wavefunction:

- Hartree Product (HP): $\Psi^{\mathrm{HP}} = \chi_1(\mathbf{x_1})\,\chi_2(\mathbf{x_2})\cdots\chi_N(\mathbf{x_N})$

- Slater determinant: antisymmetrized product (AP)

$$\Psi^{\mathrm{AP}} = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(\mathbf{x_1}) & \chi_2(\mathbf{x_1}) & \cdots & \chi_N(\mathbf{x_1}) \\ \chi_1(\mathbf{x_2}) & \chi_2(\mathbf{x_2}) & \cdots & \chi_N(\mathbf{x_2}) \\ \vdots & \vdots & & \vdots \\ \chi_1(\mathbf{x_N}) & \chi_2(\mathbf{x_N}) & \cdots & \chi_N(\mathbf{x_N}) \end{vmatrix} = \left|\chi_1(\mathbf{x_1})\,\chi_2(\mathbf{x_2})\cdots\chi_N(\mathbf{x_N})\right\rangle = \left|\chi_1\,\chi_2\cdots\chi_N\right\rangle$$

Slater determinant properties :

- $\{\chi_i\}$ must be linearly independent
- If $\chi'_i = \sum_j^N \chi_j A_{ji}$ then $\Psi' = \det(\mathbf{A})\,\Psi$
- We will assume that $\{\chi_i\}$ are orthonormal, i. e.,

$$\int d\mathbf{x}_1\ \chi_i^*(\mathbf{x}_1)\,\chi_j(\mathbf{x}_1) = \langle \chi_i | \chi_j \rangle = \delta_{ij} \Rightarrow \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}$$ Therefore $$\langle \Psi^{AP} | \Psi^{AP} \rangle = 1$$

- If $\mathbf{A}^\dagger = \mathbf{A}^{-1}$ (unitary) $\langle \Psi'^{AP} | \Psi'^{AP} \rangle = \langle \Psi^{AP} | \Psi^{AP} \rangle = 1$

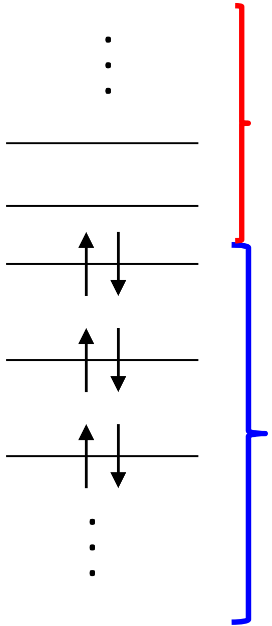
- Physically: “independent” electron model

Slater determinant classification :

Restricted

Each pair of spin-orbitals have the same spatial part

$$\chi_i\left(x_i\right)=\psi_j\left(r_i\right)\eta\left(\omega_i\right)$$

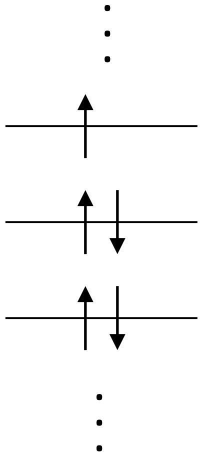


r = N+1, …∞
unoccupied or
virtual spin-orbitals

a = 1, …N
Occupied spin-orbitals

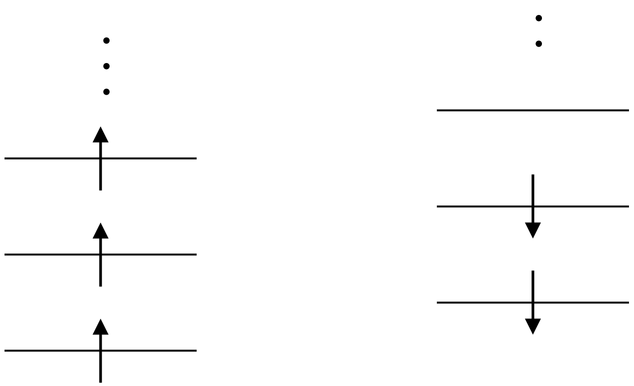
$$\boxed{\Psi^{AP} = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}}$$

closed shell



open shell

Unrestricted



Electronic energy and total energy

$$\Psi_0 = |\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_N\rangle \qquad \chi_a \quad a = 1,\ldots N$$

Electronic energy, E_0:

$$E_0 = \frac{\int d\tau\, \Psi_0^*\, H\, \Psi_0}{\int d\tau\, \Psi_0^*\, \Psi_0} = \frac{\langle \Psi_0 |\, H\, | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} = \sum_a^N \langle a |\, h\, | a \rangle + \frac{1}{2}\sum_a^N\sum_b^N \left(\langle a\,b | a\,b \rangle - \langle a\,b | b\,a \rangle \right)$$

One-electron term:

$$\langle a | h | a \rangle = \int d\mathbf{x}_1 \chi_a^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_a(\mathbf{x}_1) \qquad h(\mathbf{r}_1) \equiv h(1) = -\frac{1}{2}\nabla_1^2 - \sum_A^M \frac{Z_A}{r_{1A}}$$

Coulomb integral:

$$\langle a\,b | a\,b \rangle = \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_a^*(\mathbf{x}_1)\, \chi_b^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_a(\mathbf{x}_1)\, \chi_b(\mathbf{x}_2) \qquad |\chi_a(\mathbf{x}_1)|^2 \longleftrightarrow |\chi_b(\mathbf{x}_2)|^2$$

Exchange integral:

$$\langle a\,b | b\,a \rangle = \int d\mathbf{x}_1\, d\mathbf{x}_2\, \overbrace{\chi_a^*(\mathbf{x}_1)}\, \underbrace{\chi_b^*(\mathbf{x}_2)} \frac{1}{r_{12}} \overbrace{\chi_b(\mathbf{x}_1)}\, \underbrace{\chi_a(\mathbf{x}_2)}$$

Electronic energy and total energy

Coulomb operator, $J_b(1)$:

$$J_b(1)\,\chi(1) = \left(\int d\mathbf{x_2}\, \chi_b^*(2) \frac{1}{r_{12}} \chi_b(2) \right) \chi(1)$$

Exchange operator, $K_b(1)$:

$$K_b(1)\,\chi(1) = \left(\int d\mathbf{x_2}\, \chi_b^*(2) \frac{1}{r_{12}} \chi(2) \right) \chi_b(1)$$

Thus,

$$\langle ab|ab\rangle = \langle \chi_a(1) | J_b(1) | \chi_a(1) \rangle$$

$$\langle ab|ba\rangle = \langle \chi_a(1) | K_b(1) | \chi_a(1) \rangle$$

Total Potential Energy:

$$E_0 = \sum_a^N \langle a|\ h\ |a\rangle + \frac{1}{2}\sum_a^N \sum_b^N \left(\langle a\,b|a\,b\rangle - \langle a\,b|b\,a\rangle \right) \qquad E_{tot} = E_0 + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$$

Hartree-Fock Theory

In HF theory one assumes that the wavefunction is monodeterminantal

$$\Psi_0 = \left| \chi_1 \chi_2 \cdots \chi_a \chi_b \cdots \chi_N \right\rangle \quad \chi_a \;\; a = 1,\ldots N \qquad E_0 = \frac{\langle \Psi_0 | H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}$$

The optimal set of spin-orbitals will be those minimizing the energy (**Variational principle**)

$$\delta \langle \Psi_0 | H | \Psi_0 \rangle = 0$$

$$\delta \langle \Psi_0 | \Psi_0 \rangle = 0$$

The wavefunction must be kept normalized

$$\delta \langle \Psi_0 | H | \Psi_0 \rangle = \langle \delta\Psi_0 | H | \Psi_0 \rangle + \langle \Psi_0 | H | \delta\Psi_0 \rangle = \langle \delta\Psi_0 | H | \Psi_0 \rangle + \langle \delta\Psi_0 | H | \Psi_0 \rangle^*$$

Which means that $\mathrm{Re} \langle \delta\Psi_0 | H | \Psi_0 \rangle = 0$ And if ¬ is real $\langle \delta\Psi_0 | H | \Psi_0 \rangle = 0$

How can we vary the wavefunction? Changing the spin-orbitals ….

We can do this by ‘mixing’ an occupied orbital with a virtual one by a small amount (η << 1)

$$\chi_a \rightarrow \chi_a + \eta\, \chi_r \qquad \delta\chi_a = \eta\, \chi_r \qquad \chi_r \quad r = N+1, \ldots \infty$$

Hartree-Fock Theory

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

Then the variation in the wavefunction is:

$$\delta\Psi_0 = \left| \chi_1 \chi_2 \cdots \delta\chi_a \chi_b \cdots \chi_N \right\rangle = \left| \chi_1 \chi_2 \cdots \chi_r \chi_b \cdots \chi_N \right\rangle \eta = \Psi_a^r \eta$$

According to the variational principle: $\left\langle \delta\Psi_0 \middle| H \middle| \Psi_0 \right\rangle = \left\langle \Psi_a^r \middle| H \middle| \Psi_0 \right\rangle = 0$

a = 1, …N
r = N+1, …∞

Developing the expression of energy:

$$\left\langle \Psi_a^r \middle| H \middle| \Psi_0 \right\rangle = \langle r|h|a\rangle + \sum_b^N \left(\langle rb|ab\rangle - \langle rb|ba\rangle \right) = \langle r|\underbrace{h + \sum_b^N (J_b - K_b)}_{f}|a\rangle$$

Where f is the Fock operator, according to the variational principle

$$\langle \chi_r | f | \chi_a \rangle = 0$$

a = 1, …N
r = N+1, ...∞

Hartree-Fock Theory

Then, we need to find one-electron functions:

$$\{\chi_i\}$$

We have a one-electron operator, the fock operator:

$$f(1) = h(1) + \sum_{b}^{N}\left(J_b(1) - K_b(1)\right)$$

We now know that the best spin-orbitals are those that fulfill the condition:

$$\langle \chi_r | f | \chi_a \rangle = 0$$

We also know that the fock operator acting on a spin-orbital will give us another function that can be expressed using a complete basis of functions:

$$f\chi_a = \sum_{b}^{\infty} \chi_b \varepsilon_{ba} = \underset{\text{occupied}}{\sum_{b}^{N} \chi_b \varepsilon_{ba}} + \underset{\text{virtual}}{\cancelto{0}{\sum_{r=N+1}^{\infty} \chi_r \varepsilon_{ra}}}$$

considering $\langle \chi_r | f | \chi_a \rangle = \varepsilon_{ra} = 0$ then

$$\boxed{f\chi_a = \sum_{b}^{N} \chi_b \varepsilon_{ba}}$$

- *The fock operator acting on an occupied spin-orbital gives another spin-orbital written as a combination of occupied spin-orbitals.*

- *Of all the possible sets of spin-orbitals, there is one that simplifies the previous equation …*

Hartree-Fock Theory

$$\boxed{f\chi_a = \sum_{b}^{N} \chi_b \varepsilon_{ba}} \quad a = 1, \ldots N$$

$$\boxed{f\chi'_a = \varepsilon_a \chi'_a} \quad a = 1, \ldots N$$

$$f\chi_a = \varepsilon_{aa}\chi_a + \varepsilon_{ba}\chi_b + \ldots. + \varepsilon_{Na}\chi_N$$

$$f\chi_b = \varepsilon_{ab}\chi_a + \varepsilon_{bb}\chi_b + \ldots. + \varepsilon_{Nb}\chi_N$$

…

$$f\chi_N = \varepsilon_{aN}\chi_a + \varepsilon_{bN}\chi_b + \ldots. + \varepsilon_{NN}\chi_N$$

Unitary transformation

$$f\chi'_a = \varepsilon_{aa}\chi'_a$$

$$f\chi'_b = \varepsilon_{bb}\chi'_b$$

…

$$f\chi'_N = \varepsilon_{NN}\chi'_N$$

$$\varepsilon = \begin{pmatrix} \varepsilon_{aa} & \varepsilon_{ab} & \ldots & \varepsilon_{aN} \\ \varepsilon_{ba} & \varepsilon_{bb} & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ \varepsilon_{Na} & \ldots & \ldots & \varepsilon_{NN} \end{pmatrix}$$

$$\varepsilon_{ba} = \varepsilon^{*}_{ab}$$

$$\varepsilon = \begin{pmatrix} \varepsilon_{aa} & 0 & \ldots & 0 \\ 0 & \varepsilon_{bb} & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ 0 & 0 & \ldots & \varepsilon_{NN} \end{pmatrix}$$

Hartree-Fock Theory

$\Psi_0 = |\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_N\rangle$ χ_a a = 1,…N $E_0 = \dfrac{\langle\Psi_0|H|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}$

$$\delta\langle\Psi_0|H|\Psi_0\rangle = \langle\delta\Psi_0|H|\Psi_0\rangle + \langle\Psi_0|H|\delta\Psi_0\rangle =$$

$$= \langle\delta\Psi_0|H|\Psi_0\rangle + \langle\delta\Psi_0|H|\Psi_0\rangle^*$$

$\{\chi_a\}$ χ_r r = N+1, …∞ $\chi_a \to \chi_a + \eta\,\chi_r$ $\delta\chi_a = \eta\,\chi_r$

$$\delta\Psi_0 = |\chi_1\chi_2\cdots\delta\chi_a\chi_b\cdots\chi_N\rangle = |\chi_1\chi_2\cdots\chi_r\chi_b\cdots\chi_N\rangle\eta = \Psi_a^r\eta$$

$$\langle\Psi_a^r|H|\Psi_0\rangle = \langle r|h|a\rangle + \sum_b^N\left(\langle rb|ab\rangle - \langle rb|ba\rangle\right) = \langle r|h + \sum_b^N (J_b - K_b)|a\rangle$$

$$f\chi_a = \sum_b^N \chi_b\varepsilon_{ba}$$

$$\varepsilon_{ba} = \langle\chi_b|f|\chi_a\rangle = \langle\chi_a|f|\chi_b\rangle^* = \varepsilon_{ab}^*$$

$$\delta\langle\Psi_0|H|\Psi_0\rangle = 0$$

$$\delta\langle\Psi_0|\Psi_0\rangle = 0$$

$$\mathrm{Re}\langle\delta\Psi_0|H|\Psi_0\rangle = 0$$

$$\langle\Psi_a^r|H|\Psi_0\rangle = 0$$

$$\langle\chi_r|f|\chi_a\rangle = 0$$

$$f\chi_a = \sum_b^N \chi_b\varepsilon_{ba}$$

$$f\chi_a = \varepsilon_a\chi_a$$

a = 1, …N

Hartree-Fock Theory

Take home message about HF:

- We have transformed an N-electron problem into an N-monoelectron problem

$$H\,\Psi(x_1,\ldots.x_N) = E\,\Psi(x_1,\ldots.x_N) \quad \Rightarrow \quad f\chi_a = \varepsilon_a \chi_a \quad a = 1,\ldots N$$

- We assume that the wavefunction can be expressed as the antisymmetrized products (one determinant or configuration) of spin-orbitals

- We look for the best spin-orbitals using the variational principle

- The fock operator gives the energy of one electron in the field of the nuclei, which ‘feels’ an average interaction with the rest of electrons

Physical meaning of the HF equations & solutions

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Contents

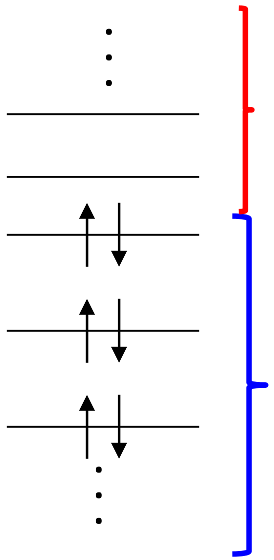
- Core, Coulomb, and exchange integrals
- Occupied and virtual orbitals
- Orbital energy and molecular energy
- Koopmans’ theorem

Physical Meaning of the HF solutions

- Fock equation: $f\left|\chi_j\right\rangle = \varepsilon_j \left|\chi_j\right\rangle \quad j = 1, 2, \ldots, \infty$

$$f = h + \sum_{b}^{N}\left(J_b - K_b\right)\left\{\begin{aligned} h &= -\frac{1}{2}\nabla_1^2 - \sum_{A}^{M}\frac{Z_A}{r_{1A}} \\ J_b(1)\,\chi(1) &= \left(\int d\mathbf{x_2}\,\chi_b^*(2)\frac{1}{r_{12}}\chi_b(2)\right)\chi(1) \\ K_b(1)\,\chi(1) &= \left(\int d\mathbf{x_2}\,\chi_b^*(2)\frac{1}{r_{12}}\chi(2)\right)\chi_b(1) \end{aligned}\right.$$

- Solutions of the Fock equation for N electrons:
  - N occupied spin-orbitals (a,b…), the rest of the spin-orbitals will be virtual or unoccupied (r,s…)



r = N+1, …∞
Unoccupied or
virtual spin-orbitals

a = 1, …N
Occupied spin-orbitals

Orbital energy

Multiplying the Fock equation by $<\chi_i|$ one obtains:

$$f|\chi_j\rangle = \varepsilon_j|\chi_j\rangle$$

$$\langle\chi_i|f|\chi_j\rangle = \varepsilon_j\langle\chi_i|\chi_j\rangle = \varepsilon_j\delta_{ij}$$

$$\varepsilon_i = \langle\chi_i|f|\chi_i\rangle = \langle\chi_i|h + \sum_b[J_b - \mathcal{K}_b]|\chi_i\rangle$$

$$\varepsilon_i = \langle\chi_i|h|\chi_i\rangle + \sum_b\left[\langle\chi_i|J_b|\chi_i\rangle - \langle\chi_i|\mathcal{K}_b|\chi_i\rangle\right]$$

$$\varepsilon_i = \langle i|h|i\rangle + \sum_b\left[\langle ib|ib\rangle - \langle ib|bi\rangle\right] = \langle i|h|i\rangle + \sum_b\langle ib||ib\rangle$$

This is the energy (kinetic and potential) of the electron alone in the field of the nuclei (h) plus the Coulomb (J) and exchange interaction (K) with all other electrons

What is the physical meaning of the Fock operator and its eigenfunctions?

Occupied orbitals

$$\left[h(1)+\sum_{b}^{N}\left(J_b(1)-K_b(1)\right)\right]\chi_a(1)=\varepsilon_a\chi_a(1) \qquad a=1,\ldots N$$

$$J_b(1)\chi_a(1)=\left(\int d\mathbf{x}_2\chi_b^*(2)\frac{1}{r_{12}}\chi_b(2)\right)\chi_a(1)$$

$$K_b(1)\chi_a(1)=\left(\int d\mathbf{x}_2\chi_b^*(2)\frac{1}{r_{12}}\chi_a(2)\right)\chi_b(1)$$

Since:

$$J_a(1)\chi_a(1)=K_a(1)\ \chi_a(1)$$

$$\left[h(1)+\sum_{b\neq a}^{N}\left(J_b(1)-K_b(1)\right)\right]\chi_a(1)=\varepsilon_a\chi_a(1) \qquad a=1,\ldots N$$

$$\varepsilon_a=\langle\chi_a|h|\chi_a\rangle+\sum_{b\neq a}^{N}\left[\langle\chi_a|\mathcal{J}_b|\chi_a\rangle-\langle\chi_a|\mathcal{K}_b|\chi_a\rangle\right]$$

Occupied spin-orbitals

- Summarizing → energy of an occupied spin-orbital:

$$\varepsilon_a = \langle \chi_a | h | \chi_a \rangle + \sum_{b\neq a}^{N} \left[\langle \chi_a | \mathcal{J}_b | \chi_a \rangle - \langle \chi_a | \mathcal{K}_b | \chi_a \rangle \right]$$

$$\varepsilon_a = \langle a | h | a \rangle + \sum_{b\neq a} \left[\langle ab | ab \rangle - \langle ab | ba \rangle \right] = \langle a | h | a \rangle + \sum_{b\neq a}^{N} \langle ab \| ab \rangle$$

- The energy of the occupied orbital includes:
  - <a|h|a> ⇒ energy of the electron alone in the field of the nuclei
  - Interaction with the other (**N-1**) electrons in the other occupied spin-orbitals b≠a:
    - <ab|ab> Coulomb interaction
    - – <ab|ba> exchange interaction

What is the physical meaning of the Fock operator and its eigenfunctions?

Occupied orbitals

$$\left[h(1)+\sum_{b}^{N}\left(J_b(1)-K_b(1)\right)\right]\chi_a(1)=\varepsilon_a\chi_a(1) \qquad a=1,\ldots N$$

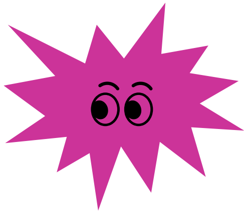
Considering: $J_a(1)\,\chi_a(1)=K_a(1)\,\chi_a(1)$

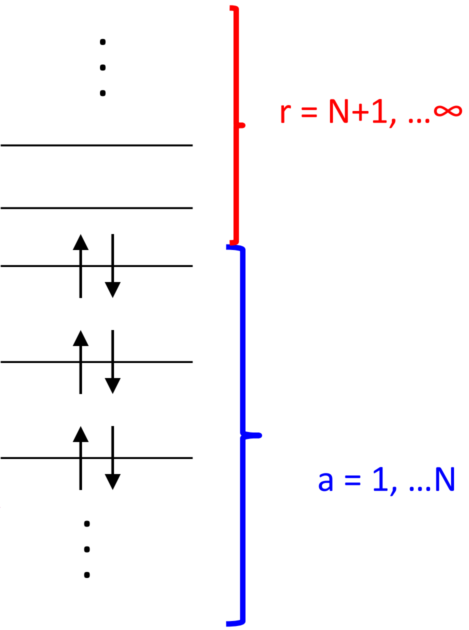
$$\left[h(1)+\sum_{b\neq a}^{N}J_b(1)-K_b(1)\right]\chi_a(1)=\varepsilon_a\chi_a(1) \qquad a=1,\ldots N$$

Virtual orbitals

$$f\chi_r=\varepsilon_r\chi_r \qquad \langle\chi_r|\chi_a\rangle=0 \qquad r=N+1,\ldots\infty$$

$$\left[h(1)+\sum_{b}^{N}\left(J_b(1)-K_b(1)\right)\right]\chi_r(1)=\varepsilon_r\chi_r(1)$$





Virtual spin-orbitals

- Summarizing: → energy of a virtual spin-orbital

$$\varepsilon_r = \langle r|h|r\rangle + \sum_{b=1}^{N} \langle rb||rb\rangle$$

$$\varepsilon_r = \langle r|h|r\rangle + \sum_{b} \left[\langle rb|rb\rangle - \langle rb|br\rangle \right]$$

- The energy of the virtual orbital includes:
  - <r|h|r> the energy of the electron alone in the field of the nuclei
  - Interaction with ***all the N electrons*** in the N occupied spin-orbitals b
    - <rb|rb> Coulomb interaction
    - – <rb|br> exchange interaction
  - It is equivalent to the energy of an ***ADDITIONAL*** electron in a system with a total of (N+1) electrons

Physical meaning of the orbital energies

$$\varepsilon_a = \langle a|h|a\rangle + \sum_{b\neq a}^{N}\left(\langle ab|ab\rangle - \langle ab|ba\rangle\right)$$

$$\varepsilon_r = \langle r|h|r\rangle + \sum_{b}^{N}\left(\langle rb|rb\rangle - \langle rb|br\rangle\right)$$

$$\sum_{a}^{N}\varepsilon_a = \sum_{a}^{N}\langle a|h|a\rangle + \sum_{a}^{N}\sum_{b}^{N}\left(\langle ab|ab\rangle - \langle ab|ba\rangle\right)$$

$$E_0 = \sum_{a}^{N}\langle a|h|a\rangle + \frac{1}{2}\sum_{a}^{N}\sum_{b}^{N}\left(\langle ab|ab\rangle - \langle ab|ba\rangle\right)$$

$$\boxed{E_0 \neq \sum_{a}^{N}\varepsilon_a}$$

Ionization potentials

- System with N electrons ⇒ Slater determinant:

$$\left|{}^{N}\Psi_0\right\rangle = \left|\chi_1\chi_2\cdots\chi_c\cdots\chi_N\right\rangle$$

- If one eliminates the electron in the spin-orbital c, provided that all other spin-orbitals are identical:

$$\left|{}^{(N-1)}\Psi_c\right\rangle = \left|\chi_1\chi_2\cdots\chi_{c-1}\chi_{c+1}\cdots\chi_N\right\rangle$$

Ionization potentials

- The ionization potential will be:

$$IP = {}^{(N-1)}E_c - {}^{N}E_0$$

$${}^{N}E_0 = \sum_a \langle a|h|a\rangle + \frac{1}{2}\sum_a \sum_b \langle ab||ab\rangle$$

$${}^{(N-1)}E_c = \sum_{a\neq c} \langle a|h|a\rangle + \frac{1}{2}\sum_{a\neq c} \sum_{b\neq c} \langle ab||ab\rangle$$

$$IP = -\langle c|h|c\rangle - \sum_b \langle cb||cb\rangle = -\varepsilon_c$$

- In this model, the ionization potential is the orbital energy with the sign changed

Electron affinity

- The electron affinity is defined as:

$$EA = {}^{N}E_0 - {}^{(N+1)}E^r$$

- The wavefunction, after adding one electron to the system, to the r virtual spin-orbital, provided that the other spin-orbitals are identical is:

$$\left| {}^{(N+1)}\Psi^r \right\rangle = \left| \chi_r \chi_1 \chi_2 \cdots \chi_N \right\rangle$$

- Therefore:

$${}^{(N+1)}E^r = {}^{N}E_0 + \varepsilon_r = \sum_a \langle a|h|a\rangle + \frac{1}{2}\sum_a \sum_b \langle ab||ab\rangle + \langle r|h|r\rangle + \sum_b \langle rb||rb\rangle$$

$$EA = -\langle r|h|r\rangle - \sum_b \langle rb||rb\rangle = -\varepsilon_r$$

Koopmans' Theorem (KT)

Given:

- A system of N electrons
- A set of spin-orbitals (*SO*)
  - Occupied SO: energies $\{\varepsilon_a\}$
  - Virtual SO: energies $\{\varepsilon_r\}$
- Ground state: Slater determinant $|{}^N\Psi_0\rangle = |\chi_1\chi_2\ldots\chi_{a-1}\chi_a\chi_{a+1}\ldots\chi_N\rangle$,

Then:

- **Ionization potential**: energy needed to obtain the cation with (N-1) electrons
  - Determinant with identical spin-orbitals: $|{}^{(N-1)}\Psi_a\rangle = |\chi_1\chi_2\ldots\chi_{a-1}\chi_{a+1}\ldots\chi_N\rangle$, obtained by eliminating the electron in the spin-orbital χ_a
  - **IP =** $-\varepsilon_a$
- **Electron affinity**: energy needed to remove an electron from the anion with (N+1) electrons
  - Determinant with identical spin-orbitals: $|{}^{(N+1)}\Psi^r\rangle = |\chi_r\chi_1\chi_2\ldots\chi_N\rangle$, obtained by adding an electron to virtual spin-orbital χ_r
  - **EA =** $-\varepsilon_r$

Koopmans’ Theorem (KT)

- Two defects:
  - Missing orbital relaxation: the orbitals of the cation and anion are assumed to be the same as for the neutral system
  - Missing the correlation effects: involved in the Hartree Fock method itself

KT Limitations: orbital relaxation

- One assumes that the spin-orbitals are "*frozen*": the positive ion (N-1 electrons) or negative ion (N+1 electrons) spin-orbitals are equal to those of the neutral system (N electrons)
  - The relaxation of the spin-orbitals that would arise if they were optimized in a specific HF calculation for the positive or negative ion is neglected.
  - Relaxation should stabilize ions, therefore KT overestimates the absolute values of IP and EA

KT limitations: Electron correlation

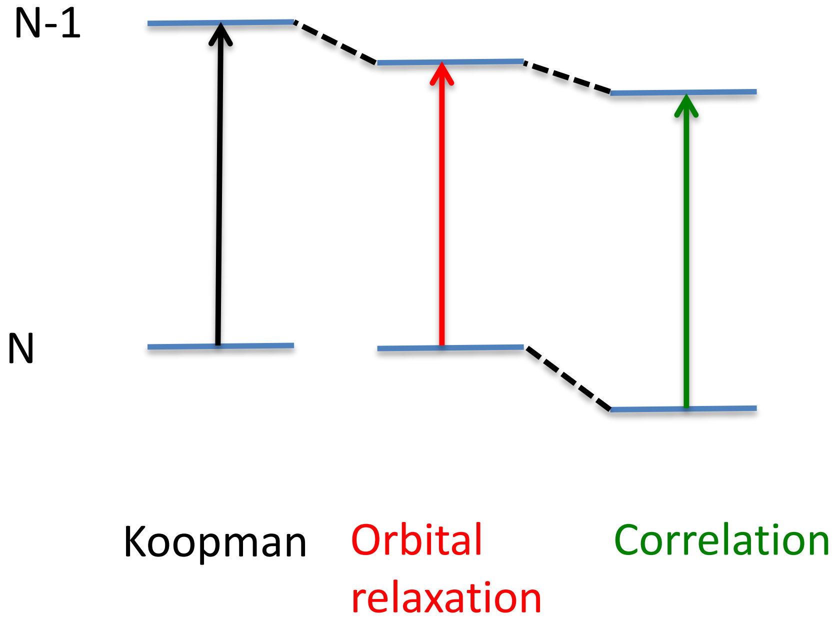
- KT does not include correlation effects:
  - Electron correlation: more important for systems with more electrons ⇒ the anion will be stabilized more than the neutral system, which in turn is stabilized more than the cation
  - If correlation energy was included, the EA would be smaller and the IP greater (in absolute values) than the values obtained by KT

KT limitations: combined effect

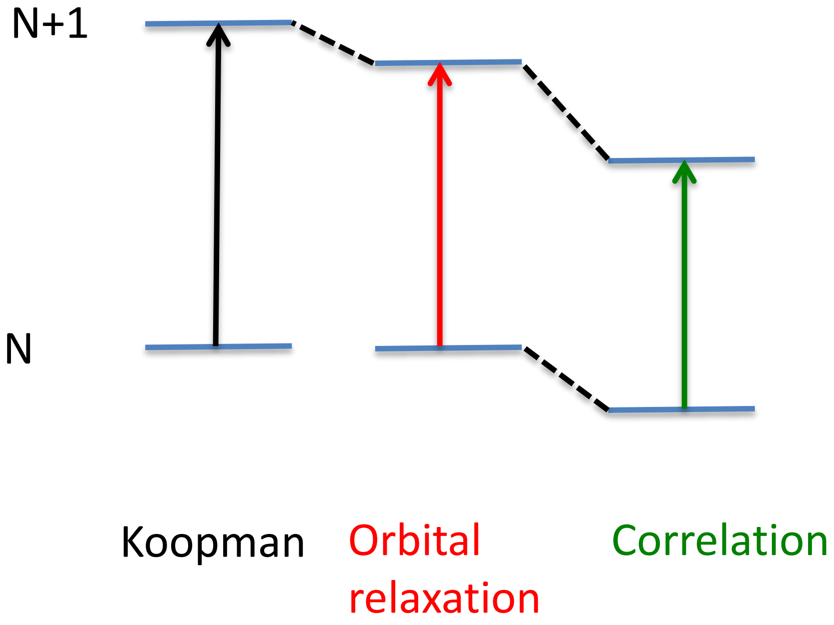
- In KT values, the relaxation and correlation errors,
  - IP: have different signs and their effects are partially compensated
  - EA: have the same sign their effects are added
  - In general, KT IPs are closer to the experimental values than EAs

KT limitations: combined effect

IP



EA



In general, KT IPs are closer to the experimental values than EAs

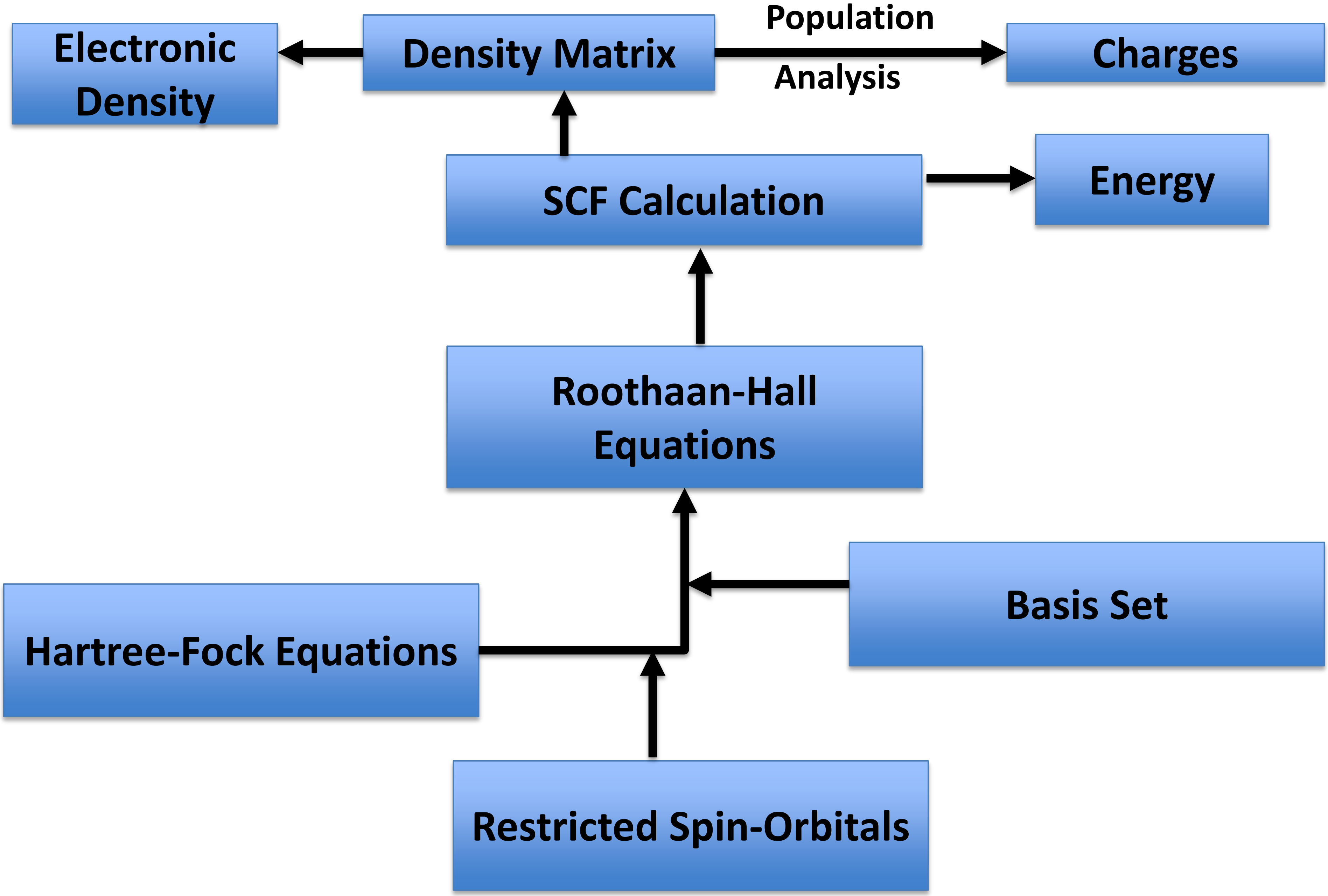
Restricted HF for closed-shell systems: Roothaan equations

Computational Chemistry
Elective Course
Chemistry Degree
4th Year

Contents

- Closed shell HF: restricted spin-orbitals
- Introduction of a basis set: Roothaan equations
- Charge density
- Expression of the Fock matrix
- SCF procedure
- Expectation values and population analysis

General Scheme for RHF



Electronic Density

Density Matrix

Population Analysis

Charges

SCF Calculation

Energy

Roothaan-Hall Equations

Basis Set

Hartree-Fock Equations

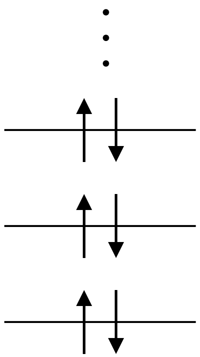
Restricted Spin-Orbitals

Restricted spin-orbitals

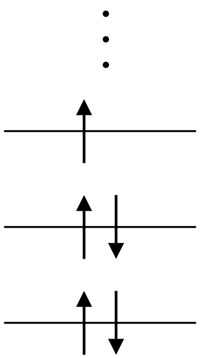
Restricted molecular spin-orbital: $\chi_i(\mathbf{x_i}) = \psi_j(\mathbf{r_i})\ \eta(\omega_i)$ $\eta(\omega_i) \begin{cases} \alpha(\omega_i) \\ \beta(\omega_i) \end{cases}$

The same spatial orbital ψ_j allows us to build a pair of spin-orbitals

- Closed shell: All spatial orbitals are doubly occupied
- Open shell: There are spatial orbitals that are only singly occupied (α or β)



Closed shell



Open shell

HF equation for closed shell

- Integro-differential HF equation :

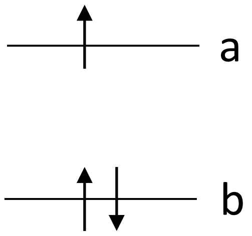
$$f\chi_a = \varepsilon_a \chi_a \quad \Rightarrow \quad f\psi_a = \varepsilon_a \psi_a$$

- Fock operator:

Pairs of electrons

$$f(1) = h(1) + \sum_{b}^{N/2} \left(2J_b(1) - K_b(1)\right)$$

- J and K operators:



$$J_b(1)\,\chi_a(1) = \left(\int d\mathbf{x}_2 \chi_b^*(2) \frac{1}{r_{12}} \chi_b(2) \right) \chi_a(1)$$

$$K_b(1)\,\chi_a(1) = \left(\int d\mathbf{x}_2 \chi_b^*(2) \frac{1}{r_{12}} \chi_a(2) \right) \chi_b(1)$$

Integral vanishes for different spins

Introduction of a basis set

- HF equations:
  - Cannot be solved analytically
  - Only a numerical solution can be obtained ⟹ Tables of values of each MO at each point in space
- Introduction of a basis set: LCBF approximation (Linear Combination of Basis Functions)
  - A set of functions is chosen: $\{\phi_\mu\}_{\mu=1\ldots K}$
  - They constitute a K-dimensional representation basis. Exact if $K \to \infty$
  - They allow us to obtain analytical expressions for MOs

$$\{\phi_\mu \mid \mu = 1,2, \ldots K\} \qquad \psi_i = \sum_{\mu=1}^{K} C_{\mu i}\, \phi_\mu \qquad i = 1,2, \ldots K$$

Introduction of a basis set

- Now the problem is to calculate the values of the coefficients $\{C_{\mu i}\}_{\mu=1\ldots K,\ i=1\ldots K}$ (indexes run over basis functions and MOs)
- By substituting ψ_i in the HF equation:

$$f(1)\sum_{\nu} C_{\nu i}\phi_{\nu}(1)=\varepsilon_i\sum_{\nu} C_{\nu i}\phi_{\nu}(1)$$

- After multiplying by $\langle\phi_\mu|$ and integrating:

$$\sum_{\nu} C_{\nu i}\boxed{\langle\phi_{\mu}|f|\phi_{\nu}\rangle}=\varepsilon_i\sum_{\nu} C_{\nu i}\boxed{\langle\phi_{\mu}|\phi_{\nu}\rangle}$$

- One can define two matrices:
  - Overlap matrix: $S_{\mu\nu} = \langle\phi_\mu|\phi_\nu\rangle$
  - Fock matrix: $F_{\mu\nu} = \langle\phi_\mu|f|\phi_\nu\rangle$

$$\Bigg\}\Rightarrow \sum_{\nu} F_{\mu\nu}C_{\nu i}=\varepsilon_i\sum_{\nu} S_{\mu\nu}C_{\nu i}$$

$$\mathbf{FC}=\mathbf{SC}\boldsymbol{\varepsilon}$$

Roothaan equations

Roothaan equations

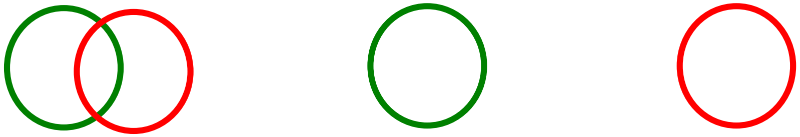
$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \varepsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i} i = 1 \ldots K \qquad \Rightarrow \qquad \mathbf{FC} = \mathbf{SC\boldsymbol{\varepsilon}}$$

$$\mathbf{C} = \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1\mathrm{K}} \\ C_{21} & C_{22} & \cdots & C_{2\mathrm{K}} \\ \vdots & \vdots & & \vdots \\ C_{\mathrm{K}1} & C_{\mathrm{K}2} & \cdots & C_{\mathrm{KK}} \end{pmatrix} \qquad \boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_1 & 0 & 0 & 0 \\ 0 & \varepsilon_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & \varepsilon_{\mathrm{K}} \end{pmatrix}$$

$$\mathbf{F} = \begin{pmatrix} F_{11} & F_{12} & \cdots & F_{1\mathrm{K}} \\ F_{21} & F_{22} & \cdots & F_{2\mathrm{K}} \\ \vdots & \vdots & & \vdots \\ F_{\mathrm{K}1} & F_{\mathrm{K}2} & \cdots & F_{\mathrm{KK}} \end{pmatrix} \qquad S = \begin{pmatrix} S_{11} & S_{12} & \cdots & S_{1\mathrm{K}} \\ S_{21} & S_{22} & \cdots & S_{2\mathrm{K}} \\ \vdots & \vdots & & \vdots \\ S_{\mathrm{K}1} & S_{\mathrm{K}2} & \cdots & S_{\mathrm{KK}} \end{pmatrix}$$

Properties of **S** and **F**

- Properties of **S**:
  - K x K Hermitian matrix
  - $0 \le |S_{\mu\nu}| \le 1$
  - $S_{\mu\mu} = 1$



$S_{\mu\nu} < 1$

$S_{\mu\nu} \approx 0$

Coefficient matrix & Density matrix

- The coefficient matrix gives the MO composition in terms of the AOs

$$\psi_i = \sum_{\mu=1}^{K} C_{\mu i}\,\phi_\mu \qquad i = 1,2, \ldots K$$

- For one electron described by $\psi_a(\mathbf{r})$, the spatial probability density is:

$$|\psi_a(\mathbf{r})|^2$$

- For a closed shell molecule described by a Slater determinant, the total charge density is:

$$\rho(\mathbf{r}) = 2\sum_{a}^{N/2} \left|\psi_a(\mathbf{r})\right|^2 \quad \Rightarrow \quad \int d\mathbf{r}\,\rho(\mathbf{r}) = N$$

- After introducing the basis set:

$$\rho(\mathbf{r}) = 2\sum_{a}^{N/2}\psi_a^*(\mathbf{r})\,\psi_a(\mathbf{r}) = 2\sum_{a}^{N/2}\sum_{\nu} C_{\nu a}^*\phi_\nu^*(\mathbf{r})\sum_{\mu} C_{\mu a}\phi_\mu(\mathbf{r}) =$$

Density matrix

$$= \sum_{\mu\nu}\left[2\sum_{a}^{N/2} C_{\mu a}C_{\nu a}^*\right]\phi_\mu(\mathbf{r})\,\phi_\nu^*(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu}\phi_\mu(\mathbf{r})\,\phi_\nu^*(\mathbf{r}) \Rightarrow \boxed{P_{\mu\nu} = 2\sum_{a}^{N/2} C_{\mu a}C_{\nu a}^*}$$

Density matrix and population analysis

$$N = 2\sum_{a}^{N/2} \int d\mathbf{r} \left|\psi_a(\mathbf{r})\right|^2 = \sum_{\mu}\sum_{\nu} P_{\mu\nu} S_{\nu\mu} = \sum_{\mu} (\mathbf{PS})_{\mu\mu} = tr(\mathbf{PS})$$

- Mulliken atomic charges:
  - Number of electrons associated to ϕ_μ: $(\mathbf{P}\,\mathbf{S})_{\mu\mu}$
  - Number of electrons associated to the atom A: $N_A = \sum_{\mu \in A} (\mathbf{PS})_{\mu\mu}$
  - Net charge associated to the atom A: $q_A = Z_A - \sum_{\mu \in A} (\mathbf{PS})_{\mu\mu}$

Fock matrix

F is a Hermitian matrix of K x K size

F matrix elements in the basis set:

$$\mathrm{f}(1)=\mathrm{h}(1)+\sum_{b}^{N/2}\left(2\mathrm{J}_b(1)-\mathrm{K}_b(1)\right) \Rightarrow \quad F_{\mu\nu}=\langle\phi_\mu|f|\phi_\nu\rangle=\langle\phi_\mu|\mathrm{h}(1)+\sum_{b}^{N/2}\left(2\mathrm{J}_b(1)-\mathrm{K}_b(1)\right)|\phi_\nu\rangle=$$

$$=\langle\phi_\mu|\mathrm{h}(1)|\phi_\nu\rangle+\sum_{b}^{N/2}\langle\phi_\mu|\left(2\mathrm{J}_b(1)-\mathrm{K}_b(1)\right)|\phi_\nu\rangle=$$

$$=H_{\mu\nu}^{core}+\sum_{b}^{N/2}\left(2\langle\mu b|\nu b\rangle-\langle\mu b|b\nu\rangle\right)=H_{\mu\nu}^{core}+G_{\mu\nu}$$

Where:

$$H_{\mu\nu}^{core}=T_{\mu\nu}+V_{\mu\nu}^{nucl}$$

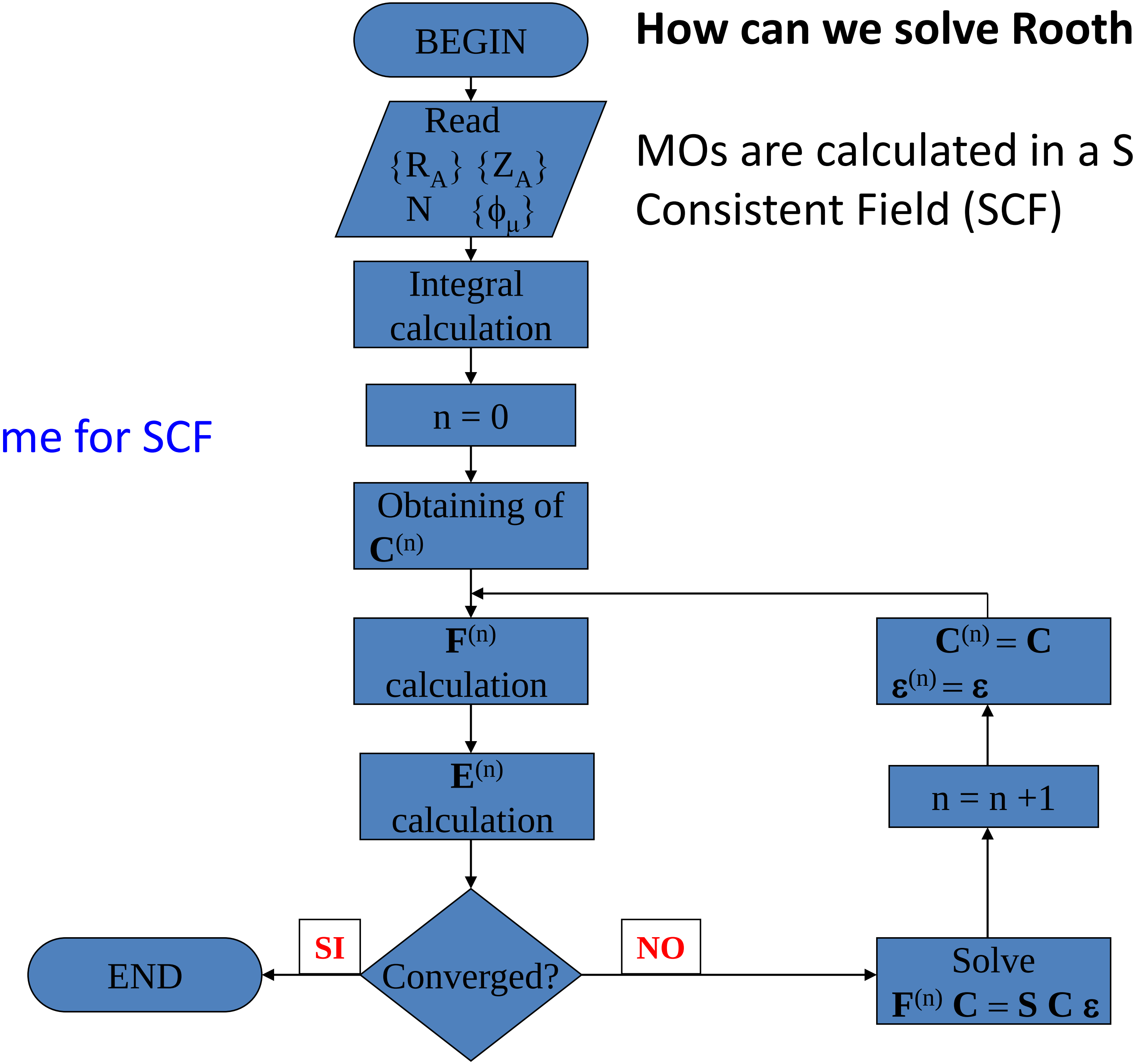
$$G_{\mu\nu}=\sum_{b}^{N/2}\left(2\langle\mu b|\nu b\rangle-\langle\mu b|b\nu\rangle\right)=\sum_{b}^{N/2}\sum_{\lambda\sigma}C_{\lambda b}C_{\sigma b}^{*}\left[2\langle\mu\sigma|\nu\lambda\rangle-\langle\mu\sigma|\lambda\nu\rangle\right]=$$

$$=\sum_{\lambda\sigma}P_{\lambda\sigma}\left[\langle\mu\sigma|\nu\lambda\rangle-\frac{1}{2}\langle\mu\sigma|\lambda\nu\rangle\right]\Rightarrow \mathbf{F}(\mathbf{C}) \quad \Rightarrow \quad \mathbf{F}(\mathbf{C})\,\mathbf{C}=\mathbf{S}\,\mathbf{C}\,\boldsymbol{\varepsilon}$$

How can we solve Roothaan eqs?

MOs are calculated in a Self-Consistent Field (SCF)

Scheme for SCF



BEGIN

Read $\{R_A\}$ $\{Z_A\}$ N $\{\phi_\mu\}$

Integral calculation

n = 0

Obtaining of $\mathbf{C}^{(n)}$

$\mathbf{F}^{(n)}$ calculation

$\mathbf{E}^{(n)}$ calculation

Converged?

SI

END

NO

Solve $\mathbf{F}^{(n)}\,\mathbf{C} = \mathbf{S}\,\mathbf{C}\,\boldsymbol{\varepsilon}$

n = n +1

$\mathbf{C}^{(n)} = \mathbf{C}$

$\boldsymbol{\varepsilon}^{(n)} = \boldsymbol{\varepsilon}$

Summary

$$\Psi_0 = \left| \psi_1 \bar{\psi}_1 \cdots \psi_a \bar{\psi}_a \cdots \psi_{N/2} \bar{\psi}_{N/2} \right\rangle \qquad f\,(\mathbf{r}_1)\,\psi_i\,(\mathbf{r}_1) = \varepsilon_i\,\psi_i\,(\mathbf{r}_1)$$

Hartree-Fock

$$\{\phi_\mu \mid \mu = 1,2,\, \ldots K\} \qquad \psi_i = \sum_{\mu=1}^{K} C_{\mu i}\,\phi_\mu \qquad i = 1,2,\, \ldots K$$

Basis set

$$\boxed{\mathbf{F}\,\mathbf{C} = \mathbf{S}\,\mathbf{C}\,\boldsymbol{\varepsilon}}$$

Roothaan eqs.

$$F_{\mu\nu} = < \phi_\mu | f |\, \phi_\nu >$$

$$S_{\mu\nu} = < \phi_\mu | \phi_\nu >$$

$$\mathbf{C} = \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1K} \\ C_{21} & C_{22} & \cdots & C_{2K} \\ \vdots & \vdots & & \vdots \\ C_{K1} & C_{K2} & \cdots & C_{KK} \end{pmatrix} \qquad \varepsilon = \begin{pmatrix} \varepsilon_1 & 0 & 0 & 0 \\ 0 & \varepsilon_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & \varepsilon_K \end{pmatrix}$$

$$\mathbf{F} = \mathbf{F}(\mathbf{C})$$

$$\mathbf{F}(\mathbf{C})\,\mathbf{C} = \mathbf{S}\,\mathbf{C}\,\boldsymbol{\varepsilon}$$

SCF

⬇

SCF procedure (*Self-Consistent Field*)

Expected values

- Total energy:

$$E_0 = \sum_{a}^{N/2} \left(h_{aa} + \varepsilon_a \right) = \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\mu\nu} \left(H_{\mu\nu}^{core} + F_{\mu\nu} \right)$$

$$E_{tot} = E_0 + \sum_{A} \sum_{B} \frac{Z_A Z_B}{R_{AB}}$$

- One-electron properties:
  - Defined by an operator as the sum of terms depending on the coordinates of a single electron:

$$\mathcal{O}_1 = \sum_{i=1}^{N} \hat{o}(i)$$

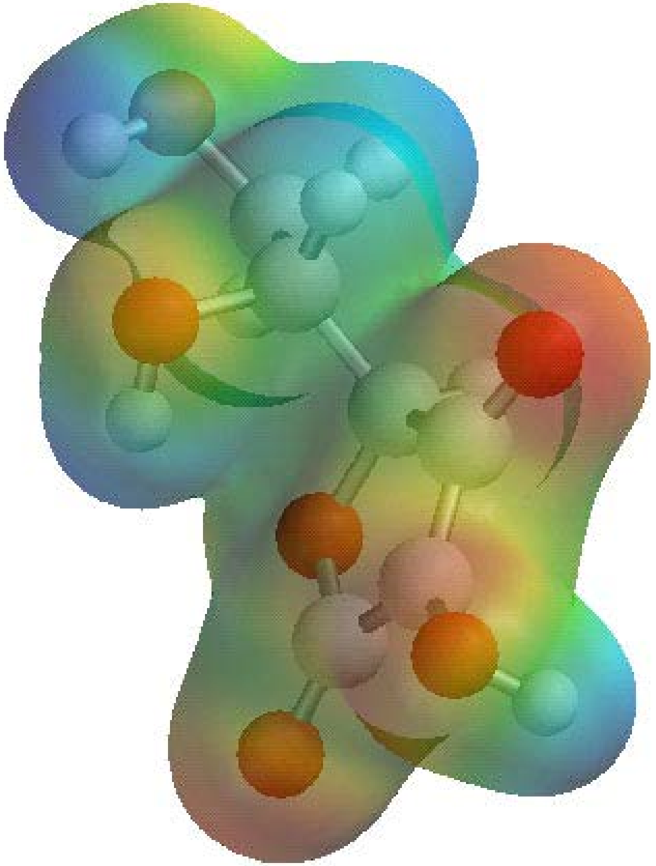
  - The average value will be:

$$\left\langle \mathcal{O}_1 \right\rangle = \left\langle \Psi_0 \middle| \mathcal{O}_1 \middle| \Psi_0 \right\rangle = \sum_{a}^{N/2} \left\langle \psi_a \middle| \hat{o} \middle| \psi_a \right\rangle = \sum_{\mu\nu} P_{\mu\nu} \left\langle \mu \middle| \hat{o} \middle| \nu \right\rangle$$

Charge density

- Charge density → displayed as contour maps
- Charge density: vitamin C molecule
- Colours
  - Negative potential in red
  - Positive potential in blue

$$\rho(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu}\phi_{\mu}(\mathbf{r})\phi_{\nu}^{*}(\mathbf{r})$$



Other population analysis

- Since tr(**A B**) = tr(**B A**):

$$N = \sum_{\mu} (\mathbf{PS})_{\mu\mu} = \sum_{\mu} \left(\mathbf{S}^{\alpha} \mathbf{PS}^{1-\alpha} \right)_{\mu\mu}$$

- Lowdin population analysis: a = ½

$$N = \sum_{\mu} \left(\mathbf{S}^{1/2} \mathbf{PS}^{1/2} \right)_{\mu\mu}$$

- Net charge associated to atom A:

$$q_A = Z_A - \sum_{\mu \in A} \left(\mathbf{S}^{1/2} \mathbf{PS}^{1/2} \right)_{\mu\mu}$$

- **P**’ density matrix in the symmetrically orthogonalized basis set

$$\mathbf{P}'_{\mu\mu} = (\mathbf{S}^{1/2}\ \mathbf{P}\ \mathbf{S}^{1/2})_{\mu\mu}$$

Basis set orthogonalization

- The basis set $\{\phi_\mu\}$ is not necessarily orthogonal ⇒ **S** matrix
- Transformation **X** from $\{\phi_\mu\}$ to $\{\phi_\mu'\}$
- **X** form: $\phi'_\mu = \sum_\nu X_{\mu\nu}\phi_\nu \leftrightarrow \langle \phi'_\mu | \phi'_\nu \rangle = \delta_{\mu\nu}$

$$\delta_{\mu\nu} = \langle \phi'_\mu | \phi'_\nu \rangle = \left\langle \sum_\lambda X_{\mu\lambda}\phi_\lambda \middle| \sum_\sigma X_{\nu\sigma}\phi_\sigma \right\rangle = \sum_\lambda \sum_\sigma X^*_{\mu\lambda} \langle \phi_\lambda | \phi_\sigma \rangle X_{\nu\sigma} = \sum_\lambda \sum_\sigma X^*_{\mu\lambda} S_{\lambda\sigma} X_{\nu\sigma}$$

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1}$$

- Two possibilities:
  - Symmetrical orthogonalization: $\mathbf{X} = \mathbf{S}^{-1/2}$
  - Canonical orthogonalization: $\mathbf{X} = \mathbf{U}\mathbf{s}^{-1/2} \Leftarrow \mathbf{s} = \mathbf{U}^\dagger\mathbf{S}\mathbf{U}$

Orthogonal basis set

- Transformation of **C**:

  $\mathbf{C}' = \mathbf{X}^{-1}\,\mathbf{C}$

  $\mathbf{C} = \mathbf{X}\,\mathbf{C}'$

- By substituting in the Roothaan eq.:

  $\mathbf{F}\,\mathbf{X}\,\mathbf{C}' = \mathbf{S}\,\mathbf{X}\,\mathbf{C}'\,\varepsilon$

  $(\mathbf{X}^{\dagger}\,\mathbf{F}\,\mathbf{X})\mathbf{C}' = (\mathbf{X}^{\dagger}\,\mathbf{S}\,\mathbf{X})\,\mathbf{C}'\,\varepsilon$

  $\mathbf{F}' = \mathbf{X}^{\dagger}\,\mathbf{F}\,\mathbf{X}$

  $\mathbf{F}'\,\mathbf{C}' = \mathbf{C}'\,\varepsilon \;\Rightarrow\; \mathbf{C} = \mathbf{X}\,\mathbf{C}'$

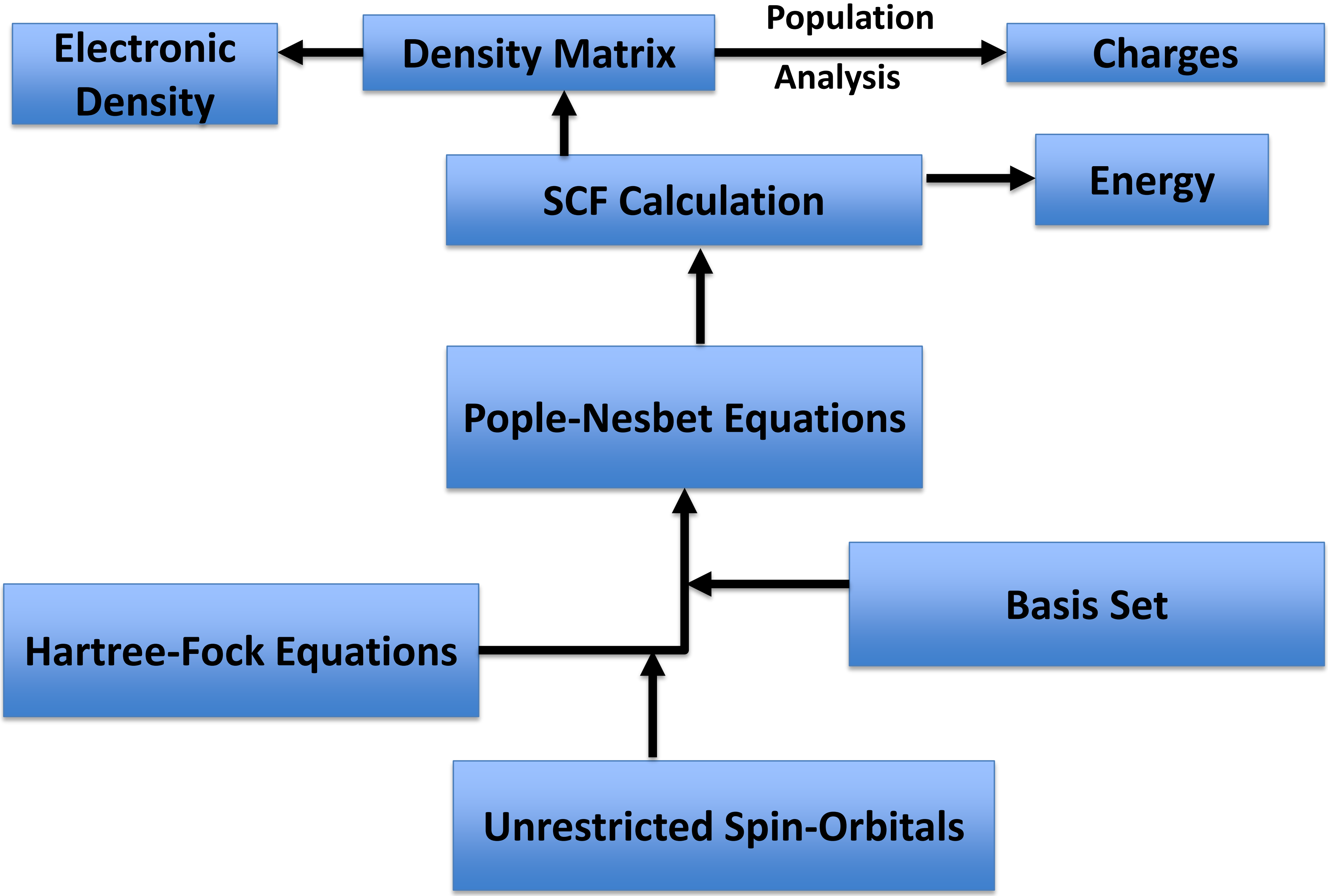
Unrestricted HF for open shell systems: Pople-Nesbet equations

Computational Chemistry
Elective Course
Degree in Chemistry
4th year

Contents

- Open shell HF: unrestricted spin-orbitals
- Introduction of a basis set: Pople-Nesbet equations
- Unrestricted density matrices
- Expression of the Fock matrices
- Solving unrestricted SCF equations
- The problem with dissociation and its unrestricted solution : the H_2 molecule as an example

General Scheme for UHF



Electronic Density

Density Matrix

Population Analysis

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SCF Calculation

Energy

Pople-Nesbet Equations

Basis Set

Hartree-Fock Equations

Unrestricted Spin-Orbitals

Restricted spin-orbitals

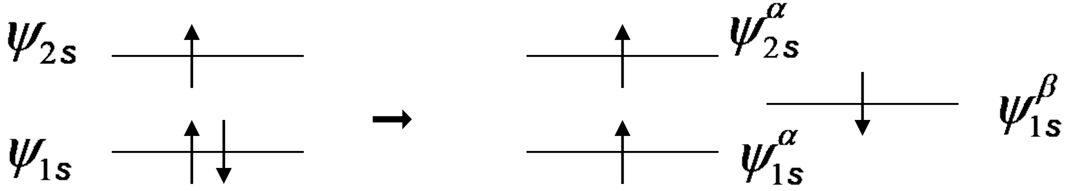
Restricted molecular spin-orbital: $\chi_i(\mathbf{x_i}) = \psi_j(\mathbf{r_i})\ \eta(\omega_i)$ $\eta(\omega_i) \begin{cases} \alpha(\omega_i) \\ \beta(\omega_i) \end{cases}$

The same spatial orbital ψ_j allows us to build a pair of spin-orbitals

- Closed shell: all spatial orbitals are doubly occupied
- Open shell: there are singly occupied spatial orbitals (α or β)

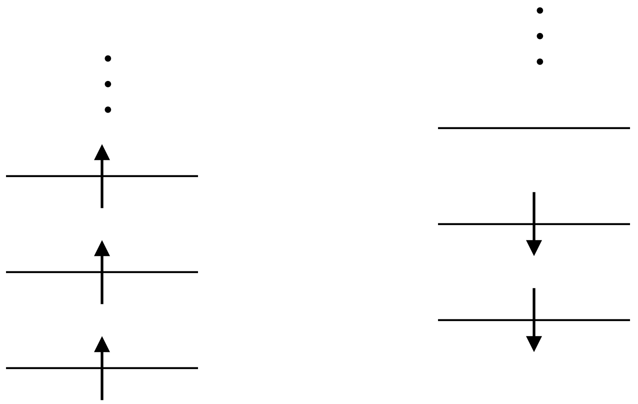
Is this correct?

- Must the spatial orbital of an electron α always be the same of an electron β?
- Let us consider a system of 3 electrons:



- The electron 1s(α) has an exchange interaction with 2s(α), but 1s(β) does not
- The electrons 1s(α) and 1s(β) feel different potentials

Unrestricted spin-orbitals



Unrestricted molecular spin-orbital:

$$\begin{cases} \chi_i^{\alpha}(\mathbf{x_i}) = \psi_i^{\alpha}(\mathbf{r_i})\ \alpha \\ \chi_j^{\beta}(\mathbf{x_i}) = \psi_j^{\beta}(\mathbf{r_i})\ \beta \end{cases}$$

There are two separated sets of spatial orbitals:

- For α spin $\Longrightarrow \{\psi_i^{\alpha}|i=1, 2, \ldots, K\}$
- For β spin $\Longrightarrow \{\psi_j^{\beta}|j=1, 2, \ldots, K\}$

Unrestricted HF equations

- If we use unrestricted spin-orbitals, then the HF equation becomes:

$$\boldsymbol{f}^{\alpha}(1)\,\psi_j^{\alpha}(1)=\varepsilon_j^{\alpha}\psi_j^{\alpha}(1)$$
$$\boldsymbol{f}^{\beta}(1)\,\psi_j^{\beta}(1)=\varepsilon_j^{\beta}\psi_j^{\beta}(1)$$

- Where the Fock operator takes the form:

$$\boldsymbol{f}^{\alpha}(\mathbf{r}_1)=\left\langle \alpha(\omega_1)\right|\boldsymbol{f}(\mathbf{r}_1,\omega_1)\left|\alpha(\omega_1)\right\rangle$$
$$\boldsymbol{f}^{\beta}(\mathbf{r}_1)=\left\langle \beta(\omega_1)\right|\boldsymbol{f}(\mathbf{r}_1,\omega_1)\left|\beta(\omega_1)\right\rangle$$

The Fock operator

- Taking into account the possible interactions:
  - Two electrons with the same spin have both Coulomb and exchange interactions
  - Two electrons with different spins have only Coulomb interactions

$$f^{\alpha}(1) = h(1) + \sum_{a}^{N^{\alpha}} \left[J_a^{\alpha}(1) - K_a^{\alpha}(1) \right] + \sum_{a}^{N^{\beta}} J_a^{\beta}(1)$$

$$f^{\beta}(1) = h(1) + \sum_{a}^{N^{\beta}} \left[J_a^{\beta}(1) - K_a^{\beta}(1) \right] + \sum_{a}^{N^{\alpha}} J_a^{\alpha}(1)$$

$$J_a^{\alpha}(1) = \left\langle \psi_a^{\alpha}(2) \middle| r_{12}^{-1} \middle| \psi_a^{\alpha}(2) \right\rangle$$

$$K_a^{\alpha}(1)\, \psi_i^{\alpha}(1) = \left\langle \psi_a^{\alpha}(2) \middle| r_{12}^{-1} \middle| \psi_i^{\alpha}(2) \right\rangle \psi_a^{\alpha}(1)$$

Fock equations

- The equations for α and β spin-orbitals are coupled due to the Coulomb interaction between electrons with different spins
- Integrals needed:
  - h_{ii}^{α}, h_{ii}^{β} : Kinetic energy and nuclear attraction
  - $J_{ij}^{\alpha\beta} = J_{ji}^{\beta\alpha}$: Coulomb interaction between α and β
  - $J_{ij}^{\alpha\alpha}$, $J_{ij}^{\beta\beta}$: Coulomb interaction between electrons of the same spin
  - $K_{ij}^{\alpha\alpha}$, $K_{ij}^{\beta\beta}$: Exchange interaction

Electronic energy

$$E_0 = \sum_a^{N^\alpha} h_{aa}^\alpha + \sum_a^{N^\beta} h_{aa}^\beta + \frac{1}{2}\sum_a^{N^\alpha}\sum_b^{N^\alpha}\left(J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}\right) + \frac{1}{2}\sum_a^{N^\beta}\sum_b^{N^\beta}\left(J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}\right) + \sum_a^{N^\alpha}\sum_b^{N^\beta} J_{ab}^{\alpha\beta}$$

$$h_{ii}^\alpha = \left\langle \psi_i^\alpha \middle| h \middle| \psi_i^\alpha \right\rangle$$

$$h_{ii}^\beta = \left\langle \psi_i^\beta \middle| h \middle| \psi_i^\beta \right\rangle$$

$$J_{ij}^{\alpha\beta} = J_{ji}^{\beta\alpha} = \left\langle \psi_i^\alpha \middle| J_j^\beta \middle| \psi_i^\alpha \right\rangle = \left\langle \psi_j^\beta \middle| J_i^\alpha \middle| \psi_j^\beta \right\rangle = \left\langle \psi_i^\alpha \psi_j^\beta \middle| \psi_i^\alpha \psi_j^\beta \right\rangle$$

$$J_{ij}^{\alpha\alpha} = \left\langle \psi_i^\alpha \middle| J_j^\alpha \middle| \psi_i^\alpha \right\rangle = \left\langle \psi_j^\alpha \middle| J_i^\alpha \middle| \psi_j^\alpha \right\rangle = \left\langle \psi_i^\alpha \psi_j^\alpha \middle| \psi_i^\alpha \psi_j^\alpha \right\rangle$$

$$J_{ij}^{\beta\beta} = \left\langle \psi_i^\beta \middle| J_j^\beta \middle| \psi_i^\beta \right\rangle = \left\langle \psi_j^\beta \middle| J_i^\beta \middle| \psi_j^\beta \right\rangle = \left\langle \psi_i^\beta \psi_j^\beta \middle| \psi_i^\beta \psi_j^\beta \right\rangle$$

$$K_{ij}^{\alpha\alpha} = \left\langle \psi_i^\alpha \middle| K_j^\alpha \middle| \psi_i^\alpha \right\rangle = \left\langle \psi_j^\alpha \middle| K_i^\alpha \middle| \psi_j^\alpha \right\rangle = \left\langle \psi_i^\alpha \psi_j^\alpha \middle| \psi_j^\alpha \psi_i^\alpha \right\rangle$$

$$K_{ij}^{\beta\beta} = \left\langle \psi_i^\beta \middle| K_j^\beta \middle| \psi_i^\beta \right\rangle = \left\langle \psi_j^\beta \middle| K_i^\beta \middle| \psi_j^\beta \right\rangle = \left\langle \psi_i^\beta \psi_j^\beta \middle| \psi_j^\beta \psi_i^\beta \right\rangle$$

Introduction of a basis set

$\{\phi_\mu \mid \mu = 1,2, \ldots K\}$

$$\psi_i^\alpha = \sum_{\mu=1}^{K} C_{\mu i}^{\alpha}\, \phi_\mu \quad i = 1,2, \ldots K$$

$$\psi_i^\beta = \sum_{\mu=1}^{K} C_{\mu i}^{\beta}\, \phi_\mu \quad i = 1,2, \ldots K$$

$$\Psi_0 = \left| \psi_1^\alpha \overline{\psi}_1^\beta \cdots \psi_a^\alpha \overline{\psi}_a^\alpha \cdots \right\rangle$$

$$f^\alpha(\mathbf{r_1})\, \psi_i^\alpha(\mathbf{r_1}) = \varepsilon_i^\alpha\, \psi_i^\alpha(\mathbf{r_1})$$

$$f^\beta(\mathbf{r_1})\, \psi_i^\beta(\mathbf{r_1}) = \varepsilon_i^\beta\, \psi_i^\beta(\mathbf{r_1})$$

$F_{\mu\nu}^{\alpha} = < \phi_\mu | f^\alpha | \phi_\nu >$

$F_{\mu\nu}^{\beta} = < \phi_\mu | f^\beta | \phi_\nu >$

$S_{\mu\nu} = < \phi_\mu | \phi_\nu >$

Pople-Nesbet eq.: $\mathbf{F}^\alpha\, \mathbf{C}^\alpha = \mathbf{S}\, \mathbf{C}^\alpha\, \boldsymbol{\varepsilon}^\alpha$

$\mathbf{F}^\beta\, \mathbf{C}^\beta = \mathbf{S}\, \mathbf{C}^\beta\, \boldsymbol{\varepsilon}^\beta$

Unrestricted Density Matrices

$$\left.\begin{aligned} \rho^\alpha(\mathbf{r}) = 2\sum_a^{N^\alpha}\left|\psi_a^\alpha(\mathbf{r})\right|^2 \quad &\Rightarrow \quad \int d\mathbf{r}\;\rho^\alpha(\mathbf{r}) = N^\alpha \\ \rho^\beta(\mathbf{r}) = 2\sum_a^{N^\alpha}\left|\psi_a^\beta(\mathbf{r})\right|^2 \quad &\Rightarrow \quad \int d\mathbf{r}\;\rho^\beta(\mathbf{r}) = N^\beta \end{aligned}\right\}$$

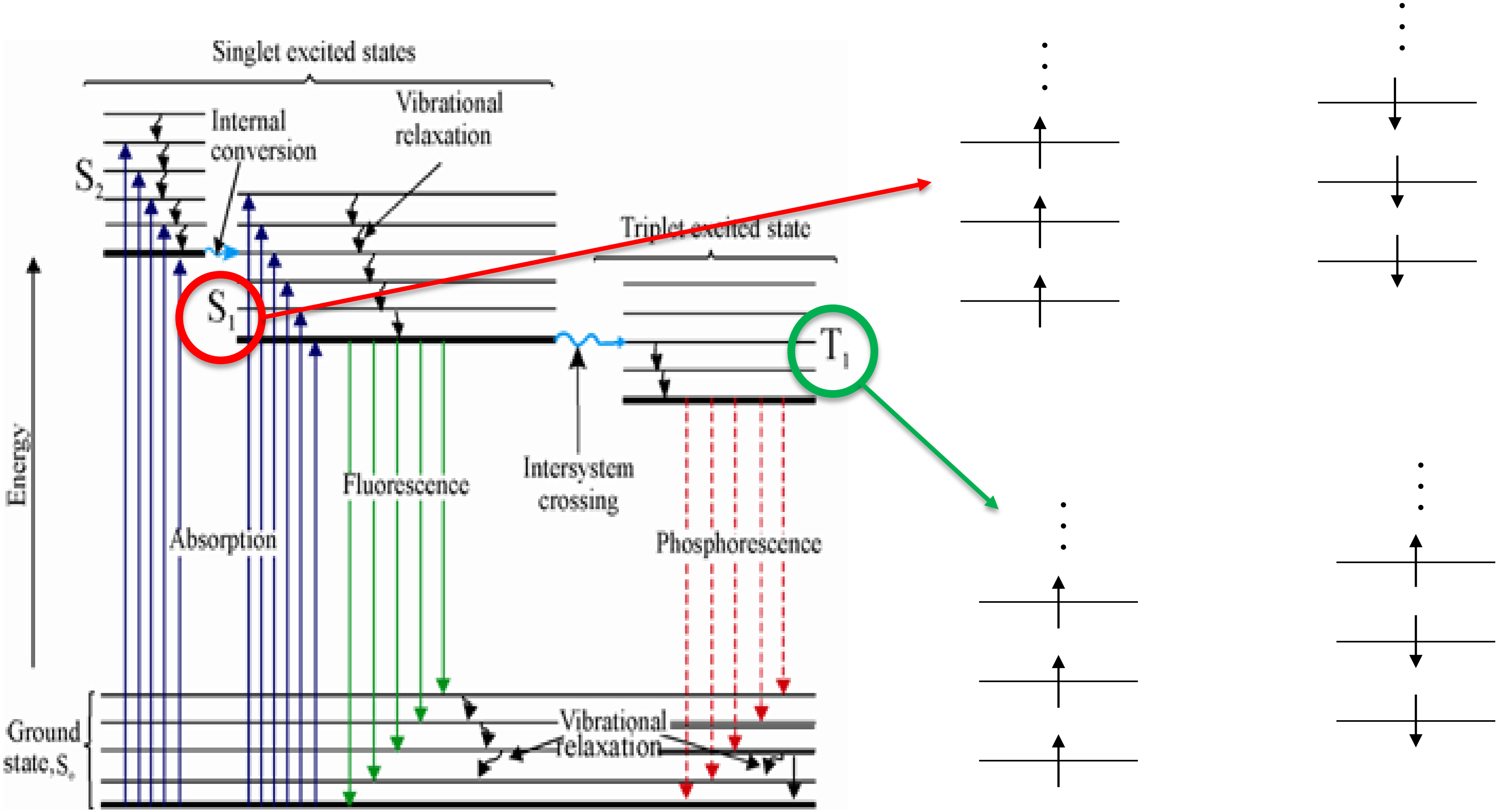
Charge Densities

$$\begin{cases} \rho^T(\mathbf{r}) = \rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r}) \quad \Rightarrow \quad \int d\mathbf{r}\;\rho^T(\mathbf{r}) = N = N^\alpha + N^\beta \\ \rho^S(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}) \end{cases}$$

Density Matrices

$$\left.\begin{aligned} \rho^\alpha(\mathbf{r}) &= \sum_a^{N^\alpha}\left|\psi_a^\alpha(\mathbf{r})\right|^2 = \sum_{\mu\nu} P^\alpha_{\mu\nu}\phi_\mu(\mathbf{r})\phi^*_\nu(\mathbf{r}) \\ \rho^\beta(\mathbf{r}) &= \sum_a^{N^\beta}\left|\psi_a^\beta(\mathbf{r})\right|^2 = \sum_{\mu\nu} P^\beta_{\mu\nu}\phi_\mu(\mathbf{r})\phi^*_\nu(\mathbf{r}) \end{aligned}\right\} \Rightarrow \boxed{\left\{\begin{aligned} P^\alpha_{\mu\nu} &= \sum_a^{N^\alpha} C^\alpha_{\mu a}\left(C^\alpha_{\nu a}\right)^* \\ P^\beta_{\mu\nu} &= \sum_a^{N^\beta} C^\beta_{\mu a}\left(C^\beta_{\nu a}\right)^* \end{aligned}\right\}} \Rightarrow \begin{cases} \mathbf{P}^T = \mathbf{P}^\alpha + \mathbf{P}^\beta \\ \mathbf{P}^S = \mathbf{P}^\alpha - \mathbf{P}^\beta \end{cases}$$

Unrestricted Density Matrices



What if $N^{\alpha} = N^{\beta}$?

- There are two possible independent solutions:
  - The restricted solution
    - $\Rightarrow \mathbf{P}^{\alpha} = \mathbf{P}^{\beta} = \mathbf{P}/2$
    - $\Rightarrow \mathbf{F}^{\alpha} = \mathbf{F}^{\beta} = \mathbf{F}$
  - In some cases an unrestricted solution of lower energy can exist
    - $\Rightarrow \mathbf{P}^{\alpha} \neq \mathbf{P}^{\beta} \Rightarrow$ Initial trial with $\mathbf{P}^{\alpha} \neq \mathbf{P}^{\beta}$, but even then the restricted solution can be obtained
    - → The dissociation problem!!!

H_2: The dissociation problem

- Closed shell system, geometry in equilibrium
  ⇒The RHF solution is OK
- At infinite distance, 2 atoms with 2 degenerated orbitals with 1 electron in each ⇒ UHF method
- There can be more than one solution for the intermediate R_{AB} depending on the starting orbitals

The hydrogen molecule

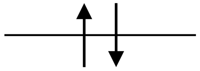
- Potential energy curves:

MOs H_2 RHF in **M**inimal **B**asis **S**et

$H_A - H_B$

(σ_u^*)

$(\sigma_g)^2$



$$\psi_2(i)=\frac{1}{\sqrt{2(1-s)}}\left(\phi_A(i)-\phi_B(i)\right)$$

$$\psi_1(i)=\frac{1}{\sqrt{2(1+s)}}\left(\phi_A(i)+\phi_B(i)\right) \qquad s=\langle\phi_A|\phi_B\rangle$$

$$\Psi_0\left({}^1\Sigma_g^+,\, R=R_{opt}\right)=\left|\psi_1\ \bar{\psi}_1\right\rangle$$

$$\Psi_0({}^1\Sigma_g^+,\, R=R_{opt})=\frac{1}{2(1+s)}\left(\underbrace{\left|\phi_A\bar{\phi}_A\right\rangle}_{H_A^-\ H_B^+}+\underbrace{\left|\phi_B\bar{\phi}_B\right\rangle}_{H_B^-\ H_A^+}+\underbrace{\left|\phi_A\bar{\phi}_B\right\rangle}_{H_A\bullet\ H_B\bullet}+\underbrace{\left|\phi_B\bar{\phi}_A\right\rangle}_{H_B\bullet\ H_A\bullet}\right)$$

When R→∞, s→0:

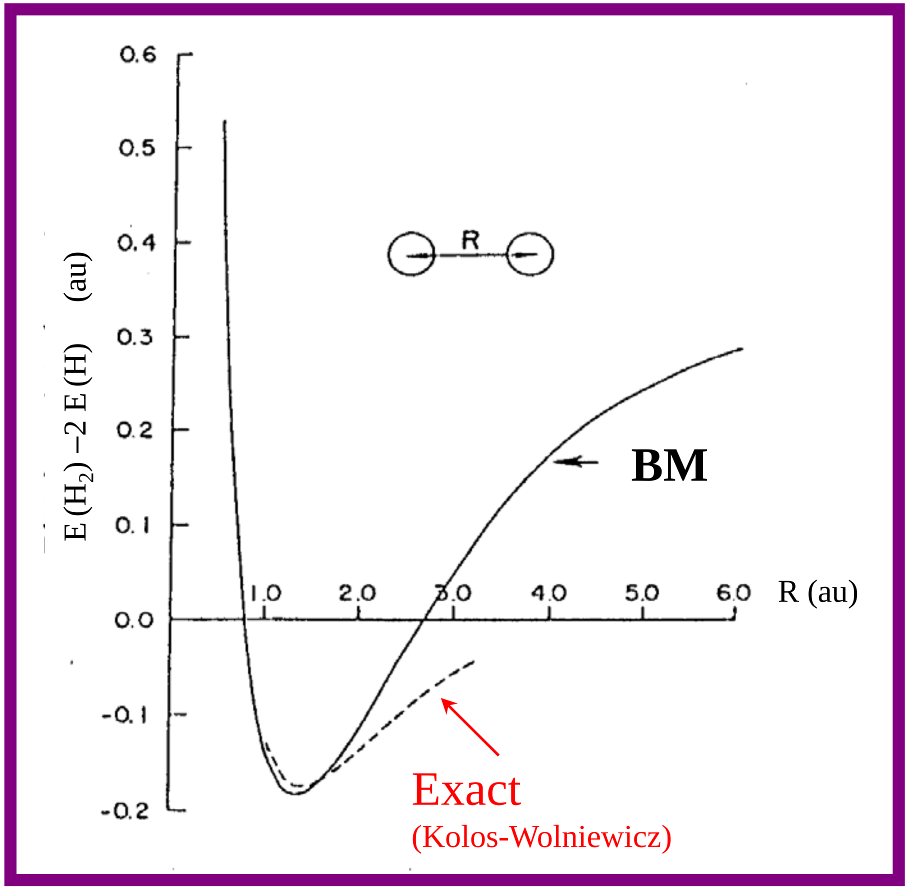
$$E_0=\frac{\langle\Psi_0|H|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}=\frac{1}{4}\left(4E(H)+2E(H^-)\right)=E(H)+\frac{1}{2}E(H^-)$$

The hydrogen molecule

When R→∞, s→0:

$$E_0 = \underbrace{E(H) + \frac{1}{2}E(H^-)}_{\neq 2\,E(H)}$$

!!!!



The hydrogen molecule

- Potential energy curves:

True ground state of H_2 at R→∞: two H(^{2}S) atoms

$$\Psi_0\left({}^1\Sigma_g^+, \mathrm{R}=\infty\right)=\frac{1}{\sqrt{2}}\left(\left|\phi_A\bar{\phi}_B\right\rangle-\left|\bar{\phi}_A\phi_B\right\rangle\right)$$

Unrestricted solution:

$$\Psi_{\mathrm{UHF}} = \left|\psi_1^{\alpha}(1)\ \bar{\psi}_1^{\beta}(2)\right\rangle$$

- If R $\leq$ 2.3 au

$$\left.\psi_1^{\alpha}=\psi_1^{\beta}=\psi_1=c_A\phi_A+c_B\phi_B\ \right\}\quad c_A=c_B$$

Restricted Solution

- If R $>$ 2.3 au

$$\left.\begin{aligned}\psi_1^{\alpha}&=c_A\phi_A+c_B\phi_B\\ \psi_1^{\beta}&=c_B\phi_A+c_A\phi_B\end{aligned}\ \right\}\quad c_A\neq c_B$$

Unrestricted Solution

- If R→∞

$$\Psi_{\mathrm{UHF}}(\mathrm{R}\rightarrow\infty) = \left|\phi_A(1)\ \bar{\phi}_B(2)\right\rangle$$

Dissociation Energy: OK!

Wavefunction: ~~O~~K!

Why?

Let’s write the unrestricted MOs as a linear combination of the restricted MOs:

$$\begin{aligned}\psi_1^{\alpha} &= \boxed{\cos\theta}\,\psi_1 + \boxed{\sin\theta}\,\psi_2 \\ \psi_1^{\beta} &= \cos\theta\,\psi_1 - \sin\theta\,\psi_2\end{aligned}$$

Two normalized coefficients

By substituting the expression of ψ_1 and ψ_2:

$$\left.\begin{aligned}\psi_1^{\alpha} &= c_1\phi_1 + c_2\phi_2 \\ \psi_1^{\beta} &= c_2\phi_1 + c_1\phi_2\end{aligned}\right\}\begin{cases} c_1 = \dfrac{1}{\sqrt{2(1+s)}}\cos\theta + \dfrac{1}{\sqrt{2(1-s)}}\sin\theta \\[2ex] c_2 = \dfrac{1}{\sqrt{2(1+s)}}\cos\theta - \dfrac{1}{\sqrt{2(1-s)}}\sin\theta \end{cases}$$

Limiting values:

- If $\theta = 0^{o}$ ⇒ **restricted solution:** $c_1 = c_2 = [2(1 + s)]^{-1/2}$
- If $s = 0$ and $\theta = 45^{o}$ ⇒ $c_1 = 1$ and $c_2 = 0$, then: $\psi_1^{\alpha} = \phi_1$ and $\psi_1^{\beta} = \phi_2$ ⇒ 2 separated atoms
- If θ has values between 0^{o} and 45^{o} ⇒ ψ_1^{α} and ψ_1^{β} have intermediate compositions
- θ varies with the internuclear distance, R

How does E_0 depend on θ?

Electronic energy of an unrestricted determinant $|\psi_1^{\alpha}(1)\alpha(1)\ \psi_1^{\beta}(2)\beta(2)>$

$$E_0(\theta) = 2\cos^2\theta\, h_{11} + 2\sin^2\theta\, h_{22} + \cos^4\theta\, J_{11} + \sin^4\theta\, J_{22} + 2\sin^2\theta\cos^2\theta\left(J_{12} - 2K_{12}\right)$$

For θ = 0º ⇒ restricted solution: $E_0(\theta = 0) = 2h_{11} + J_{11}$

Optimal value of θ:

$$\frac{dE_0(\theta)}{d\theta} = 4\cos\theta\sin\theta\left[h_{22} - h_{11} + \sin^2\theta\, J_{22} - \cos^2\theta\, J_{11} + \left(\cos^2\theta - \sin^2\theta\right)\left(J_{12} - 2K_{12}\right)\right] = 0$$

That has two solutions:

1. $\cos\theta\sin\theta = 0 \Rightarrow \theta = 0 \rightarrow$ restricted solution
2. $h_{22} - h_{11} + \sin^2\theta\, J_{22} - \cos^2\theta\, J_{11} + \left(\cos^2\theta - \sin^2\theta\right)\left(J_{12} - 2K_{12}\right) = 0 \Rightarrow$

$$\cos^2\theta = \frac{h_{22} - h_{11} + J_{22} - J_{12} + 2K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}} = f(R)$$

The value of integrals depends on R

How does E_0 depend on θ?

Classification of the end value:

For $\theta = 0^\circ$ ⇔ restricted solution:

$$\left[\frac{d^2E_0(\theta)}{d\theta^2}\right]_{\theta=0^\circ} = 4\left(h_{22}-h_{11}-J_{11}+J_{12}-2K_{12}\right)$$

The sign of the second derivative depends on R

The sign of the second derivative changes when this is equal to zero:

$$h_{22}-h_{11}=J_{11}-J_{12}+2K_{12} \Rightarrow \left[\frac{d^2E_0(\theta)}{d\theta^2}\right]_{\theta=0^\circ}=0$$

Saddle Point:
Occurs at R ~ 1.2 Å

- For R < 1.2 Å ⇒ **RHF** SOLUTION MINIMUM ⇔ $\left[\frac{d^2E_0(\theta)}{d\theta^2}\right]_{\theta=0^\circ}<0$
- For R > 1.2 Å ⇒ **RHF** SOLUTION MAXIMUM ⇔ $\left[\frac{d^2E_0(\theta)}{d\theta^2}\right]_{\theta=0^\circ}>0$

How does E_0 depend on θ?

Classification of the end value:

For $\cos^2\theta = \dfrac{h_{22} - h_{11} + J_{22} - J_{12} + 2K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}}$ ⟺ unrestricted solution:

- At R < 1.2 Å ⇒ $\cos^2\theta > 1$ ⇒ **UHF** SOLUTION UNDEFINED
- At R > 1.2 Å ⇒ $\cos^2\theta < 1$ ⇒ $\left[\dfrac{d^2E_0(\theta)}{d\theta^2}\right]_\theta > 0$ ⇒ **UHF** SOLUTION MINIMUM
- At R = ∞ ⇒ $\cos^2\theta = ½$ ⇒ $\theta = 45^o$ ⇒ 2 H atoms

R Intervals

R (Å)	2nd derivative	Class	Minimum Energy Solution
< 1.2	> 0	MINIMUM	RHF
1.2	= 0	SADDLE POINT	
> 1.2	< 0	MAXIMUM	RHF
> 1.2	> 0	MINIMUM	UHF

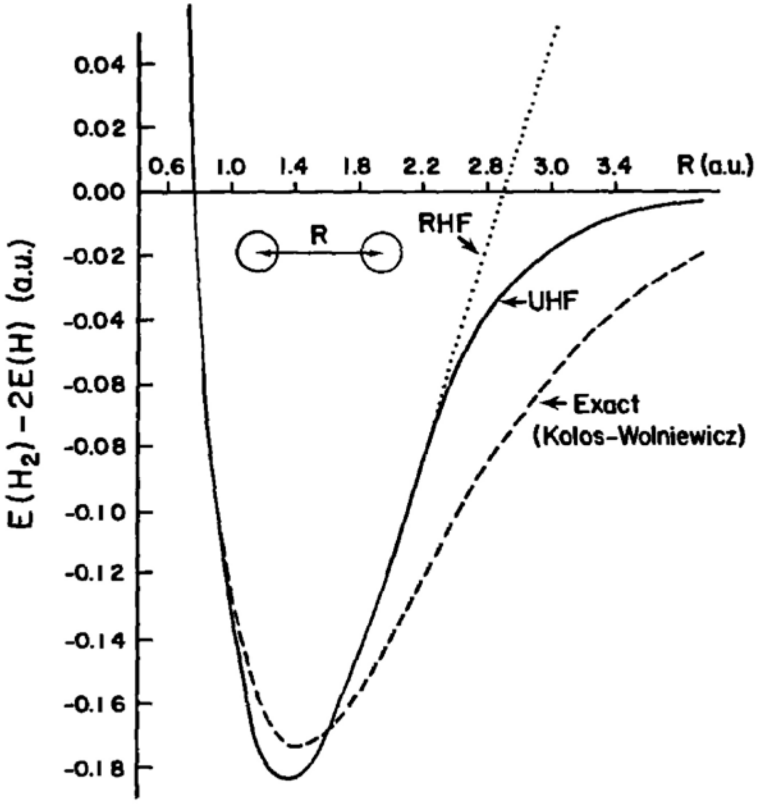


Figure 3.18 STO-3G potential curves for H_2.

CONCLUSION
For R > 2,3 au (≈1.2 Å) TWO SOLUTIONS exist:

- Restricted solution ⇒ MAXIMUM
- Unrestricted solution ⇒ MINIMUM
- **Obtaining one or the other depends on the starting set of MOs (initial estimate)**

Density Functional Theory (DFT)

Computational Chemistry
Elective Course
Degree in Chemistry
4th Year

Contents

- Basic principles of the density functional theory (DFT)
- Kohn-Sham approximation
- Applications of DFT
- DFT strengths and weaknesses

Wavefunction and electron density

For a system of N electrons

- Wavefunction:
  - depends on 4N variables (3N spatial variables and N spin variables)

$$\Psi\left(x_1, y_1, z_1, \sigma_1, \ldots, x_N, y_N, z_N, \sigma_N\right) = \Psi\left(\mathbf{r}_1, \sigma_1, \ldots, \mathbf{r}_N, \sigma_N\right) = \Psi\left(\mathbf{x}_1, \ldots, \mathbf{x}_N\right)$$

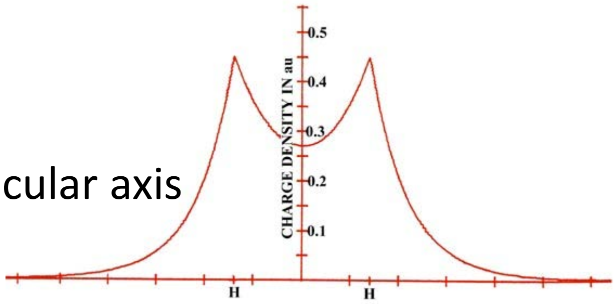
- Electron density:
  - Represents the density of probability to find any of the electrons in the system
  - Depends on **ONLY** 3 variables (x,y,z)

$$\rho\left(\mathbf{r}_1\right) = N \sum_{\forall \sigma_i} \int \cdots \int d\mathbf{r}_2\, d\mathbf{r}_3 \ldots d\mathbf{r}_N \left|\Psi\left(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N\right)\right|^2$$

Electron density properties

- Non-negative functional with only **3 variables**, independent of the total number of electrons, N
  - Tends towards zero at infinite: $\rho(\mathbf{r}\longrightarrow\infty) = 0$
  - Integrates to N: $\int d\mathbf{r}\, \rho(\mathbf{r}) = N$
- It can be measured experimentally (X-Ray diffraction, electron diffraction, …)
- At the position of the nuclei, the electron density gradient is discontinuous and a cusp appears

Electron density of the H_2 molecule along the molecular axis



DFT methods

- Solve the state of N-electron systems using $\rho(\mathbf{r})$ instead of $\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)$
  - For a 10-electron system
    - Wavefunction depends on 40 coordinates
    - Electron density depends on 3 coordinates
  - For a system with 1000 electrons
    - Wavefunction depends on 4000 coordinates
    - Electron density depends on 3 coordinates
- PROBLEM: The exact $\rho(\mathbf{r})$ is unknown

1^{st} Hohenberg-Kohn theorem

- **First HK theorem** : The properties of a molecule in its ground state are completely determined by the electron density of the ground state $\rho_0(x,y,z)$. ⇒ any property (E, for ex.) of the ground state is a functional of ρ_0: $E_0=F[\rho_0(\mathbf{r})]$

- Only states the existence of the functional and not how to find it ⇒ *That is the question!*

- It is assumed that approximate functionals give reasonable approximations of the properties of the system

2^{nd} Hohenberg-Kohn theorem

Second HK theorem: Any electron density functional will give an energy value greater than or equal to the true ground state energy

- Let $v(\mathbf{r})$ be the *external* potential of the system (nuclei potential) and $E_v[\rho]$ the functional of the electronic energy
- Let ρ_t be an approximation of the electron density of the ground state satisfying
  - $\int d\mathbf{r}\, \rho_t(\mathbf{r}) = N \Rightarrow$ The electron number must be conserved
  - $\rho_t(\mathbf{r}) \geq 0 \ \forall \mathbf{r} \Rightarrow$ The electron number cannot be negative
- Let $E_0(\rho_0)$ be the true ground state energy
- Then:

$$\boxed{E_v[\rho_t] \geq E_0(\rho_0)}$$

- It is analogous to the variational principle
- $E_v[\rho]$ is an unknown functional… ⇒ if one uses approximate functionals ⇒ IT IS NOT VARIATIONAL

Kohn-Sham (KS) equations

- Are analogous to Hartree Fock but in the context of DFT
- Are the basis of DFT calculations
- What do we need?:
  - A good approximation of the density ρ_0
  - The exact functional of energy $E_v[\rho]$

    ⇒ direct calculation of the energy
  - ANY OF THE 2 CONDITIONS CAN BE ACHIEVED
- KS equations:
  - Express the energy as a sum of terms, one of them is the “unknown”, assumed to be “small” relative to the other
  - Use a trial density to initiate calculations, and they will be improved iteratively

KS equations

- In KS equations a non-interacting reference system is used:
  - *Fictitious*
  - The electrons do not interact, but…
  - $\rho_r = \rho_0$ (the system real density)
  - The deviation of the real behavior is accumulated in a small term that we must *build*
- The total energy is obtained by:

$$E_0 = <T[\rho_0]> + <V_{Ne}[\rho_0]> + <V_{ee}[\rho_0]>$$

- Where
  - T is the electronic kinetic energy
  - V_{ne} is the interaction between nuclei and electrons
  - V_{ee} is the interaction between electrons
  - The three are functionals of ρ_0
  - All terms are average values

KS energy

- Reference system: non-interacting electrons with the same electronic distribution as the real system

$$\psi_r = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1^{KS}(1)\alpha(1) & \cdots & \boxed{\psi_{N/2}^{KS}}(1)\beta(1) \\ \vdots & \ddots & \vdots \\ \psi_1^{KS}(N)\alpha(N) & \cdots & \psi_{N/2}^{KS}(N)\beta(N) \end{vmatrix}$$

KS orbitals

- Kinetic electron energy of the *reference* system:

$$\left\langle T[\rho_0] \right\rangle_{ref} = \left\langle \psi_r \middle| \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 \middle| \psi_r \right\rangle$$

$$\left\langle T[\rho_0] \right\rangle_{ref} = -\frac{1}{2}\sum_{i=1}^{N} \left\langle \psi_i^{KS}(1) \middle| \nabla_1^2 \middle| \psi_i^{KS}(1) \right\rangle$$

- Kinetic energy of the *real* system is the energy of the reference, plus a small deviation:

$$\left\langle T[\rho_0] \right\rangle_{real} = \left\langle T[\rho_0] \right\rangle_{ref} + \Delta\left\langle T[\rho_0] \right\rangle$$

KS Energy

- Nuclei-electron interaction:

$$V_{Ne} = \sum_{i=1}^{N}\sum_{I=1}^{M} -\frac{Z_I}{\boldsymbol{r}_{iI}} = \sum_{i=1}^{N} v\left(\boldsymbol{r}_i\right)$$

$v(\mathbf{r}_i)$ ➞ external attractive potential between the ith electron and all nuclei

$$v\left(\boldsymbol{r}_i\right) = \sum_{I=1}^{M} -\frac{Z_I}{\boldsymbol{r}_{iI}}$$

- In general, one can write:

$$\int d\tau \; \psi^* \sum_{i=1}^{N} f\left(\mathbf{r}_i\right) \psi = \int d\mathbf{r} \; \rho\left(\mathbf{r}\right) f\left(\mathbf{r}\right)$$

- Average electron-nucleus interactions will be:

$$\left\langle V_{Ne}\right\rangle = \int d\mathbf{r} \; \rho_0\left(\mathbf{r}\right) v\left(\mathbf{r}\right) \qquad \rho_0 = \sum_{i=1}^{N} \left|\psi_i^{KS}(1)\right|^2$$

KS Energy

- The energy of interaction between electrons in the *real* system is obtained by the sum of the interaction in the *reference* system and a term that accounts for the difference:

$$\left\langle V_{ee}\left[\rho_0\right]\right\rangle_{real} = \frac{1}{2}\int\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho_0\left(\mathbf{r}_1\right)\rho_0\left(\mathbf{r}_2\right)}{\mathbf{r}_{12}} + \Delta\left\langle V_{ee}\left[\rho_0\right]\right\rangle$$

- Differences between the real and reference systems are due to correlation and exchange

KS energy and XC potential

- The Kohn-Sham energy can be written:

$$E_0 = \int d\mathbf{r}\; \rho_0(\mathbf{r})\, v(\mathbf{r}) + \left\langle T[\rho_0] \right\rangle_{ref} + \frac{1}{2}\int\int d\mathbf{r}_1\, d\mathbf{r}_2\, \frac{\rho_0(\mathbf{r}_1)\rho_0(\mathbf{r}_2)}{\mathbf{r}_{12}} + \Delta\left\langle T[\rho_0] \right\rangle + \Delta\left\langle V_{ee}[\rho_0] \right\rangle$$

- Correlation-exchange (XC) energy:
  - The deviation of the kinetic energy with respect to the reference: correlation kinetic energy
  - The deviation of the e-e repulsion from the classical system: correlation and exchange potential

$$E_{XC}[\rho_0] \equiv \Delta\left\langle T[\rho_0] \right\rangle + \Delta\left\langle V_{ee}[\rho_0] \right\rangle$$

- KS energy:

$$E_0 = \int d\mathbf{r}\; \rho_0(\mathbf{r})\, v(\mathbf{r}) + \left\langle T[\rho_0] \right\rangle_{ref} + \frac{1}{2}\int\int d\mathbf{r}_1\, d\mathbf{r}_2\, \frac{\rho_0(\mathbf{r}_1)\rho_0(\mathbf{r}_2)}{\mathbf{r}_{12}} + E_{XC}[\rho_0]$$

KS energy and XC potential

- KS energy:

$$E_0 = -\sum_{I=1}^{M} Z_I \int d\mathbf{r}_1 \frac{\rho_0(\mathbf{r}_1)}{\mathbf{r}_{1I}} - \frac{1}{2}\sum_{i=1}^{N} \left\langle \psi_i^{KS}(1) \middle| \nabla_1^2 \middle| \psi_i^{KS}(1) \right\rangle + \frac{1}{2}\int\int d\mathbf{r}_1\, d\mathbf{r}_2 \frac{\rho_0(\mathbf{r}_1)\rho_0(\mathbf{r}_2)}{\mathbf{r}_{12}} + E_{XC}\left[\rho_0\right]$$

$$\rho_0 = \rho_{ref} = \sum_{i=1}^{N} \left| \psi_i^{KS}(1) \right|^2$$

- XC energy:
  - Problematic term
  - It is assumed to be small
  - Requires the design of adequate functionals: principal problem in DFT

Kohn-Sham equations

- By substituting in E_0, taking the first derivative with respect to the ψ_i^{KS} (which is made equal to zero) and requiring them to be orthonormal ➞ KS equations:

$$\left[-\frac{1}{2}\nabla_i^2-\sum_{I=1}^{M}\frac{Z_I}{\mathbf{r}_{1I}}+\frac{1}{2}\int d\mathbf{r}_2\frac{\rho(\mathbf{r}_2)}{\mathbf{r}_{12}}+v_{XC}(1)\right]\psi_i^{KS}(1)=\varepsilon_i^{KS}\psi_i^{KS}(1)\leftrightarrow\hat{h}^{KS}(1)\,\psi_i^{KS}(1)=\varepsilon_i^{KS}\psi_i^{KS}(1)$$

  - ε_i^{KS} ➞ KS orbital energies
  - $v_{XC}(1)$ ➞ correlation-exchange potential
  - N/2 equations (closed shell)
  - $h^{KS}(1)$ ➞ Kohn-Sham operator

$$v_{xc}(1)=\frac{\delta E_{xc}\left[\rho(1)\right]}{\delta\rho(1)}$$

KS equations are equivalent to HF

HF and KS comparison

- KS:
  - Orbitals → artefact for computation
  - Exact KS energy, if known
    - $\rho_0(\mathbf{r})$
    - $E_{XC}[\rho_0]$
  - Gives an approximate solution to an exact equation
  - There are no means to systematically improve the results → IT IS NOT variational
- HF:
  - Approximation that does not properly include the correlation
  - Gives an exact solution to an approximate equation
  - Allows a systematic improvement of the results
    - Better basis sets
    - Larger perturbation order in MP or CC
    - More extensive CI

Solving KS equations

1. Expand the KS orbitals in a basis set of dimension K (i.e. 6-31G*):

$$\psi_i^{KS} = \sum_{\mu}^{K} C_{\mu i}\phi_\mu \quad i = 1, 2, \ldots, K$$

2. Substitute the KS MO into the equations
3. Multiply by $<\phi_\nu|$ $\Rightarrow$ equations in matrix form :

$$\mathbf{h\ C = S\ C}\ \boldsymbol{\varepsilon}$$

   - Requires calculation of the matrix $h_{\mu\nu} = <\phi_\mu|h^{KS}|\phi_\nu>$
   - Trial density ➞ sum of atom densities

Iterative procedure

1. Specify geometry, charge and multiplicity
2. Specify basis set
3. Trial initial ρ ➞ superposition of ρ of atoms
4. Calculate $v_{XC}(\mathbf{r})=\delta E_{XC}/\delta\rho$, by means of the chosen E_{XC} functional
5. Calculate the h^{KS} operator
6. Calculate the matrix $h_{\mu\nu} = <\phi_\mu|h^{KS}|\phi_\nu>$
7. Orthogonalize the h matrix and diagonalize it, deorthogonalize the coefficient matrix
8. Calculate an improved ρ with the KS OM of 7
9. Come back to 4 with the new ρ. Verify the convergence in 7
10. After convergence calculate the KS E_0
11. With the derivatives of E_0 with respect to R_I, one can optimize the geometry

Which E_{XC} functional do we choose?

By searching the “divine functional”. Successive approximations…

- LDA: Local Density Approximation
- LSDA: Local Spin Density Approximation
- GGA: Generalized Gradient Approximation
- MGGA: Meta-GGA
- HGGA: hybrid GGA
- HMGGA: hybrid MGGA
- Completely non-local theory

Jacob’s ladder

“Divine” functional

Scientists inventing functionals

Kohn dreaming of the perfect functional

L(S)DA: Local (Spin) Density Approximation

- Uniform electron gas: e^-s move over a background with a uniformally positive charge distribution, in such a way that the ensemble is neutral

$$E_{XC}^{LDA}[\rho] = \int d\mathbf{r}\, \rho(\mathbf{r})\varepsilon_{XC}(\rho(\mathbf{r}))$$

  - $\varepsilon_{XC}(\rho(\mathbf{r}))$ ➞ exchange-correlation energy by particle of an electron uniform gas of density $\rho(\mathbf{r})$
  - The energy per particle is weighed with $\rho(\mathbf{r})$
  - $\varepsilon_{XC}(\rho(\mathbf{r})) = \varepsilon_X(\rho(\mathbf{r})) + \varepsilon_C(\rho(\mathbf{r}))$
  - $\varepsilon_X = -(3/4)(3\rho(\mathbf{r})/\pi)^{1/3}$ (Bloch, Dirac, end of the 20's)
  - ε_C is obtained from simulations of quantum Monte-Carlo of the homogeneous e- gas

- Bond lengths of ~2%

GGA: Generalized Gradient Approximation

- Information on the density gradient is used to obtain XC $\nabla\rho(\mathbf{r}) \Rightarrow$ inhomogeneity of the true $\rho(\mathbf{r})$

$$E_{XC}^{GGA}\left[\rho_\alpha, \rho_\beta\right] = \int d\mathbf{r}\ f\left(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta\right)$$

- Becke hybrid functional

$$E_{XC}^{hyb} = \alpha\ E_X^{KS} + (1 - \alpha)\ E_{XC}^{GGA}$$

  - E_X^{KS} ➞ Calculated with the KS wavefunction and MOs
  - E_{XC}^{GGA} ➞ An appropriate GGA functional
  - α an adjustable parameter
- Reduce the LDA errors by a factor of 3 to 5

DFT Applications

- Molecular structures : bond lengths (Å)

Bond		LDA	BLYP	BP86	Exp.
H–H	R(H–H)	0,765	0,748	0,752	0,741
CH_3–CH_3	R(C–C)	1,510	1,542	1,535	1,526
	R(C–H)	1,101	1,100	1,102	1,088
HCCH	R(C–C)	1,203	1,209	1,210	1,203
	R(C–H)	1,073	1,068	1,072	1,061

- Vibrational frequencies (cm^{-1}): set of 122 molecules

method	RMS	Error Molec >10%	Desv > 100 cm^{-1}
BP86	41	6	142(H2), 115(HF), 106(F2)
B3LYP	34	6	132(HF), 125(F2), 121(H2)

DFT Applications

- Atomization Energies:
  - → LDA < GGA < hybrid functional
  - – Deviation [kcal/mol] between calculated and experimental

molecule	LDA	BLYP	molecule	LDA	BLYP
CH	7	0	F_2	47	18
CH_3	31	-2	O_2	57	19
CH_4	44	-3	N_2	32	6
C_2H_2	50	-6	CO	37	1
C_2H_4	86	-6	CO_2	82	11

DFT: Strengths and Weaknesses

- Strengths :
  - Includes correlation from the beginning
  - Cost is similar to HF and achieves precision comparable to methods that include correlation (e. g. MP2)
  - Saturates the basis set faster than *ab initio*
  - Works with electron density, experimentally accessible

- Weaknesses:
  - Exact $E_{XC}[\rho_0]$ is unknown
  - There are no ways to systematically improve the functional
  - Progress is based on experience and intuition, verified with the experiments ⇒ philosophy somewhat semiempirical
  - Some functionals include semiempirical parameters
  - It is not a variational method, except with the exact functional, which is unknown
  - One cannot know *a priori* if a given functional is appropriate to a given problem
  - Problems with van der Waals molecules or those with weak interactions

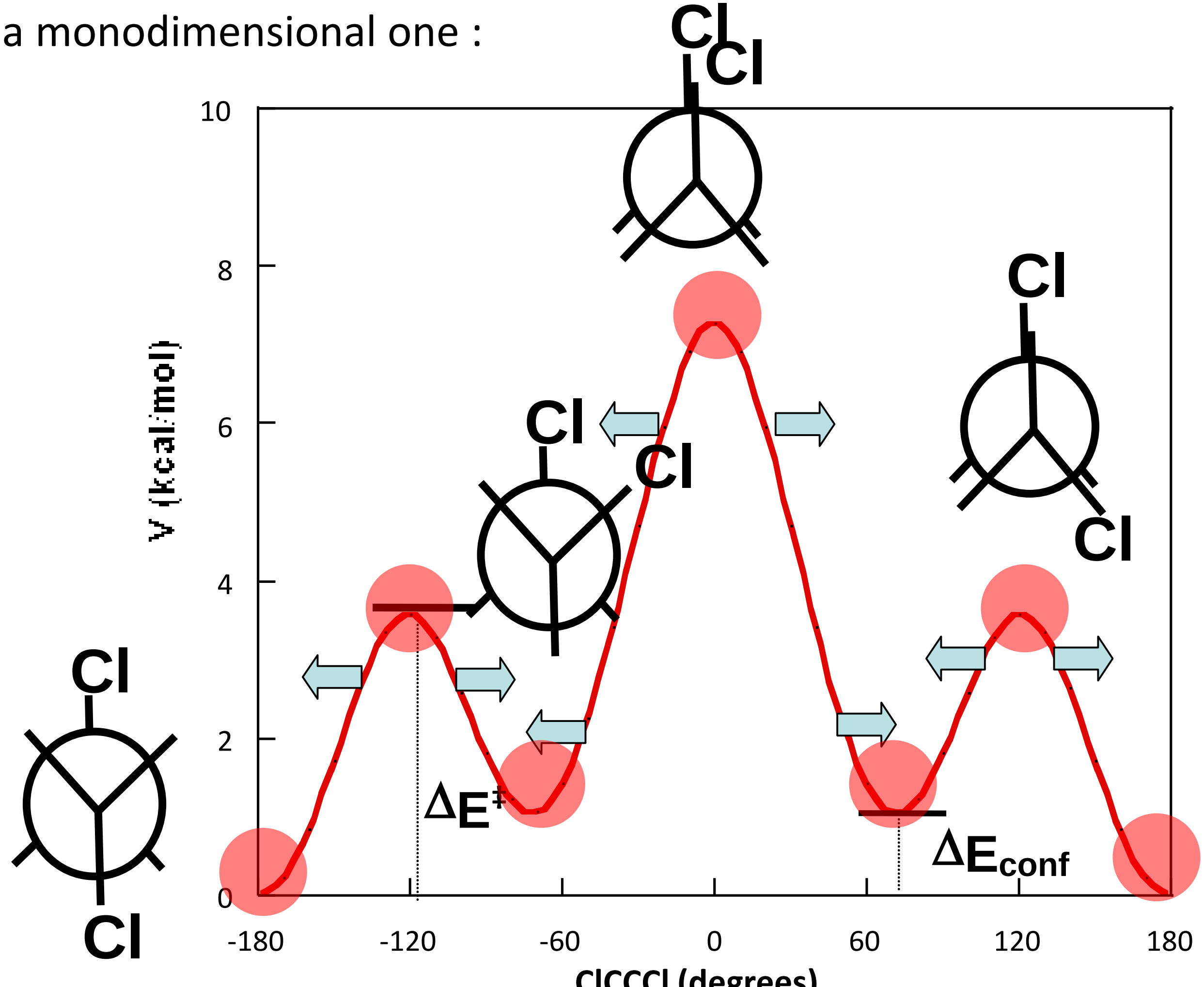
Introduction
to
Chemical Reactivity

Computational Chemistry
Elective Course
Degree in Chemistry
4th Year

Introduction

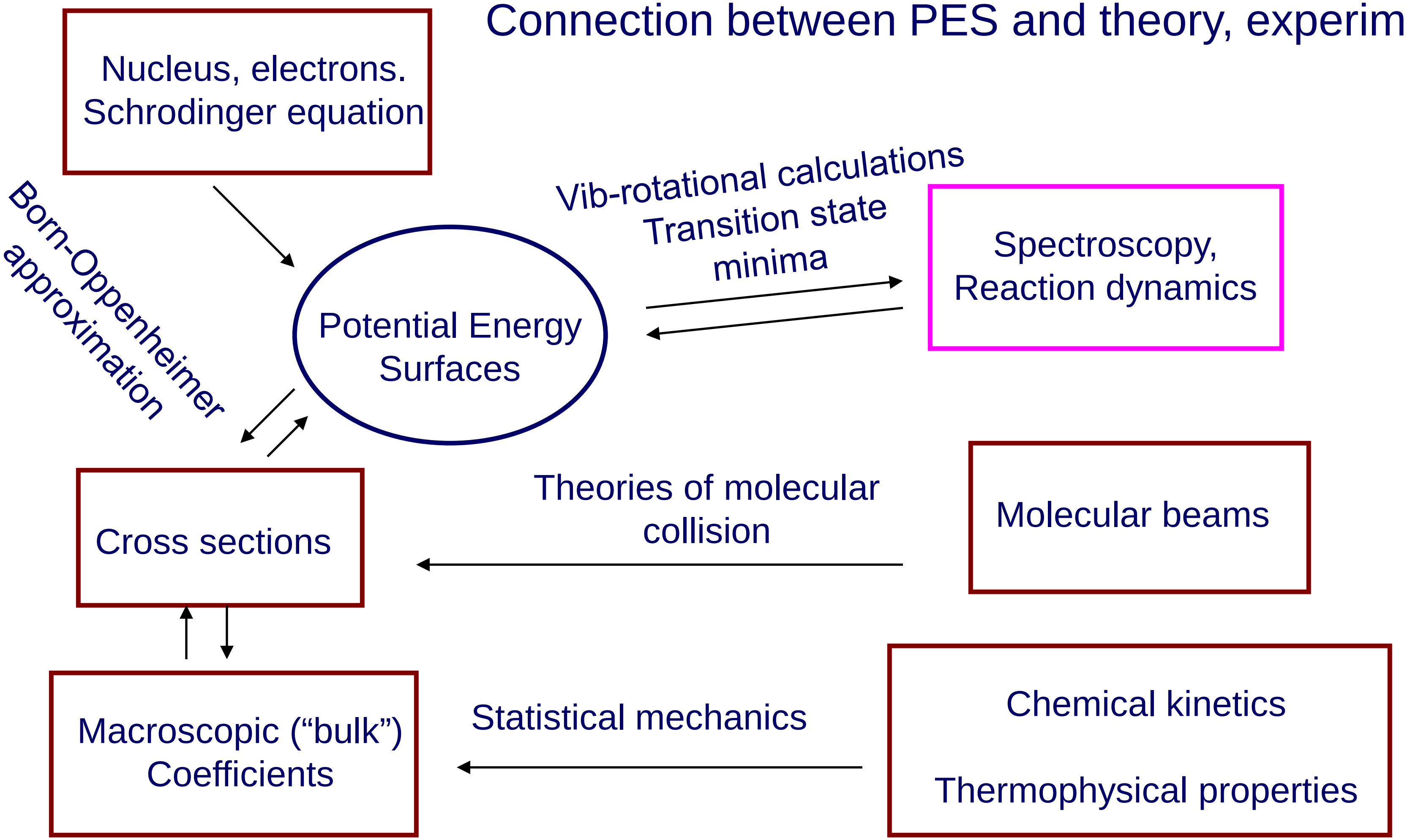
In a PES (Potential Energy Surface), stable species appear as valleys. Therefore, in a chemical reaction, the transformation of one stable species into another will correspond to a path between one valley and another. The speed of the transformation can be obtained from the minimum energy required to pass from reactant to product.

The simplest PES is a monodimensional one :



Introduction

Connection between PES and theory, experiment



Nucleus, electrons.
Schrodinger equation

Born-Oppenheimer
approximation

Potential Energy
Surfaces

Vib-rotational calculations
Transition state
minima

Spectroscopy,
Reaction dynamics

Cross sections

Theories of molecular
collision

Molecular beams

Macroscopic (“bulk”)
Coefficients

Statistical mechanics

Chemical kinetics

Thermophysical properties

Introduction

What happens if we have to look at more coordinates?

Let us look at a simple example, the reaction between H and the H_2 molecule. The first problem is choosing the appropriate coordinates to study the corresponding reaction PES

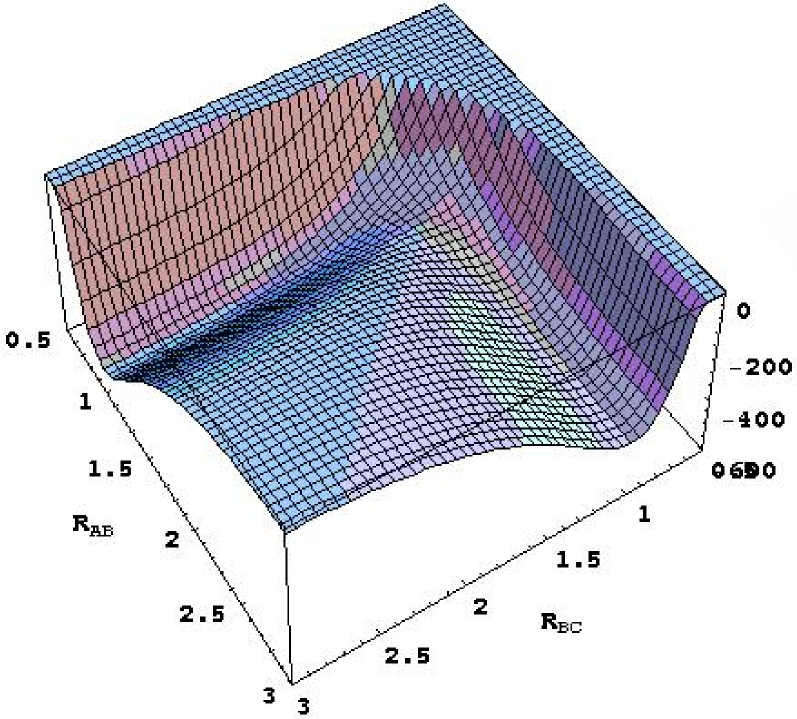
$$H_a + H_bH_c \longrightarrow H_aH_b + H_c$$

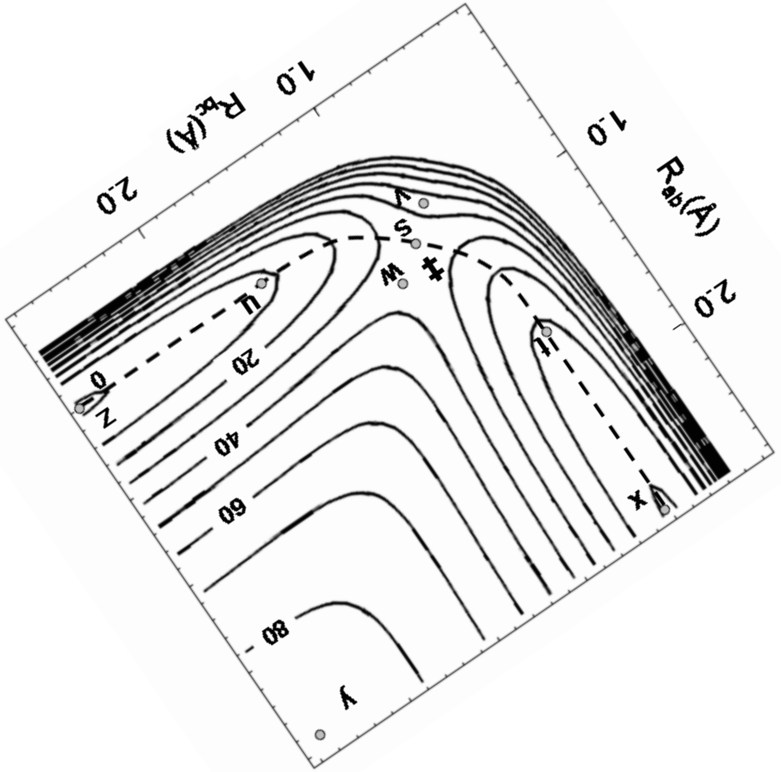
3*3 – 6 = 3 variables $\left\{ \begin{array}{l} R_{ab} \text{ increases} \\ R_{bc} \text{ decreases} \\ \theta_{abc} \text{ takes the optimum value} \end{array} \right.$

3-D PES $\Rightarrow$ $R_{ab}\ ;\ R_{bc}\ ;\ V$

$$H_a + H_bH_c \longrightarrow H_aH_b + H_c$$

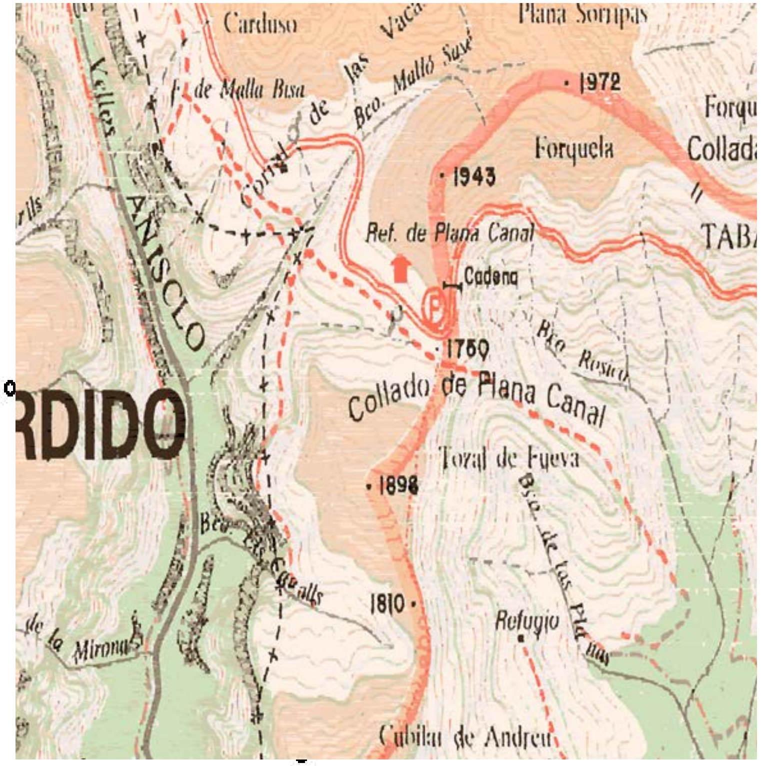
We calculate the potential energy of the system for different pairs of values over the coordinates that we have selected to follow the reaction (Rab; R_{bc}), optimizing the rest. The result, which can be represented in 3D or contour, is known as the potential energy surface (PES)

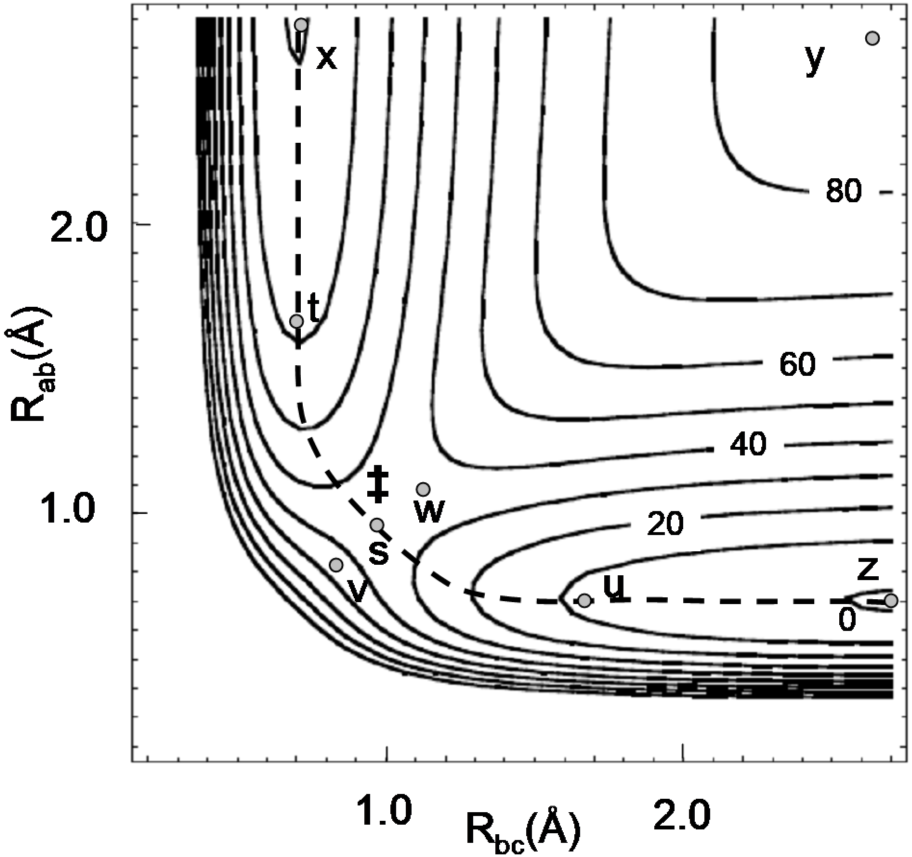




$$H_a + H_bH_c \longrightarrow H_aH_b + H_c$$

In the representation by contour levels, the value of the curve corresponds to the potential energy of the system, while the axes are the distinguished coordinates

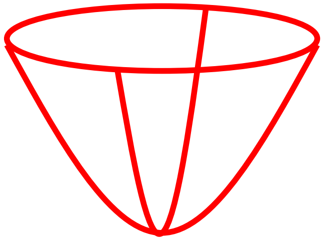


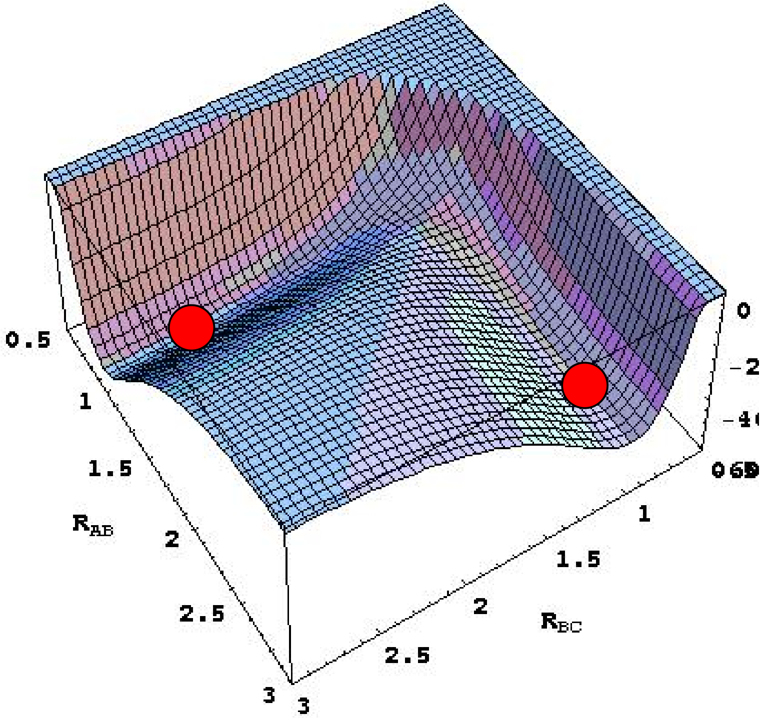


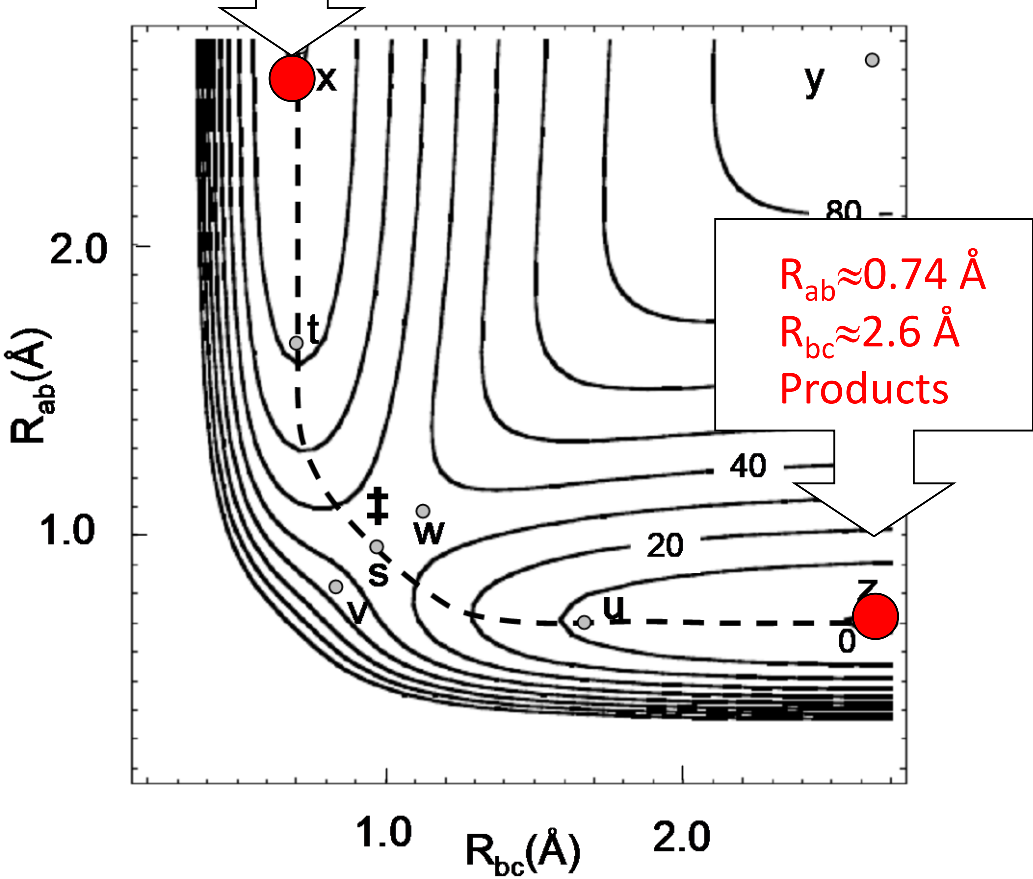
$H_a + H_bH_c \longrightarrow H_aH_b + H_c$

Stable structures on the PES (reactants, products, intermediates) are minima in both directions, and correspond to valleys on the map

R_{bc}≈0.74 Å
R_{ab}≈2.6 Å
Reactants





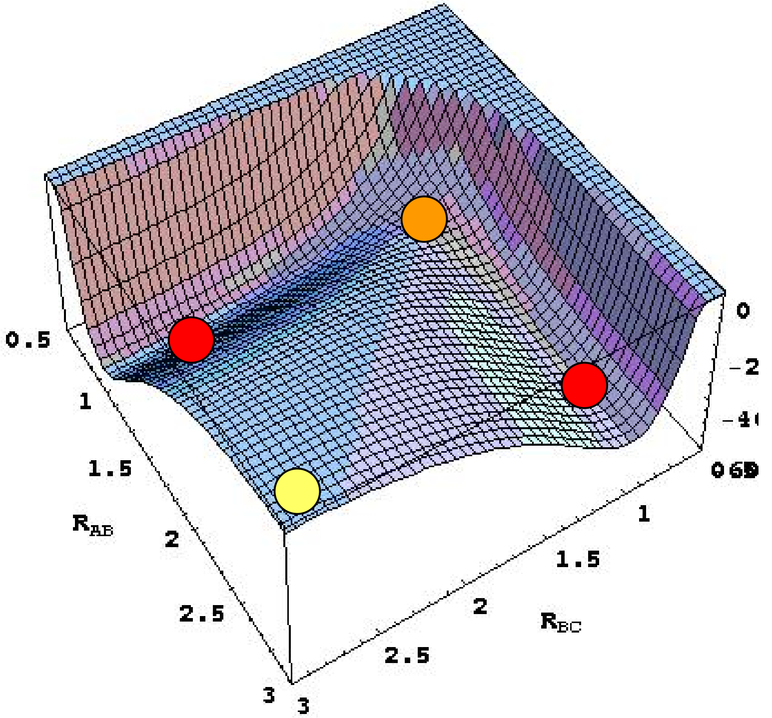


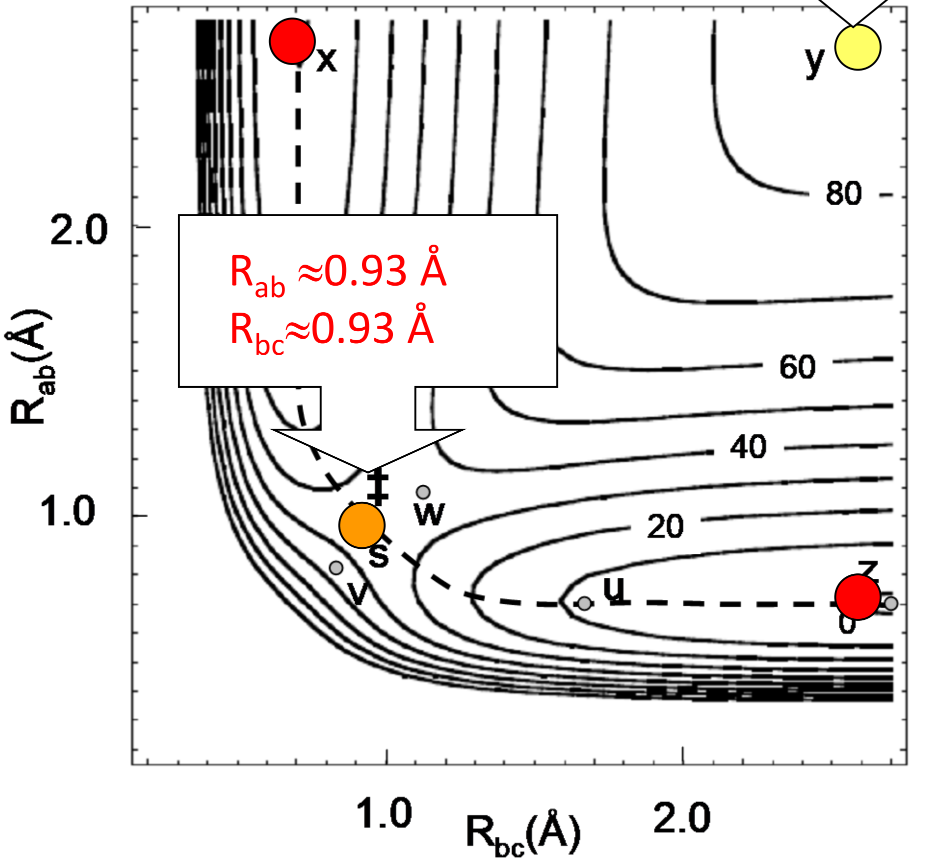
R_{ab}≈0.74 Å
R_{bc}≈2.6 Å
Products

$H_a + H_bH_c \longrightarrow H_aH_b + H_c$

There are other stationary structures that are minima in all directions except for those which are maxima. These structures have the minimum energy required to move from one minimum to another, and are known as **transition structures**.

$R_{ab} \rightarrow \infty$
$R_{bc} \rightarrow \infty$

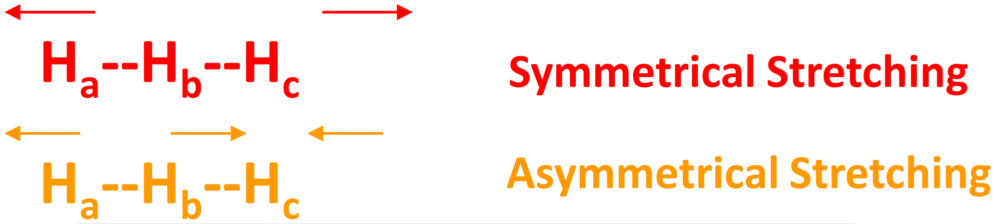




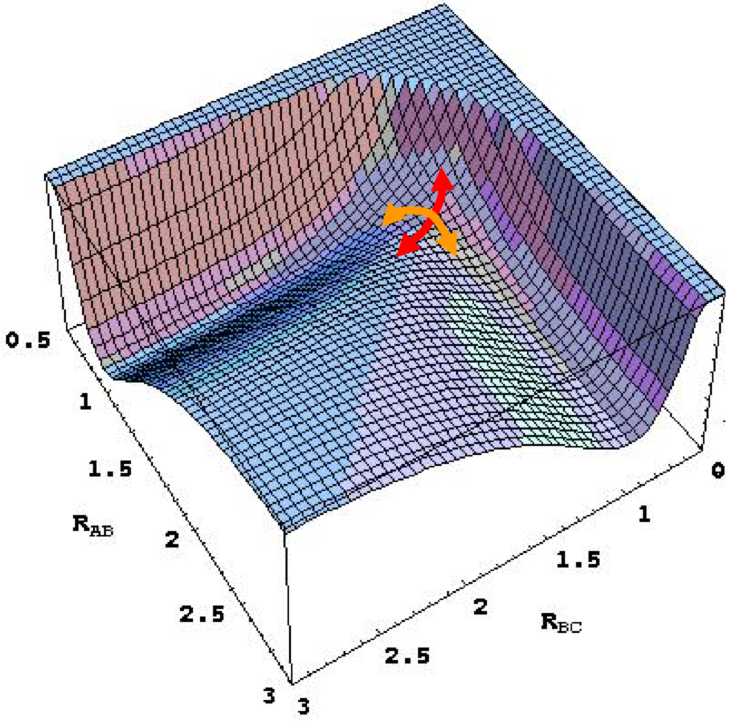
R_{ab} ≈0.93 Å
R_{bc}≈0.93 Å

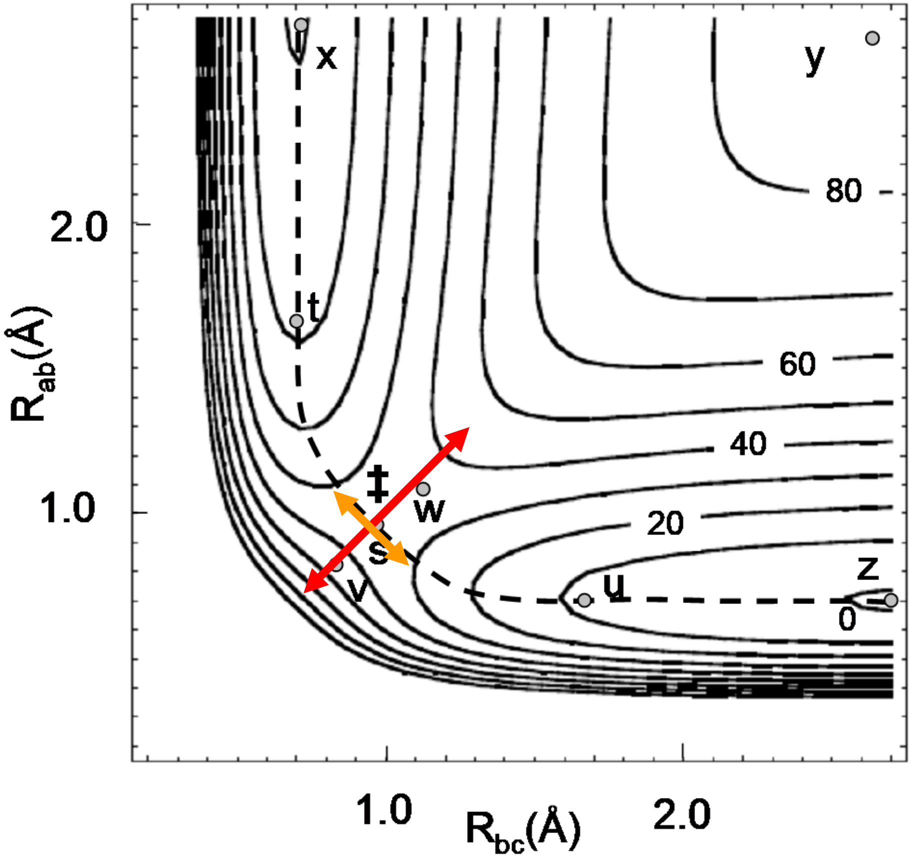
H_a--H_b--H_c

On the PES we can follow two directions. The TS is a minimum along one of these directions and a maximum along the other.


H_a--H_b--H_c **Symmetrical Stretching**

H_a--H_b--H_c **Asymmetrical Stretching**



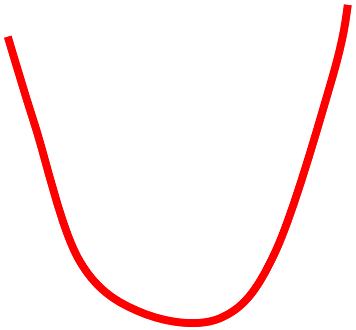


The ONLY direction in which the TS is a maximum is known as the transition vector. It is a normal mode of vibration that allows the TS to transform into reagents or products. This normal mode is characterized by having one imaginary frequency.

$\leftarrow \qquad \qquad \rightarrow$

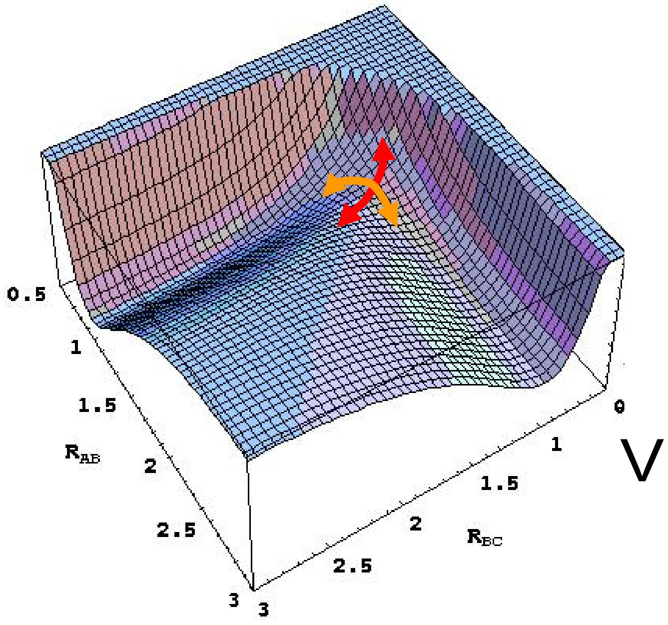
H_a--H_b--H_c

Symmetrical Stretching



$$V = \frac{1}{2}k_F(\Delta x)^2$$

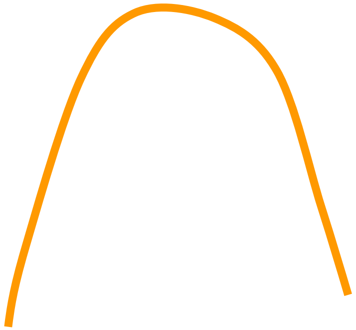
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k_F}{m}}$$



$\leftarrow \qquad \rightarrow \qquad \leftarrow$

H_a--H_b--H_c

Asymmetrical Stretching



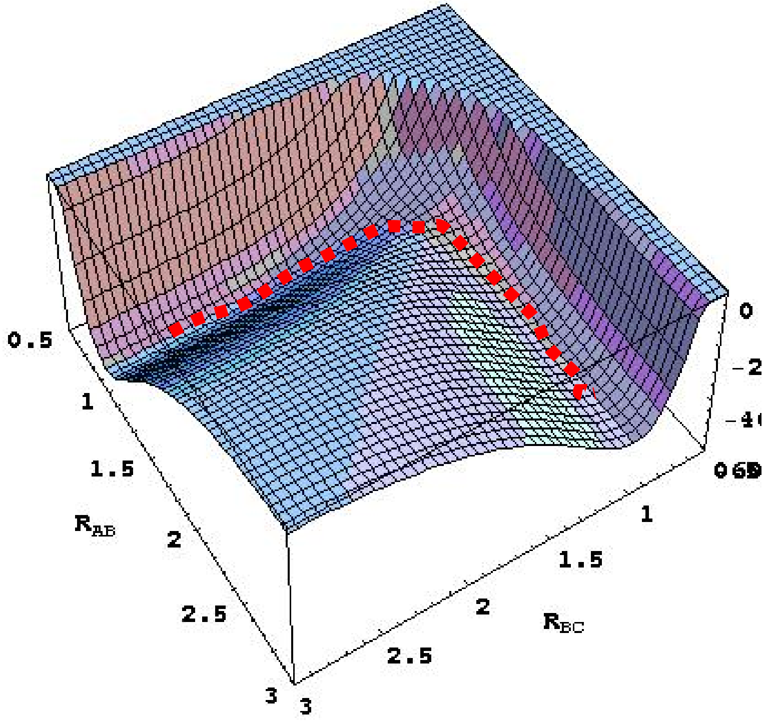
$$V = \frac{1}{2}k_F(\Delta x)^2 \Rightarrow k_F < 0$$

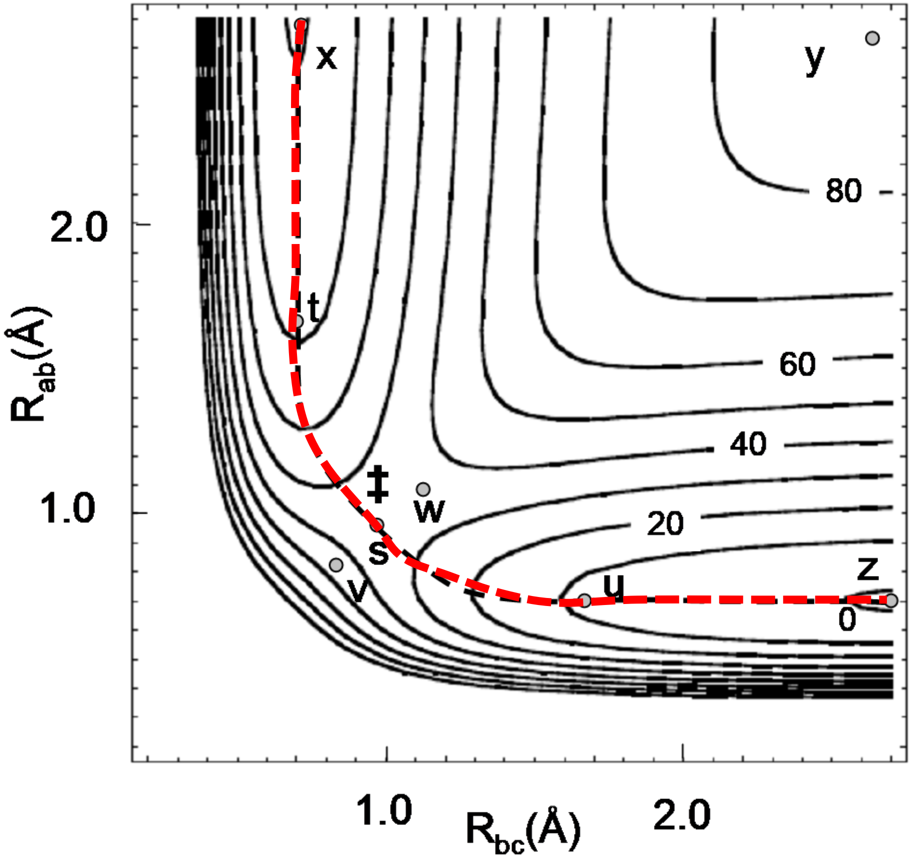
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k_F}{m}} \Rightarrow \text{imag.}$$

$H_a + H_bH_c \longrightarrow H_aH_b + H_c$

When reactants are transformed into products, they can follow any possible trajectory on the PES, but most will pass near the TS. The path of minimum potential energy going from the TS to the reactants and products tells us how the reaction occurs.

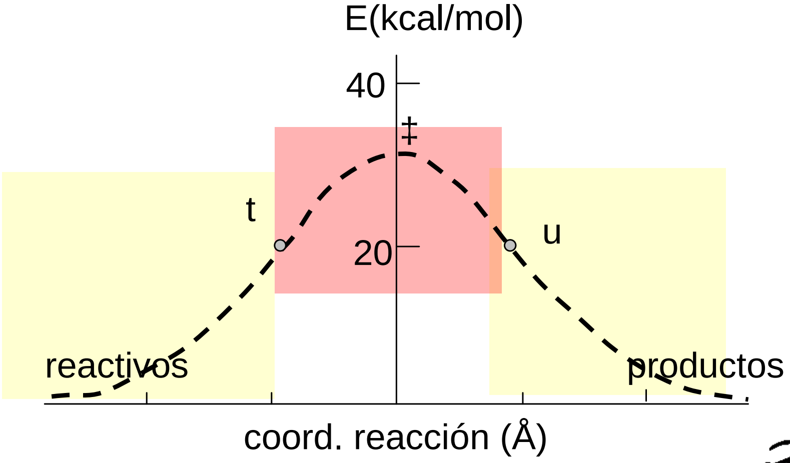
Minimum Energy Path

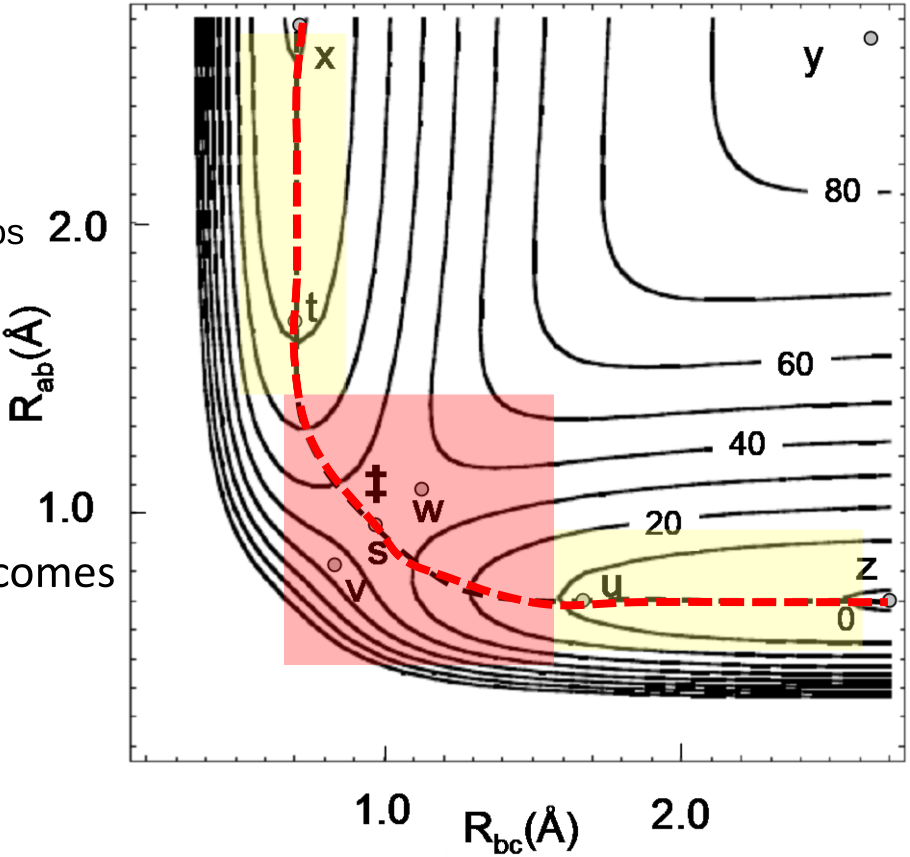




$H_a + H_bH_c \longrightarrow H_aH_b + H_c$

Minimum energy path





1) Approach of H_a (H_b-H_c ≈ constant)

2) H_a-H_b becomes shorter and H_b-H_c becomes longer

3) H_c leaves (H_a-H_b ≈ cte)

Transition State Theory

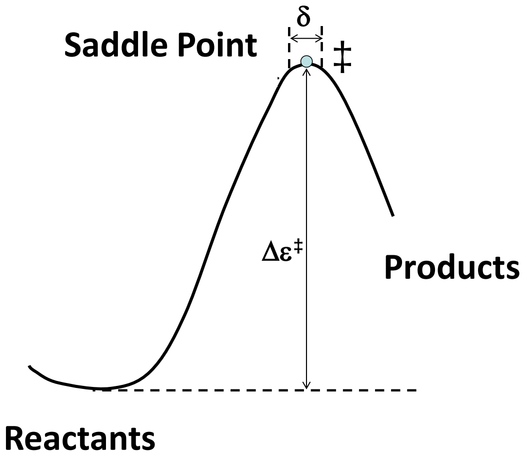
i) We assume that all reactants reaching the dividing surface will proceed to the product

ii) We assume that the reactants keep an equilibrium distribution corresponding to the temperature, T

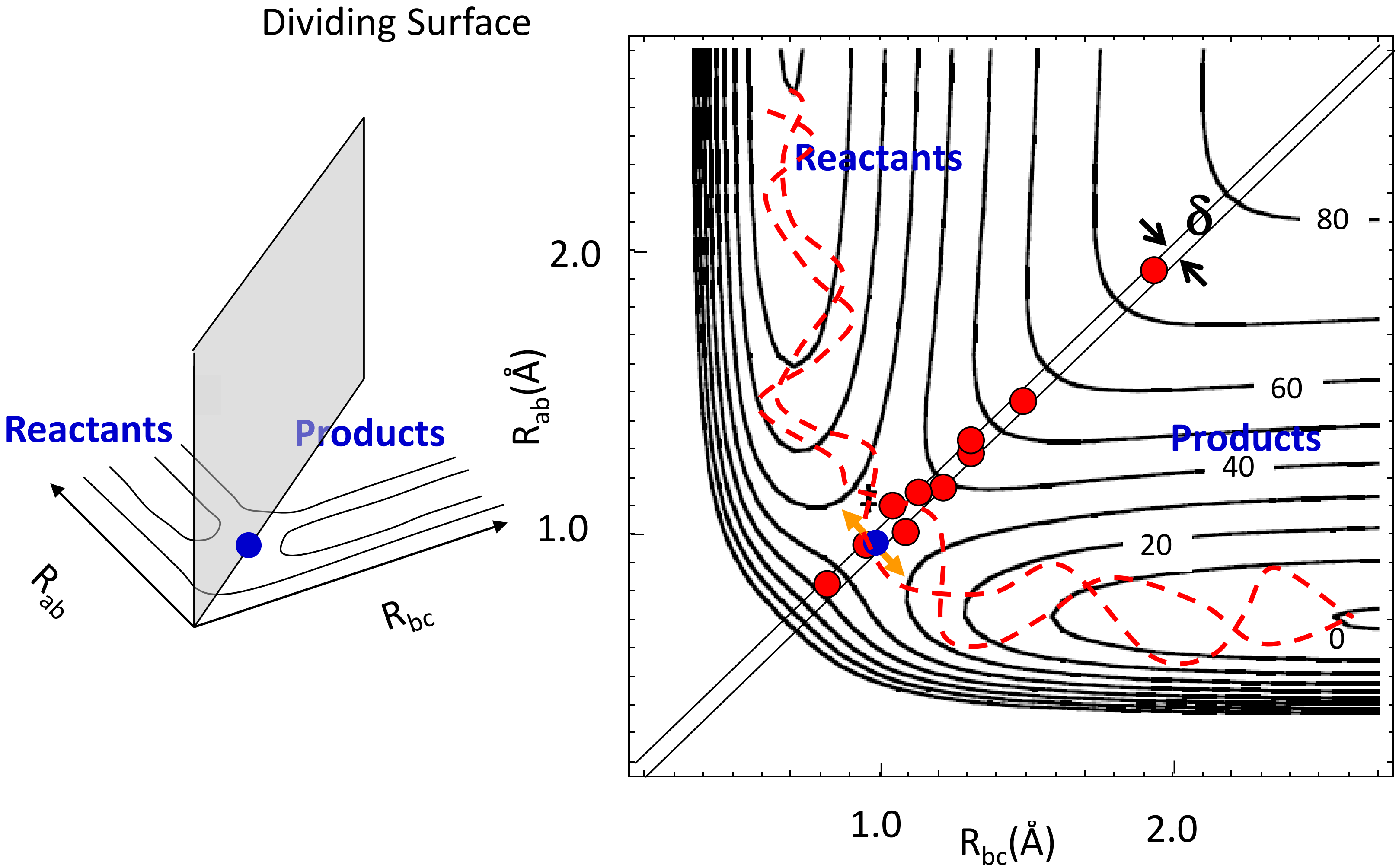
iii) We will assume that the ensemble of structures along the dividing surface (the transition state) also keeps an equilibrium distribution corresponding to temperature, T

iv) The motion along the reaction coordinate is described classically.

$$\mathbf{B + C \leftrightarrows X^{\ddagger} \rightarrow Products}$$

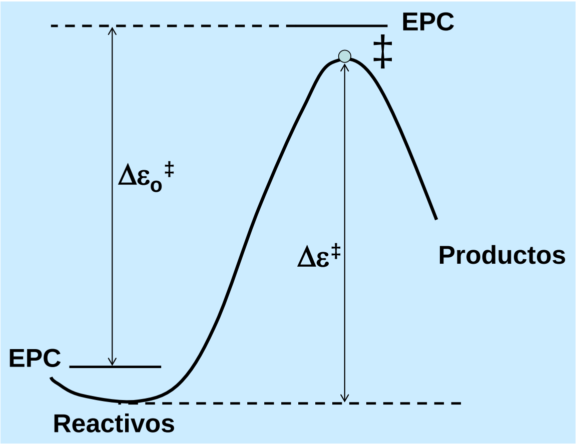


$B + C \leftrightarrows X^{\ddagger} \rightarrow$ Products



Using TST it is possible to find an expression for the rate constant according to the microscopic properties of reactants and the transition state. In particular, the rate constant can be obtained from the partition functions as well as the energy difference between their fundamental states.

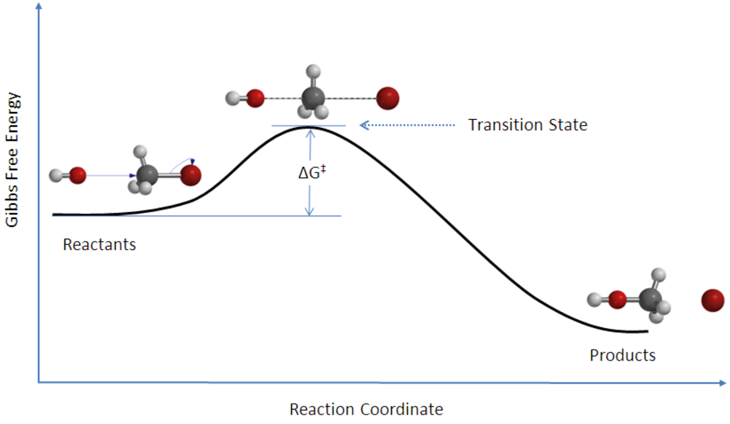
$$k_r = \frac{kT}{h}\,\frac{\bar{q}^{\ddagger}/N_A V}{\mathrm{q}_{\mathrm{react}}/N_A V}\exp\left(-\frac{\Delta\varepsilon_0^{\ddagger}}{kT}\right)$$



Alternatively, one can find the rate constant from the difference in free energy between the TS and the reactants. This free energy difference can refer to different standard States (i.e. 1 bar or 1 M) and depends on the number of molecular species we present in the reactants (n):

$$k_r = \frac{kT}{h}\left(\frac{RT}{P^0}\right)^{n-1}\exp\left(-\frac{\Delta G_P^{0\ddagger}}{RT}\right)$$

$$k_r = \frac{kT}{h}\left(C^0\right)^{1-n}\exp\left(-\frac{\Delta G_C^{0\ddagger}}{RT}\right)$$



Reaction: $HO^- + CH_3Br \rightarrow [HO\text{---}CH_3\text{---}Br]^{\ddagger} \rightarrow CH_3OH + Br^-$

Semiempirical Methods

Computational Chemistry
Elective Course
Degree in Chemistry
4th Year

Table of Contents

Summary HF:
Roothaan equations (closed shell)

Potential energy

$$E_{tot} = \frac{1}{2}\sum_{\mu}\sum_{\nu} P_{\mu\nu}\left[H_{\mu\nu}^{core} + F_{\mu\nu}\right] + \sum_{A}\sum_{B}\frac{Z_A Z_B}{R_{AB}}$$

Density matrix elements

$$P_{\mu\nu} = 2\sum_{a}^{N/2} C_{\mu a} C_{\nu a}$$

($c_{\mu j}$: Mol. Orb. coefficients)

Fock matrix elements

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\lambda}\sum_{\sigma} P_{\lambda\sigma}\left[\langle\mu\sigma|\nu\lambda\rangle - \frac{1}{2}\langle\mu\sigma|\lambda\nu\rangle\right]$$

Bielectronic integrals

$$\langle\mu\nu|\lambda\eta\rangle = \int \phi_\mu(1)^*\phi_\nu(2)^*\frac{1}{r_{12}}\phi_\lambda(1)\phi_\eta(2)d\mathbf{r}_1 d\mathbf{r}_2$$

Roothaan equations

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$$

(ε: Mol. Orb. eigenvalues)

(**S**: overlap matrix **C**: matrix of Mol. Orb. coefficients)

Summary HF:
SCF algorithm and cost

Step	Cost
1) Computation of mono- and bielectronic integrals	***$O(N^4)$***
2) Construction of core Hamiltonian $\mathbf{H}^c$	
3) Estimation of an initial density matrix	
4) Construction of Fock matrix **F**	
5) Orthogonalization using $\mathbf{S}^{1/2}$ → $\mathbf{F'C'} = \varepsilon\,\mathbf{C'}$	*$O(N^3)$*
6) Diagonalization of the Fock matrix **F'** **C'** coefficients are obtained	*$O(N^3)$*
7) Inverse transformation **C'** → **C**	
8) Construction of the new density matrix Back to 4) unless convergence	*$O(N^3)$*

Introduction to semiempirical methods

- They aim to reduce the computational cost and introduce electronic correlation
- Equations are simplified to decrease the computation time (the cost of integrals decreases from $O(N^4)$ to $O(N^2)$)
- Some parameters are added to correct the simplification
- Those parameters are obtained by fitting to experimental data (empiric parameters)
  - Electronic correlation
- The name (semiempirical) comes from the combination of quantum theory and the use of experimental information
- More stable than classical mechanics because they are based on quantum chemistry

General approximations in semiempirical methods

- Only valence electrons
  - Core electrons are treated in an averaged manner by decreasing the nuclear charge or adding special core functions
- Minimal basis set, normally Slater functions
- Certain bielectronic integrals are deleted
- Sometimes, monoelectronic integrals are also deleted

Classification of semiempirical methods

- Pariser-Parr-Pople (PPP) – 1950s
- Extended Hückel – 1960s
- Zero differential overlap (ZDO)
  - Neglect of diatomic differential overlap (NDDO) – 1960s
    - Modified neglect of differential overlap (MNDO) – 1977
    - Austin Model 1 (AM1) – 1985
    - Parameter Model 3 (PM3) – 1989
    - Parameter Model 6 (PM6) – 2007
    - Parameter Model 7 (PM7) – 2013
  - Intermediate neglect of differential overlap (INDO), MINDO – 1960s
  - Complete neglect of differential overlap (CNDO) – 1960s

Extended Hückel

$$H\ C_i\ =\ S\ C_i\ E_i$$

- H – Hamiltonian matrix
- C_i – Mol. Orbs. coefficients
- E_i – Orbital energies
- H_{ii} – Ionization potentials of the valence shell
- $H_{ij}\ =\ K\ S_{ij}\ (Hii\ +\ Hjj)$ / 2, where $K\ =$ 1,75

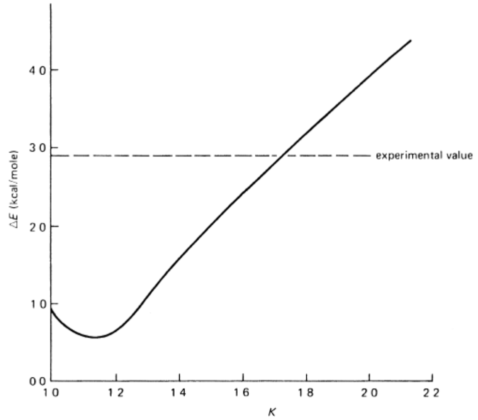
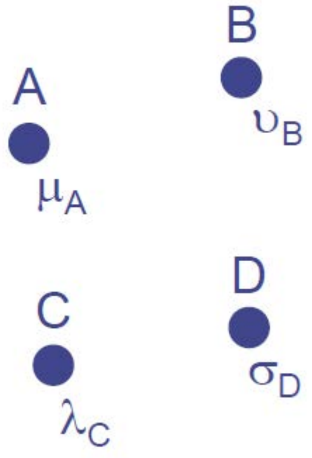


Figure 10-7 ▸ Extended Hückel energy difference between staggered and eclipsed ethanes as a function of K .

ZDO

- Common approximation in the most popular semiempirical methods
- Imposes $\mu_A(r)\nu_B(r)=0$ for μ, ν in different atoms ($A \neq B$)
- Thus, bielectronic integrals $<\mu\nu|\lambda\sigma>$ with 3 and 4 centers (the most numerous ones) are neglected
- To compensate this elimination, parameters are added into (some of) the remaining integrals



Atomic orbital μ_A is centered on atom A, etc.

NDDO, INDO, CNDO

- Semiempirical method based on ZDO
- For bielectronic integrals (ZDO):
  - $<\mu_A \nu_C | \lambda_B \sigma_D> = \delta_{AB}\delta_{CD} <\mu_A \nu_C | \lambda_B \sigma_D>$
- For monoelectronic integrals:
  - Neglect those involving 3 centers

$$\hat{h} = -\frac{1}{2}\nabla^2 - \sum\nolimits_A \frac{Z'_A}{|\vec{R}_A - \vec{r}|} = -\frac{1}{2}\nabla^2 - \sum\nolimits_A V_A$$

$$\langle \mu_A | \hat{h} | \nu_A \rangle = \left\langle \mu_A \middle| -\frac{1}{2}\nabla^2 - V_A \middle| \nu_A \right\rangle - \sum\nolimits_{B \neq A} \langle \mu_A | V_B | \nu_A \rangle$$

$$\langle \mu_A | \hat{h} | \nu_B \rangle = \left\langle \mu_A \middle| -\frac{1}{2}\nabla^2 - V_A - V_B \middle| \nu_B \right\rangle$$

$$\langle \mu_A | V_C | \nu_B \rangle = 0$$

NDDO (MNDO, AM1, PM3), INDO, CNDO

- Atomic parameters are used to compensate for the approximations

$$\langle \mu_A | \hat{h} | \nu_A \rangle = \left\langle \mu_A \middle| -\frac{1}{2}\nabla^2 - V_A \middle| \nu_A \right\rangle - \sum_{B\neq A} \langle \mu_A | V_B | \nu_A \rangle$$

$$=\langle \mu_A | \nu_B \rangle \frac{1}{2}(\beta_\mu + \beta_\nu)$$

- The MNDO, AM1 y PM3 variants only differ in the treatment of the core and how parameters are assigned (see Exercise 2 in the practical session)

NDDO, **INDO**, CNDO

- Semiempirical method based on ZDO
- For bielectronic integrals (ZDO):
  - ZDO: $<\mu_A\nu_C|\lambda_B\sigma_D> = \delta_{AB}\delta_{CD}<\mu_A\nu_C|\lambda_B\sigma_D>$
  - Also neglect 2-center integrals in which the AO on the atom are different; only keep
    - $<\mu_A\nu_B|\mu_A\nu_B>$ – 2-center integrals
    - $<\mu_A\nu_A|\lambda_A\sigma_A>$ – 1-center integrals
- For monoelectronic integrals:
  - Same as for NDDO

NDDO, **INDO (MINDO)**, CNDO

- Empirical parameters and fitted diatomic parameters are added

$$\langle \mu_A | \hat{h} | \nu_A \rangle = \left\langle \mu_A \middle| -\frac{1}{2}\nabla^2 - V_A \middle| \nu_A \right\rangle - \sum_{B \neq A} \langle \mu_A | V_B | \nu_A \rangle$$

$$= \langle \mu_A | \nu_B \rangle \beta_{AB} (I_\mu + I_\nu)$$

  - I_μ: Ionization potential of an electron in atomic orbital μ
  - β_{AB}: Fitted diatomic parameter
- Largely superseded by NDDO models based on atomic parameters (MNDO, AM1, PM3)

NDDO, INDO, **CNDO**

- Semiempirical methods based on ZDO
- Most drastic approximations in the series NDDO, INDO, CNDO
- For bielectronic integrals (ZDO):
  - Keep only:
    - $<(\mu_A \nu_B | \mu_A \nu_B>$ – 2-center integrals
    - $<\mu_A \nu_A | \mu_A \nu_A>$ – 1-center integrals

MNDO, AM1, PM3

- MNDO
  - Superseded by AM1, PM3
  - Problems:
    - Exaggerated steric effects
    - Unreliable hydrogen bonds
    - Hypervalent molecules too unstable
    - TSs are too high for bond formation/breaking
- AM1
  - M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **107**, 3902-3909 (1985)
  - Reparametrization of the core functions (with respect to MNDO)
  - Improvements to MNDO
    - Hydrogen bond energies more or less correct (bad geometries)
    - Improved activation energies
    - Better treatment of hypervalent molecules (still significant errors)
  - Problems
    - Alkyl groups too stable (~2 kcal/mol por CH_2)
    - Nitro groups too unstable
    - Peroxide bonds too short
- PM3
  - J. J. P. Stewart, *J. Comput. Chem.* **10**, 209-220 (1989)
  - Automatic reoptimization of the parameters (before by hand)
  - Only a few atoms available
  - General improvement with respect to MNDO y AM1 (average errors of bond lengths and y ΔH_f decrease)
  - Problems
    - Hydrogen bonds ~0.1 Å too short
    - Almost all *sp*^{3} nitrogen atoms are pyramidal
    - Charges in N atoms sometimes not very reliable
    - Si – halogen bonds very short
    - Wrong structures for NH_2NH_2 y ClF_3

MNDO, AM1, PM3 (performance)

Average error for formation enthalpies
ΔH_f *(kcal/mol)*

Compounds	**MNDO**	**AM1**	**PM3**	**MNDO/d**
Al, Si, P, S, Cl, Br, I, Zn, Hg (488 compounds)	29.2	15.3	10.0	4.9
Si, P, S, Cl, Br, I (404 compounds)	31.4	16.1	9.5	5.1

Data from Frank Jensen, *Introduction to Computational Chemistry* (Wiley, New York, 1999)

MNDO, AM1, PM3 (general problems)

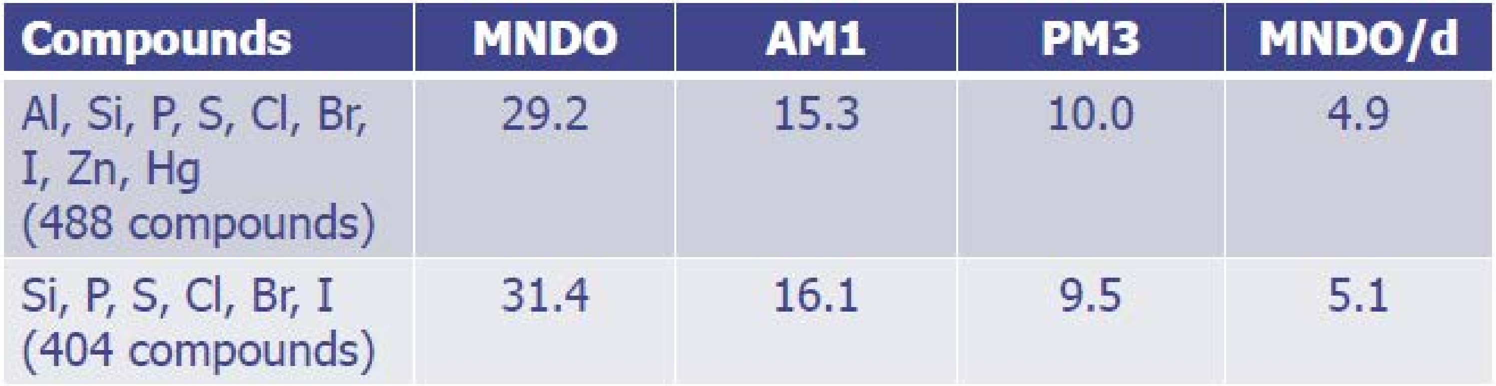
- Barriers of rotation around partial double bonds too low
- Parameters for metals based on few data
- Bad description of dispersion forces and weak interactions

MNDO/d

- Adds *d* type functions to MNDO
- Relevant for metals
- Improves the description of polarization in 2nd row atoms
- General improvement with respect to MNDO, AM1 y PM3

MNDO, AM1, PM3, MNDO/d (performance)

Average error in the enthalpies of formation ΔH_f (kcal/mol)



Compounds	MNDO	AM1	PM3	MNDO/d
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Si, P, S, Cl, Br, I (404 compounds)	31.4	16.1	9.5	5.1

Data from Frank Jensen, *Introduction to Computational Chemistry* (Wiley, New York, 1999)

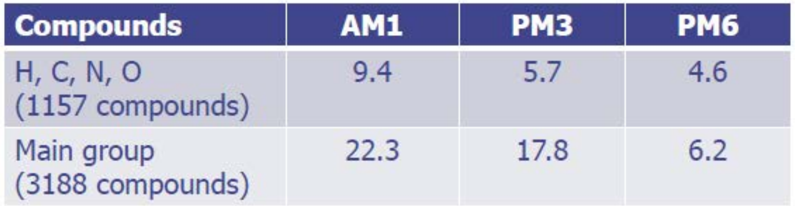
PM6

- NDDO method with improved parameters and improved core-core interaction terms (diatomic parameters are used as in MINDO)
- 70 parametrized elements
- Corrects problems with AM1 and PM3
- Add *d* functions for metals, like in MNDO/d

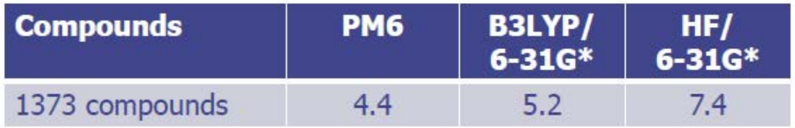
J. J. P. Stewart, *J. Mol. Model***13**, 1173-1123 (2007)

AM1, PM3, PM6 (performance)

Average error in ΔH_f (kcal/mol)

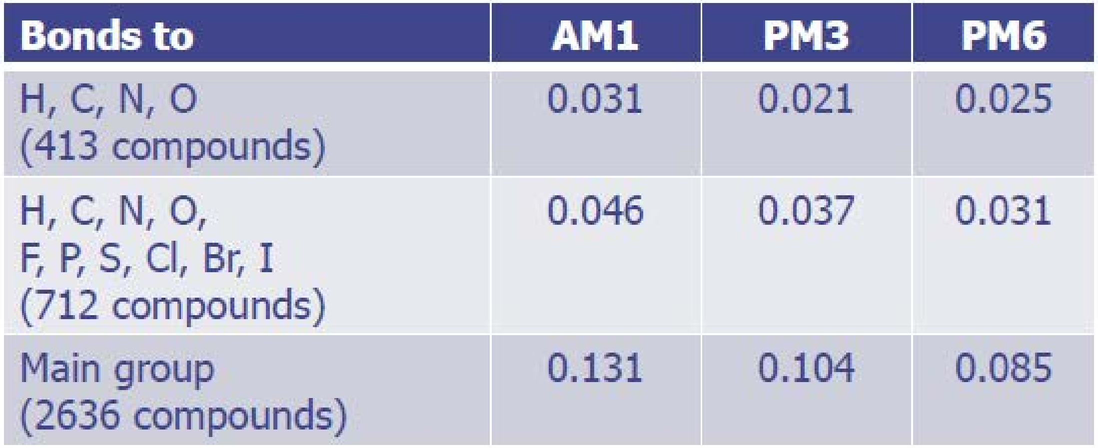


Compounds	AM1	PM3	PM6
H, C, N, O (1157 compounds)	9.4	5.7	4.6
Main group (3188 compounds)	22.3	17.8	6.2



Compounds	PM6	B3LYP/ 6-31G*	HF/ 6-31G*
1373 compounds	4.4	5.2	7.4

Average error in bond lengths (Å)



Bonds to	AM1	PM3	PM6
H, C, N, O (413 compounds)	0.031	0.021	0.025
H, C, N, O, F, P, S, Cl, Br, I (712 compounds)	0.046	0.037	0.031
Main group (2636 compounds)	0.131	0.104	0.085

J. J. P. Stewart, *J. Mol. Model.* **13**, 1173-1123 (2007)

Improvements in PM6 (non-covalent interactions)

- PM6-DH, PM6-DH2, PM6-D3H4X
- Adds terms for an accurate description of dispersion (C_6/R^6)
- Similar to the dispersion corrections in DFT
- Also adds terms for an accurate description of hydrogen bonds

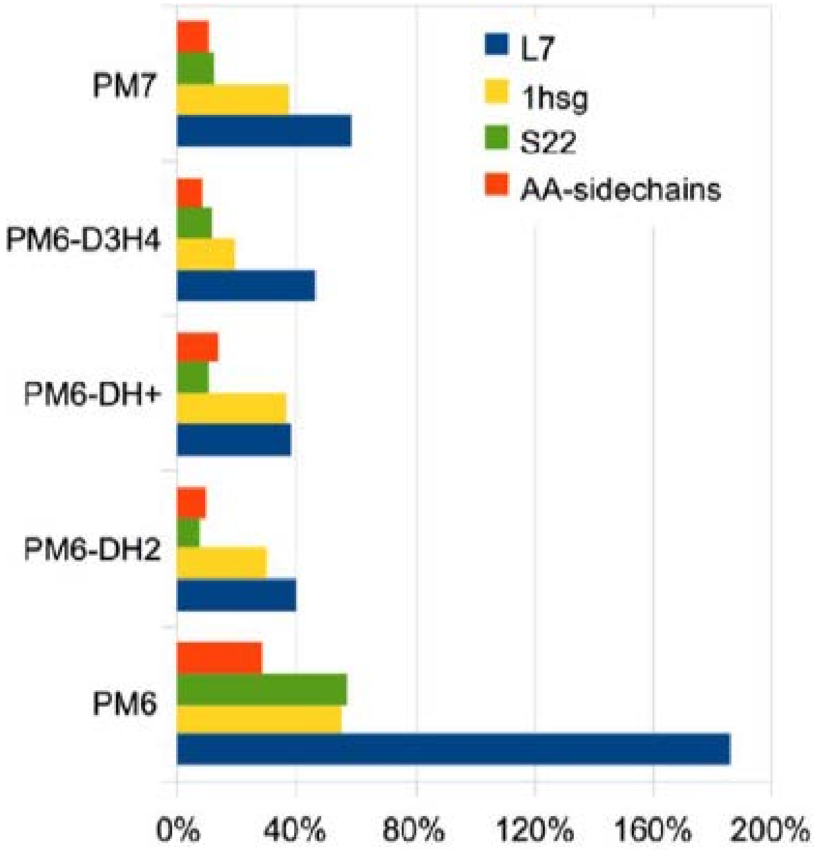
PM6-DH: J. Rezac, J. Fanfrlik, D. Salahub, and P. Hobza, *J. Chem. Theory Comput.* **5**, 1749-1760 (2009)
PM6-DH2: M. Korth, M. Pitonak, J. Rezac, and P. Hobza, *J. Chem. Theory Comput.***6**, 344 (2010)
PM6-D3H4X: J. Rezac and P. Hobza, *J. Chem. Theory Comput.* **8**, 141 (2012)

PM7…

- J. J. P. Stewart, *J. Mol. Model.* **19**, 1-32 (2013)
- Subsequent improvements to PM6
- Adds explicit terms to treat non-covalent interactions, based on the –DH2, –DH+, –D3H4 corrections to PM6
- Aimed to expand use to systems other than those used in the calibration
- Reduces bond length errors (5%) and enthalpy of formation errors (10%) (in organic solids 60%) with respect to PM6

PM6, PM6-D, PM7 (performance)

RMS error (%) in intermolecular interaction energies



J. Rezac, P. Hobza, *Chem. Phys. Lett.* **568**, 161 (2013)

General Bibliography

- K. I. Ramachandran, *et al.* “Computational Chemistry and Molecular Modeling”. Springer: Berlin, Heidelberg (2008)
- F. Jensen. “Introduction to Computational Chemistry”. Wiley: New York (1999)
- W. Thiel ,“Semiempirical Methods”. In: Modern Methods and Algorithms of Quantum Chemistry, Proceedings, Second Edition, J. Grotendorst (Ed.), John von Neumann Institute for Computing: Jülich, Vol. 3, pp. 261-283 (2000).
- The Sherrill Group. “Notes”. Georgia Institute of Technology, USA. http://vergil.chemistry.gatech.edu (October, 2018)

Post-HF Methods:
Electron Correlation

Computational Chemistry
Elective Course
Chemistry Degree
4th Year

Contents

- Electron correlation
- Electron correlation methods
  - Configuration Interaction (CI)
  - Perturbation theory (Møller-Plesset; MPn)
  - Coupled-cluster (CC)
- Formal properties of methods:
  - Extensivity
  - Size-consistency
  - N-dependence

Chemical precision

- **Chemical Precision:** Modelling of experiments with a precision equivalent to experimental values, $\sim$ 1 kcal·mol^{-1}

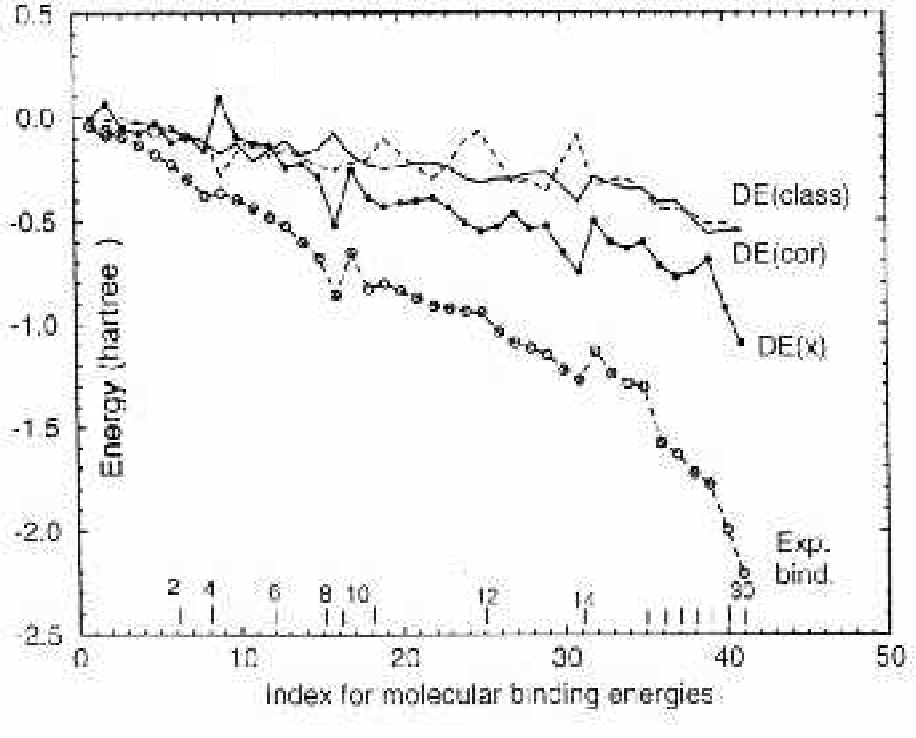
- The energy of a medium sized molecule ~10^5-10^6 kcal·mol $^{-1}$ $\rightarrow$ Accuracy of 1 in ~1.000.000 (reached in ~1995, medium sized molecules)

Problems… computational chemistry

- Chemistry $\Rightarrow$ small energy differences
  - Spectroscopy: 2 energy levels
  - Thermochemistry: reaction products and reactants
  - Stereochemistry-energetics: different molecular conformations
  - Ionization Potentials or Electron Affinities: between an atom or molecule and an ion
  - Chemical kinetics: reactants and transition states
- ~1% of total energy $\Rightarrow$ small errors in the calculation of total energies $\Rightarrow$ large errors in the differences

Some orders of magnitude

- DE_{class}; DE_{ex} ; DE_{cor} as a function (more or less) of the electron number along with the experimental bond energy
- ALL ARE OF THE SAME ORDER!!!
- No component of the electron-electron energy can be neglected



How costly is a good calculation?

Contribution	Cost	Methane Value (N=10)	Benzene Value (N=42)
E_{HF}	$\sim O(N^6)$	1×10^6	$5{,}5 \times 10^9$
E_{cor} Exact	$\sim O([2N]!/N!)$	7×10^{11}	$2{,}4 \times 10^{75}$
E_{cor} Approx	$\sim O(N^6)$	1×10^6	$5{,}5 \times 10^9$
E_{cor} Good	$\sim O(N^8)$	1×10^8	$9{,}8 \times 10^{12}$

What is electron correlation?

- N-electron system (atom or molecule)
  - In HF theory the wavefunction is approximated as a Slater Determinant:

$$\left|\Psi\right\rangle = \frac{1}{N!}\left|\chi_1\chi_2\cdots\chi_N\right\rangle$$

  - SOs are obtained by diagonalizing the Fock matrix

$$\hat{F} = \sum_i \hat{f}_i$$

What is electron correlation?

- Fock operator: repulsion among electrons is included in an ***averaged form***
- The real operator includes the instantaneous e^--e^- repulsion term: $(r_{12})^{-1}$
- Electron Correlation: electrons move in an attempt to minimize particle-particle interactions

What is electron correlation?

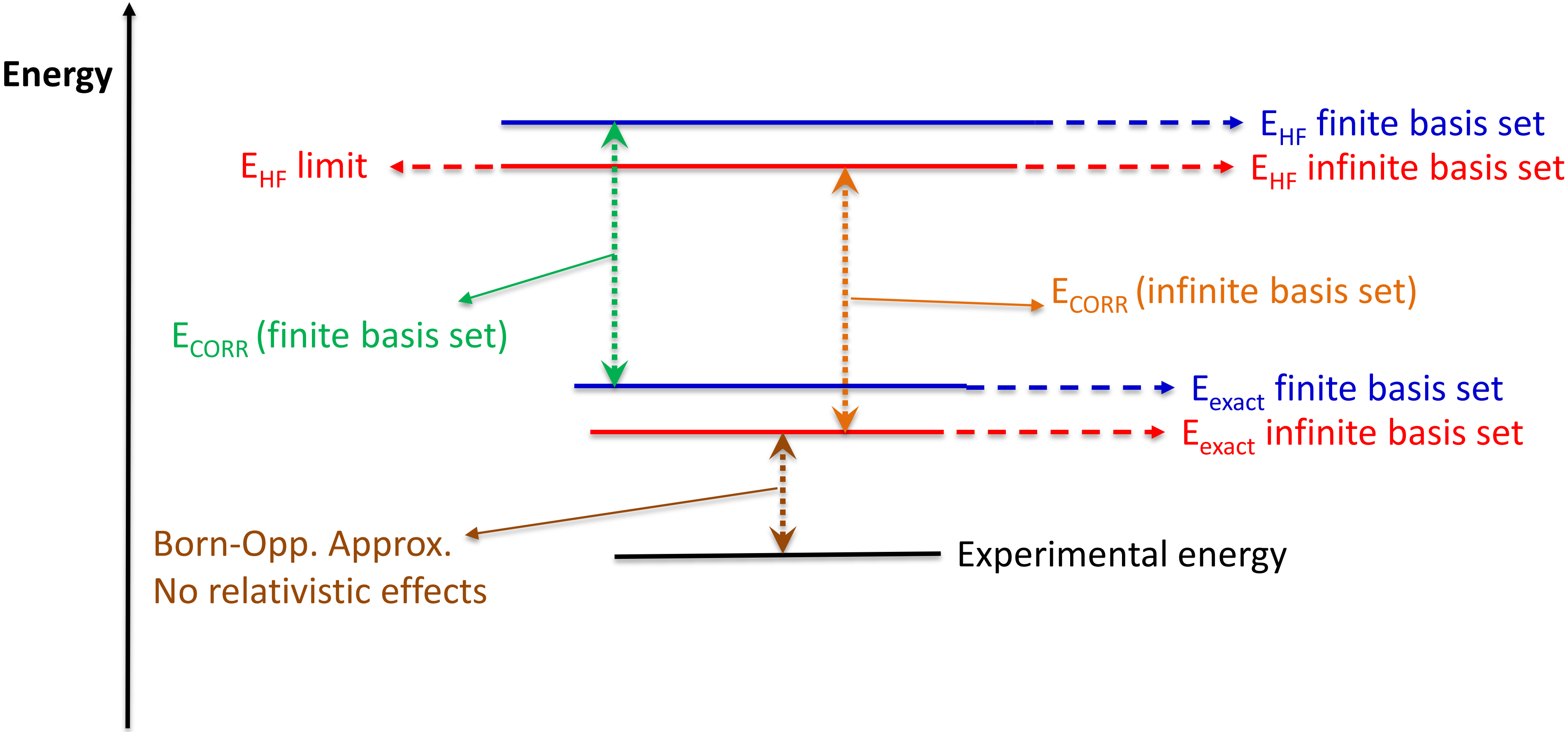
- HF energy: E_0
- Exact energy for a given basis set: $\mathcal{E}_0$
- Correlation energy for a given basis set:

$$E_{corr} = \mathcal{E}_0 - E_0$$

- If the basis set were complete:

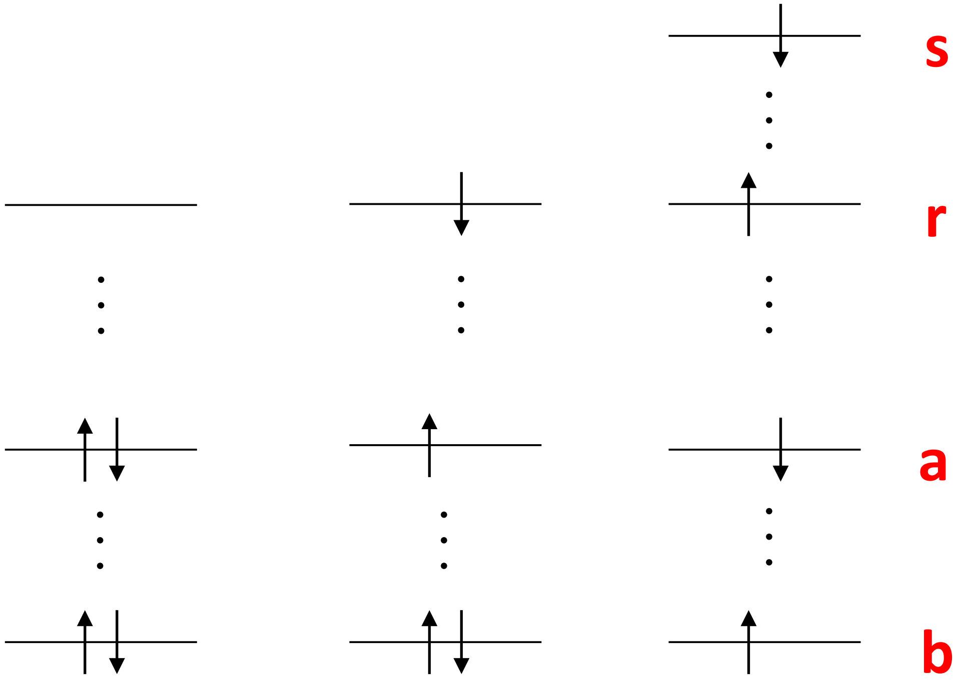
$$E_{corr} \rightarrow E_{corr}\ \text{exact}$$

What is electron correlation?



How is electron correlation introduced?

- HF gives K orbitals, where N/2 are occupied (for closed shell)
- The other orbitals can be used to build excited configurations
- Degree:
  - S: single
  - D: double
  - T: triple
  - Q: quadruple
  - …
- The wavefunction can be completed with them



Ground Conf. $|\Psi_0>$

Single Conf. $|\Psi_a^r>$

Double Conf. $|\Psi_{ab}^{rs}>$

Electron correlation methods

- 3 fundamental types:
  - CI: Configuration Interaction
    - Linear combination of configurations
    - Linear variations
    - Different methods according to the excited conf.: DCI, SDCI, SDTQCI
    - All possible configurations: FCI, exact in the basis set
  - MPn: perturbational methods
    - Series development of the HF function using excited conf.
    - Different orders of perturbation: MP2, MP4…
  - CC: *Coupled Cluster* methods
    - Exponential development of the HF function
    - Different excitation levels: CCD, CCSD, CCSDT, CCSD(T), CCSDTQ

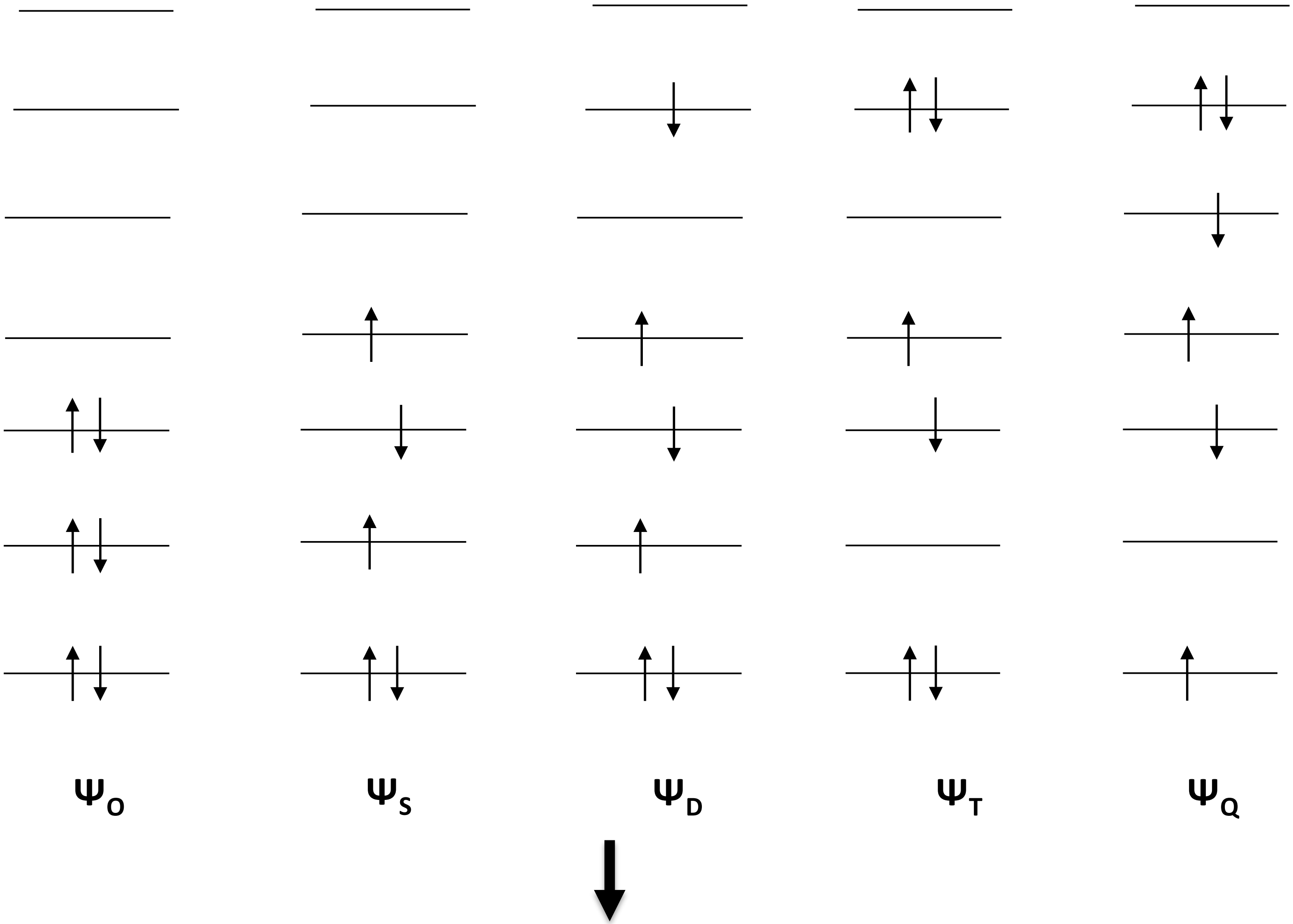
Configuration interaction

- Conceptually simple, computationally complex
- Diagonalize the **H** matrix in the basis of N-electron functions (Slater determinants)
- Wave function:

$$\left|\Phi_0\right\rangle = c_0\left|\Psi_0\right\rangle + \sum_{a,r} c_a^r \left|\Psi_a^r\right\rangle + \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs}\left|\Psi_{ab}^{rs}\right\rangle + \sum_{\substack{a<b<c\\ r<s<t}} c_{abc}^{rst}\left|\Psi_{abc}^{rst}\right\rangle + \cdots$$

$$\left|\Phi_0\right\rangle = c_0\left|\Psi_0\right\rangle + c_S\left|\Psi_S\right\rangle + c_D\left|\Psi_D\right\rangle + c_T\left|\Psi_T\right\rangle + c_Q\left|\Psi_Q\right\rangle + \cdots$$

Coefficients can be determined using the Variational Principle!



One occupied S.O. of the HF determinant is replaced by **one virtual** (unoccupied) S.O.

But, how many determinants?

- N electrons
- K basis functions → 2K spin-orbitals
- Determinant: Take N from 2K spin-orbitals, regardless of the order:

Full Configuration Interactions

- For N=40, K=100 → $\binom{2K}{N}$

2050157995198589154962348028592667411382810 ≈ 2×10^{42}

- We need to use truncated CI →

the most important contributions are given by configurations with less excitations: double CI (DCI), single and double CI (SDCI) …. Because we need to consider the configurations with bigger interactions with Ψ_O

DCI: Hydrogen molecule

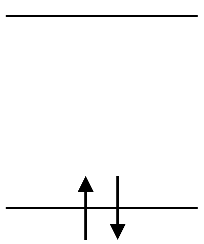
$H_A - H_B$

Normalization constants

H_2 RHF MOs in MBS

(σ_u^*)

$(\sigma_g)^2$



$$\psi_2(\mathrm{i}) = \frac{1}{\sqrt{2(1-s)}}\left(\phi_A(\mathrm{i}) - \phi_B(\mathrm{i})\right)$$

$$\psi_1(\mathrm{i}) = \frac{1}{\sqrt{2(1+s)}}\left(\phi_A(\mathrm{i}) + \phi_B(\mathrm{i})\right) \qquad s = \langle \phi_A | \phi_B \rangle$$

$$|\Psi_0\rangle = |\psi_1 \;\; \bar{\psi}_1\rangle$$

$$|\Psi_0\rangle = \frac{1}{2(1+s)}\left(|\phi_A\bar{\phi}_A\rangle + |\phi_B\bar{\phi}_B\rangle + |\phi_A\bar{\phi}_B\rangle + |\phi_B\bar{\phi}_A\rangle\right)$$

$H_A^- \; H_B^+$ $\quad$ $H_B^- \; H_A^+$ $\quad$ $H_A\bullet \; H_B\bullet$ $\quad$ $H_B\bullet \; H_A\bullet$

Ionic Conf.

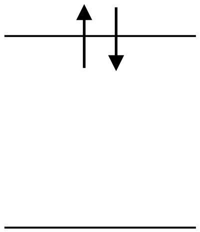
Covalent Conf.

DCI: Hydrogen molecule

$H_A – H_B$

H_2 RHF MOs in MBS

$(\sigma_u^*)^2$



(σ_g)

$$\psi_2(\mathrm{i}) = \frac{1}{\sqrt{2(1-s)}}\left(\phi_A(\mathrm{i}) - \phi_B(\mathrm{i})\right)$$

$$\psi_1(\mathrm{i}) = \frac{1}{\sqrt{2(1+s)}}\left(\phi_A(\mathrm{i}) + \phi_B(\mathrm{i})\right) \qquad s = \langle \phi_A | \phi_B \rangle$$

$$\left|\Psi_{1\bar{1}}^{2\bar{2}}\right\rangle = \left|\psi_2 \ \bar{\psi}_2\right\rangle$$

$$\left|\Psi_{1\bar{1}}^{2\bar{2}}\right\rangle = \frac{1}{2(1+s)}\left(\left|\phi_A\bar{\phi}_A\right\rangle + \left|\phi_B\bar{\phi}_B\right\rangle - \left|\phi_A\bar{\phi}_B\right\rangle - \left|\phi_B\bar{\phi}_A\right\rangle\right)$$

H_A^- H_B^+ H_B^- H_A^+ H_A• H_B• H_B• H_A•

Ionic Conf.

Covalent Conf.

H_2 DCI: The role of D

$$\left|\Psi_0\right\rangle = \frac{1}{2(1+s)}\left(\left|\phi_A\bar{\phi}_A\right\rangle + \left|\phi_B\bar{\phi}_B\right\rangle + \left|\phi_A\bar{\phi}_B\right\rangle + \left|\phi_B\bar{\phi}_A\right\rangle\right)$$

$$\left|\Psi_{1\bar{1}}^{2\bar{2}}\right\rangle = \frac{1}{2(1+s)}\left(\left|\phi_A\bar{\phi}_A\right\rangle + \left|\phi_B\bar{\phi}_B\right\rangle - \left|\phi_A\bar{\phi}_B\right\rangle - \left|\phi_B\bar{\phi}_A\right\rangle\right)$$

DCI:

$$\left|\Phi_0\right\rangle = \left|\Psi_0\right\rangle + \lambda\left|\Psi_{1\bar{1}}^{2\bar{2}}\right\rangle$$

$$\left|\Phi_0\right\rangle = \frac{1}{2(1+s)}\left[\left(1\boxed{+\lambda}\right)\left(\underbrace{\left|\phi_A\bar{\phi}_A\right\rangle}_{H_A^- \; H_B^+} + \underbrace{\left|\phi_B\bar{\phi}_B\right\rangle}_{H_B^- \; H_A^+}\right) + \left(1\boxed{-\lambda}\right)\left(\underbrace{\left|\phi_A\bar{\phi}_B\right\rangle}_{H_A\bullet \; H_B\bullet} + \underbrace{\left|\phi_B\bar{\phi}_A\right\rangle}_{H_B\bullet \; H_A\bullet}\right)\right] \leftrightarrow \boxed{\lambda < 0}$$

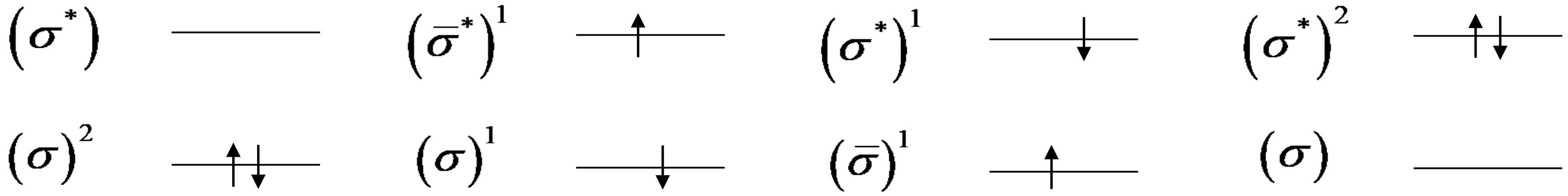
Decreases the weight of ionic conf.
Increases the weight of the covalent conf.

R_e greater than HF
D_e smaller than HF

SDCI: The S configurations

HHe$^+$ RHF MOs in MBS

$$\psi_1(\text{i})=\phi_\text{A}(\text{i})+c\,\phi_\text{B}(\text{i}) \qquad \psi_2(\text{i})=\phi_\text{A}(\text{i})-c\,\phi_\text{B}(\text{i})$$



$$|\Phi_0\rangle=|\Psi_0\rangle+\mu\left(|\Psi_1^2\rangle-|\Psi_{\bar{1}}^{\bar{2}}\rangle\right)+\lambda|\Psi_{1\bar{1}}^{2\bar{2}}\rangle$$

$$=|\psi_1\ \bar{\psi}_1\rangle+\mu\left(|\bar{\psi}_1\ \psi_2\rangle-|\psi_1\ \bar{\psi}_2\rangle\right)+\lambda|\psi_2\ \bar{\psi}_2\rangle$$

$$|\Phi_0\rangle=(1+\lambda\boxed{+2\mu})\underset{\text{He}^-\ \ \text{H}^+}{|\phi_\text{A}\bar{\phi}_\text{A}\rangle}+c^2(1+\lambda\boxed{-2\mu})\underset{\text{H}^-\ \ \text{He}^+}{|\phi_\text{B}\bar{\phi}_\text{B}\rangle}-$$

$$-c(1-\lambda-2\mu)\underset{\text{He}\bullet\ \ \text{H}\bullet}{|\phi_\text{A}\bar{\phi}_\text{B}\rangle}-c(1-\lambda+2\mu)\underset{\text{H}\bullet\ \ \text{He}\bullet}{|\phi_\text{B}\bar{\phi}_\text{A}\rangle}$$

S: Repolarize the wavefunction

As ionic conf. increases, the other decreases

H-He$^+$: Properties

HF, DCI and SDCI with STO-3G using G09

Method	R_e/Å	μ/D	ν/cm^{-1}	E/a.u.
HF	0.930	2.094	2524.9	-2.85427
DCI	0.913	1.917	2737.7	-2.86224
SDCI	0.914	1.910	2739.5	-2.86269

Configuration interactions

- Linear variation method
- **H** is built on the basis of determinants and then diagonalized
- All determinants → FCI:
  - Lowest E → Ground State
  - Higher E → Excited States
  - Exact solution in the basis set
  - Upper limit to the system energy

Rayleigh-Schrödinger perturbation theory

- Partition of the Hamiltonian:

$$H = H_0 + V \rightarrow \begin{cases} H\left|\Phi_i\right\rangle = \left(H_0 + V\right)\left|\Phi_i\right\rangle = \mathcal{E}_i\left|\Phi_i\right\rangle \\ H_0\left|\Psi_i^{(0)}\right\rangle = E_i^{(0)}\left|\Psi_i^{(0)}\right\rangle \rightarrow H_0\left|i\right\rangle = E_i^{(0)}\left|i\right\rangle \end{cases}$$

  - H is not exactly solvable
  - H_0 can be solved exactly :
    - $\{E_i^{(0)},\Psi_i^{(0)}\}$ are the zero order solutions
    - We expect $\{\Phi_i,\mathcal{E}_i\}$ to be close to $\{\Psi_i^{(0)},E_i^{(0)}\}$
    - Enhancement procedure of $\{\Psi_i^{(0)},E_i^{(0)}\}$, approaching $\{\Phi_i,\mathcal{E}_i\}$
- H_0 is the Fock operator and $E_i^{(0)}$ the sum of orbital energies

$$H_0 = \sum_i \hat{f}_i \qquad E_0^{(0)} = \sum_a \varepsilon_a$$

Series development

- Taking $H = H_0 + \lambda V \qquad 0 \le \lambda \le 1$
- We develop $\{\Phi_i, \mathcal{E}_i\}$ in the Taylor series with λ

$$\mathcal{E}_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \cdots$$

$$\left|\Phi_i\right\rangle = \left|i\right\rangle + \lambda\left|\Psi_i^{(1)}\right\rangle + \lambda^2\left|\Psi_i^{(2)}\right\rangle + \cdots$$

- Target: to write $\{\Phi_i, \mathcal{E}_i\}$ as a function of

$E_i^{(0)}$, |i> and <i|V|j>

Further development

- By substituting the developments in the exact Schrödinger equation:

$$\left(H_0 + \lambda V\right)\left(\left|i\right\rangle + \lambda\left|\Psi_i^{(1)}\right\rangle + \lambda^2\left|\Psi_i^{(2)}\right\rangle + \cdots\right) =$$

$$= \left(E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \cdots\right)\left(\left|i\right\rangle + \lambda\left|\Psi_i^{(1)}\right\rangle + \lambda^2\left|\Psi_i^{(2)}\right\rangle + \cdots\right)$$

- Assuming intermediate normalization and that |i> is normalized:

$$\left.\begin{aligned}\left\langle i\middle|i\right\rangle &= 1\\ \left\langle \Phi_i\middle|i\right\rangle &= 1\end{aligned}\right\} \rightarrow 1 = \left\langle i\middle|\Phi_i\right\rangle = \left\langle i\middle|i\right\rangle + \lambda\left\langle i\middle|\Psi_i^{(1)}\right\rangle + \lambda^2\left\langle i\middle|\Psi_i^{(2)}\right\rangle + \cdots \Rightarrow$$

$$\Rightarrow \left\langle i\middle|\Psi_i^{(n)}\right\rangle = 0\ \forall n \neq 0$$

Even further development

- By equating terms with equal **n** power of λ

$$\begin{cases} n=0 \rightarrow H_0|i\rangle = E_i^{(0)}|i\rangle \\ n=1 \rightarrow H_0\left|\Psi_i^{(1)}\right\rangle + V|i\rangle = E_i^{(0)}\left|\Psi_i^{(1)}\right\rangle + E_i^{(1)}|i\rangle \\ n=2 \rightarrow H_0\left|\Psi_i^{(2)}\right\rangle + V\left|\Psi_i^{(1)}\right\rangle = E_i^{(0)}\left|\Psi_i^{(2)}\right\rangle + E_i^{(1)}\left|\Psi_i^{(1)}\right\rangle + E_i^{(2)}|i\rangle \\ n=3 \rightarrow H_0\left|\Psi_i^{(3)}\right\rangle + V\left|\Psi_i^{(2)}\right\rangle = E_i^{(0)}\left|\Psi_i^{(3)}\right\rangle + E_i^{(1)}\left|\Psi_i^{(2)}\right\rangle + E_i^{(2)}\left|\Psi_i^{(1)}\right\rangle + E_i^{(3)}|i\rangle \\ \quad \ldots \\ n \rightarrow H_0\left|\Psi_i^{(n)}\right\rangle + V\left|\Psi_i^{(n-1)}\right\rangle = \sum_{j=1}^{n} E_i^{(n-j)}\left|\Psi_i^{(j)}\right\rangle + E_i^{(n)}|i\rangle \end{cases}$$

Initial equations: energy of order n

By multiplying by <i| →

$$\begin{cases} E_i^{(0)} = \langle i | H_0 | i \rangle \\ E_i^{(1)} = \langle i | V | i \rangle \\ E_i^{(2)} = \langle i | V | \Psi_i^{(1)} \rangle \\ E_i^{(3)} = \langle i | V | \Psi_i^{(2)} \rangle \\ \ldots \\ \boxed{E_i^{(n)} = \langle i | V | \Psi_i^{(n-1)} \rangle} \\ \ldots \end{cases}$$

The energy of order n is obtained from the n-1 order function

$$\mathcal{E}_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \cdots$$

Initial equations: energy of order n

MP2

MP-n

$$\mathcal{E}_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \cdots$$

$$E_0 = E_0^{(0)} + E_0^{(1)} = \sum_a \varepsilon_a - \frac{1}{2}\sum_{ab} \langle ab \| ab \rangle = E_0(HF) = \langle \Psi_0 | H | \Psi_0 \rangle$$

Hartree-Fock energy includes orders 0 and 1 in the Möller-Plesset partition

Wavefunction: superposition principle

$$\left|\Phi_i\right\rangle = \left|i\right\rangle + \lambda\left|\Psi_i^{(1)}\right\rangle + \lambda^2\left|\Psi_i^{(2)}\right\rangle + \cdots$$

- The wavefunction at any order is developed as a linear combination of the zero order wavefunctions:

$$\left|\Psi_i^{(k)}\right\rangle = \sum_j \left|\Psi_j^{(0)}\right\rangle c_j^{(k)} = \sum_j \left|j\right\rangle c_j^{(k)}$$

- Each component of the wavefunction can be obtained from the scalar product of the unitary vector in a given direction times the function:

$$c_j^{(k)} = \left\langle j \middle| \Psi_i^{(k)}\right\rangle = \left\langle \Psi_j^{(0)} \middle| \Psi_i^{(k)}\right\rangle$$

First order wavefunction

$$H_0\left|\Psi_i^{(1)}\right\rangle + V|i\rangle = E_i^{(0)}\left|\Psi_i^{(1)}\right\rangle + E_i^{(1)}|i\rangle$$

multiplying by $\langle n| \rightarrow \boxed{\langle n|H_0|}\Psi_i^{(1)}\rangle + \langle n|V|i\rangle = E_i^{(0)}\left\langle n\middle|\Psi_i^{(1)}\right\rangle + E_i^{(1)}\cancel{\langle n|i\rangle}$

resulting in $\rightarrow \boxed{E_n^{(0)}\langle n|}\Psi_i^{(1)}\rangle + \langle n|V|i\rangle = E_i^{(0)}\left\langle n\middle|\Psi_i^{(1)}\right\rangle$

obtaining $\rightarrow c_n^{(1)} = \left\langle n\middle|\Psi_i^{(1)}\right\rangle = \dfrac{\langle n|V|i\rangle}{E_i^{(0)} - E_n^{(0)}} \Rightarrow$

$$\Rightarrow \left|\Psi_i^{(1)}\right\rangle = \sum_{n\neq i}|n\rangle\left\langle n\middle|\Psi_i^{(1)}\right\rangle = \sum_{n\neq i}|n\rangle\frac{\langle n|V|i\rangle}{E_i^{(0)} - E_n^{(0)}}$$

Second order energy

- From the obtained result:

$$\left.\begin{aligned} E_i^{(2)} &= \left\langle i \middle| V \middle| \Psi_i^{(1)} \right\rangle \\ \left| \Psi_i^{(1)} \right\rangle &= \sum_{n \neq i} |n\rangle \left\langle n \middle| \Psi_i^{(1)} \right\rangle \end{aligned}\right\} \Rightarrow$$

$$E_i^{(2)} = \sum_{n \neq i} \langle i|V|n\rangle \left\langle n \middle| \Psi_i^{(1)} \right\rangle = \sum_{n \neq i} \frac{\langle i|V|n\rangle\langle n|V|i\rangle}{E_i^{(0)} - E_n^{(0)}}$$

Third order energy

$$E_i^{(3)} = \boxed{\sum_{n\neq i}\sum_{m\neq i}\frac{\langle i|V|n\rangle\langle n|V|m\rangle\langle m|V|i\rangle}{\left(E_i^{(0)}-E_n^{(0)}\right)\left(E_i^{(0)}-E_m^{(0)}\right)} - E_i^{(1)}\sum_{n\neq i}\frac{\langle i|V|n\rangle\langle n|V|i\rangle}{\left(E_i^{(0)}-E_n^{(0)}\right)^2}}$$

DEPENDS on N^2!!

Summarizing

- The energy of order **n** is obtained from the wavefunction of **n-1** order
- In $E^{(3)}$ (and $E^{(4)}$), a term depending on N^2 appears
- At higher orders, terms of N^3, N^4, etc. appear

General formulation of coupled cluster (CC)

- Approaching the exact function:
  - **n**, the maximum order of excitation to be considered, is chosen
    - CCSD: Double
    - CCSDT: Triple
  - For determinants of order > **n**:

    coefficients ≈ product of coefficients of determinants with order ≤ **n**

- For example, in CCSD
  - Includes only mono and diexcitations
  - C_T, C_Q, … are approximated as a product of C_S and C_D among them

The trick…

the exponential ansatz

- The exact wavefunction is obtained from an operator acting on the HF solution

$$\left|\Phi_0\right\rangle = \hat{\Omega}_0\left|\Psi_0\right\rangle$$

Ω_0 Wave Operator

- The operator is an exponential of operators creating mono-, di-, and tri-… excitations

$$\hat{\Omega}_0 = e^{\hat{T}}$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots$$

$$\hat{T}_1\left|\Psi_0\right\rangle = \left|\Psi_a^r\right\rangle$$

The trick…
the exponential ansatz

$$\left|\Phi_0\right\rangle = \hat{\Omega}_0\left|\Psi_0\right\rangle$$

Ω_0 Wave Operator

- Developing the exponential as a Taylor expansion

$$e^x = 1 + \frac{1}{1!}x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots$$

$$\hat{\Omega}_0 = e^{\hat{T}} = 1 + \frac{1}{1!}\hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \cdots$$

The trick…
the exponential ansatz

$$\left|\Phi_0\right\rangle = \hat{\Omega}_0\left|\Psi_0\right\rangle$$

Ω_0 Wave Operator

- In order to obtain the CCSD solution we must include mono- and diexcitations

$$CCSD \Leftrightarrow \hat{T} = \hat{T}_1 + \hat{T}_2$$

$$\hat{\Omega}_0 = e^{\hat{T}} = 1 + \frac{1}{1!}\left(\hat{T}_1 + \hat{T}_2\right) + \frac{1}{2!}\left(\hat{T}_1 + \hat{T}_2\right)^2 + \frac{1}{3!}\left(\hat{T}_1 + \hat{T}_2\right)^3 + \cdots =$$

$$= 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{6}\hat{T}_1^3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{2}\hat{T}_1\hat{T}_2^2 + \frac{1}{6}\hat{T}_2^3 + \cdots$$

CC methods

- Configurations of different order appear:
  - S: T_1 (*Cluster*)
  - D: T_2 (linked *Cluster*) and T_1^2 (unlinked *Cluster*)
  - T: T_1^3 and T_1T_2 (unlinked *Clusters*)
  - Q: T_1^4, $T_1^2T_2$ and T_2^2 (unlinked *Clusters*)
  - Etc. until ∞
- In general, each excited configuration can be obtained as a sum of several elementary contributions:

$$\mathrm{S}:\left(\hat{T}_1\right)\left|0\right\rangle$$

$$\mathrm{D}:\left(\frac{1}{2}\hat{T}_1^2+\hat{T}_2\right)\left|0\right\rangle$$

$$\mathrm{T}:\left(\frac{1}{6}\hat{T}_1^3+\hat{T}_1\hat{T}_2+\hat{T}_3\right)\left|0\right\rangle$$

$$\mathrm{Q}:\left(\frac{1}{24}\hat{T}_1^4+\frac{1}{2}\hat{T}_1^2\hat{T}_2+\frac{1}{2}\hat{T}_2^2+\hat{T}_1\hat{T}_3+\hat{T}_4\right)\left|0\right\rangle$$

$$\vdots$$

Formal properties

- If the limit is attained in CI, CC or MP-n:

  ⇒ The solution is exact in the basis set (FCI)

- What if you cannot reach the limit? (the usual situation)
  - CI: Upper limit to E in truncated CI (**variational**).
  - CC and MP-n: **non-variational**, they can give $E<E_{exac}$

Formal properties

How do the methods behave for N electrons as N grows?

- ***N-Dependency***: The calculated E for N **identical** **non-interacting** systems must be equal to N times the E of one of the systems
- ***Size-Consistency***: The calculated E for N **different** **non-interacting** systems must be equal to the sum of the fragment Es: Method must dissociate correctly
- ***Size-Extensivity***: The calculated E for systems of **different size** must give results depending on the first power of the number of electrons N

Formal properties

- Truncated CI: **IS NOT** size-consistent, nor size-extensive, nor has the correct N-dependence
- MP: **IS** in each perturbation order
- CC: **IS** in each truncation level

Comparison of methods for acetone

Method/basis set	Input	Energy /au	time/min
HF/6–31G* opt	AM1 geom, Hessian	-191.96224	7
HF/6–31G* opt + freq	AM1 geom, Hessian	-191.96224	14
MP2/6–31G* single point (sp)	HF/6–31G* geom	-192.5216	1
MP2/6–311G** sp	HF/6–31G* geom	-192.64662	7
MP2/6–31G* opt	AM1 geom, Hessian	-192.5239	11
MP2/6–31G* opt + freq	AM1 geom, Hessian	-192.5239	91
MP4SDTQ/6–31G* sp	MP2/6–31G* geom	-192.57982	33
MP4SDTQ/6–311G** sp	MP2/6–31G* geom	-192.71075	245
QCISD(T)/6–31G* sp	MP2/6–31G* geom	-192.57883	93
QCISD(T)/6–311G** sp	MP2/6–31G* geom	-192.70884	490
CCSD(T)/6–31G* sp	MP2/6–31G* geom	-192.57808	132
CCSD(T)/6–311G** sp	MP2/6–31G* geom	-192.70798	725

PentiumPro 200 MHz G94W

Molecular Mechanics (MM)

Computational Chemistry
Elective Course
Chemistry Degree
4th Year

Contents

Bibliography

C. J. Cramer
Essentials of Computational Chemistry
John Wiley and Sons, West Sussex, 2002

A. R. Leach
Molecular Modelling
Longman, London, 1996

J. Andrés & J. Bertrán (eds)
Química Teórica y Computacional
UJI, Castellón, 2007

1. Introduction

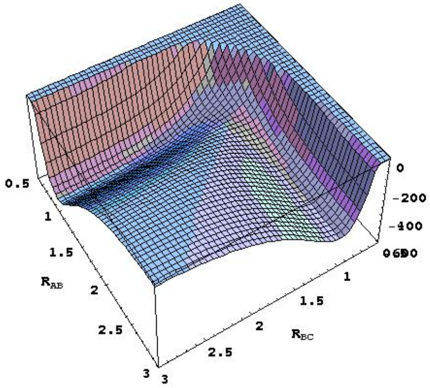
Chemistry can be considered as an exercise on potencial energy surfaces (PES):

- A vibrational spectrum is obtained from the molecular motion in a potential energy well.

- A reaction or a conformational change is defined as the molecular transit from one well on the PES to another.

- An electronic transition is considered as the transit from one PES to another.

A PES is a set of molecular potential energy values corresponding to every possible configuration of the nuclei forming it.



1. Introduction

There are different methods to obtain the PES for a system. We can easily classify them by:

Ab Initio or Density Functional Theory

- These methods explicitly consider all electrons in the system, and therefore can be applied to any kind of molecule

- These methods can be used for any structure on a given PES (minima, saddle points…) as well as for excited states

- The only limitation is the computational cost. They are usually applied to systems with less than 100 atoms (although this number changes as new computers, methods and algorithms are developed).

- For the same reason, it is difficult to carry out rigorous treatment of the environments (solvent, solid surfaces, protein) in which the process under study takes place

1. Introduction

Semiempirical methods

- In semiempirical methods, some parameters are used in order to compensate the fact that certain Hamiltonian terms are not explicitly calculated

- These parameters can be deduced from either experimental properties or ab initio calculations on a model system

- They can be applied to any system depending on the chosen parametrization, as well as to excited states

- Its use is restricted to systems containing 10^2-10^3 atoms

1. Introduction

Molecular mechanics (MM) methods

- In molecular mechanics methods, electrons are not treated explicitly

- Potential energy is obtained from a function that only contains nuclear coordinates and parameters

- These parameters can be obtained from experimental properties or ab initio calculations on model systems

- They can be applied to any system depending on the function and the chosen parametrization, although it is difficult to deal with processes containing electronic reorganization

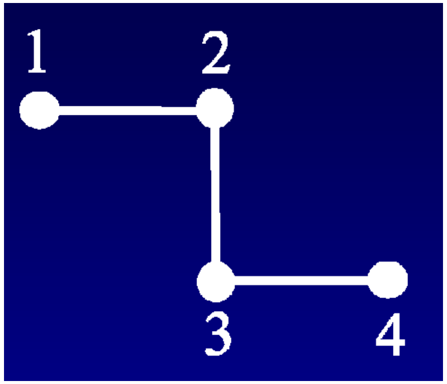
- It can be used with huge systems (more than 10^4 atoms), allowing us to include environmental effects in the study of chemical processes

1. Introduction

Molecules are considered as a group of atoms in space joined by bonds and governed by mechano-classical potential energy functions

The general form of the potential energy in MM methods is:

V = Intramolecular + Intermolecular



Normally intramolecular potential energy is written as a series of terms associated to variables defining the molecular geometry (distances, angles and dihedral angles) while intermolecular contribution is often written as a sum of electrostatic and van der Waals terms

V = Bond + Angle + Dihedral + Improper Dihedral + Crossed terms + van der Waals + Electrostatic

1. Introduction

An example of an energy function which is widespread in many force fields would be:

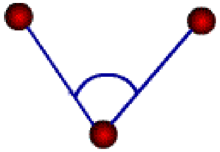
$$V(\mathbf{r}^N) = \sum_{\text{enlaces}} \frac{1}{2} k_{r,ij}\left(r_{ij} - r_{ij,0}\right)^2 + \sum_{\substack{\text{ángulos}\\ \text{enlace}}} \frac{1}{2} k_{\phi,ijl}\left(\phi_{ijl} - \phi_{ijl,0}\right)^2 + \sum_{\substack{\text{ángulos}\\ \text{torsión}}} \frac{1}{2} \sum_{n=0} V_{n,ijkl}\left[1 + \cos\left(n\theta_{ijkl} - \delta_{ijkl}\right)\right] + \sum_i \sum_j \left\{ \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]\right\}$$

① ② ③ ④ ⑤

①

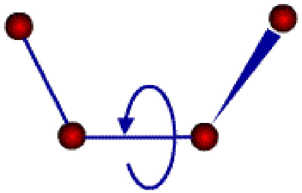
Bond stretching

②



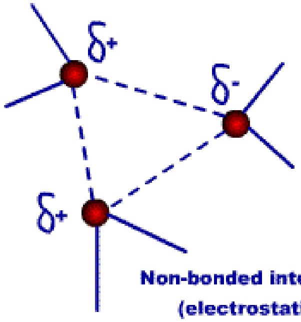
Angle Bending

③



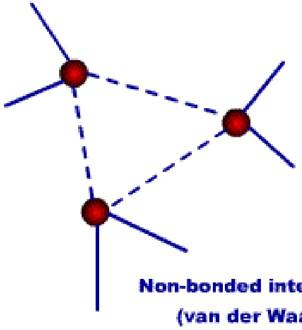
Bond rotation (torsion)

④



Non-bonded interactions
(electrostatic)

⑤



Non-bonded interactions
(van der Waals)

1. Introduction

The justification of molecular mechanics methods resides in the observation that bond properties are often transferable from one molecule to another:

- Spectroscopy studies show that bond lengths and force constants are nearly the same for each type of bond, no matter the molecule

- Thermodynamic properties, such as the enthalpy of formation, can be calculated from bond energies. These energies can also be considered as approximately constant.

We should then be able to obtain molecular geometries and energies from the bonds in the molecule, or the “type” of atoms involved in the bonds, where “type of atoms” refers to any variant of atom implied in bond formation

Example: a C atom can present different modes of bonding: simple, aromatic, double or triple. What the C is bonded to (e.g. whether the C is terminal or not) can also determine the definition of a new type of atom.

1. Introduction

The definition of a force field includes:

- The energy terms appearing in the energy function (which type of functionals are chosen for each contribution)
- The types of atoms included (the larger the types of atoms included, the more precision the force field will have, but its development will be more difficult)
- The set of values chosen for the evaluation of the different parameters appearing in the energy terms, which depend on the type of atoms

The parameters’ transferability is an important characteristic in a force field. Therefore, it should be possible to use the same parameters to treat propane, butane or pentane molecules, for example. It would only make sense to develop a new group of parameters in very small systems in which high precision is required.

2. Energy terms

Bond Stretching

In principle, the potential energy of a system can always be expressed as Taylor's expansion. Therefore, for a diatomic molecule in which the potential energy depends only on the distance, we could write (taking the energy minimum (r_0) as the origin of expansion):

$$V(r) = V(r_0) + \left(\frac{dV}{dr}\right)_{r=r_0}(r-r_0) + \frac{1}{2!}\left(\frac{d^2V}{dr^2}\right)_{r=r_0}(r-r_0)^2 + \frac{1}{3!}\left(\frac{d^3V}{dr^3}\right)_{r=r_0}(r-r_0)^3 \ldots.$$

The first term can be taken as zero by convention, while the second term is zero since it is evaluated at the minimum position. For small displacements, we can approximate the energy by means of a quadratic function of the distance (this conclusion will be valid for small displacements in any other variable: distances, angles…)

$$V(r) = \frac{1}{2}k(r-r_0)^2$$

Where k, is the force constant:

$$k = \left(\frac{d^2V}{dr^2}\right)_{r=r_0}$$

2. Energy terms

Only when considering small displacements with respect to the equilibrium position is the quadratic functional valid. Since the force constants associated to the bond tension are usually large (typically 10^3 kJ·mol^{-1}·Å^{-2}), the variations in distance are moderate (except under drastic temperature or energy conditions), then this approximation does usually give good results.

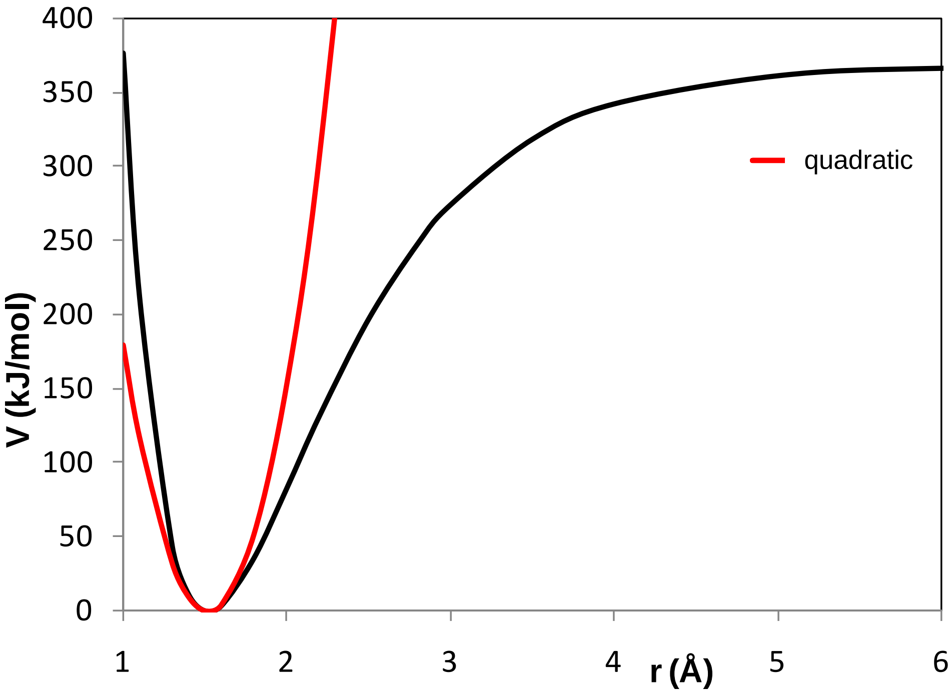
Some typical values for simple, double and triple carbon bonds, taken from de MM2 force field are:

enlace	**k (kJ·mol^{-1}·Å^{-2})**	**r_0 (Å)**
Csp3-Csp3	1330	1.523
Csp3-Csp2	1330	1.497
Csp2-Csp2	2890	1.337

2. Energy terms

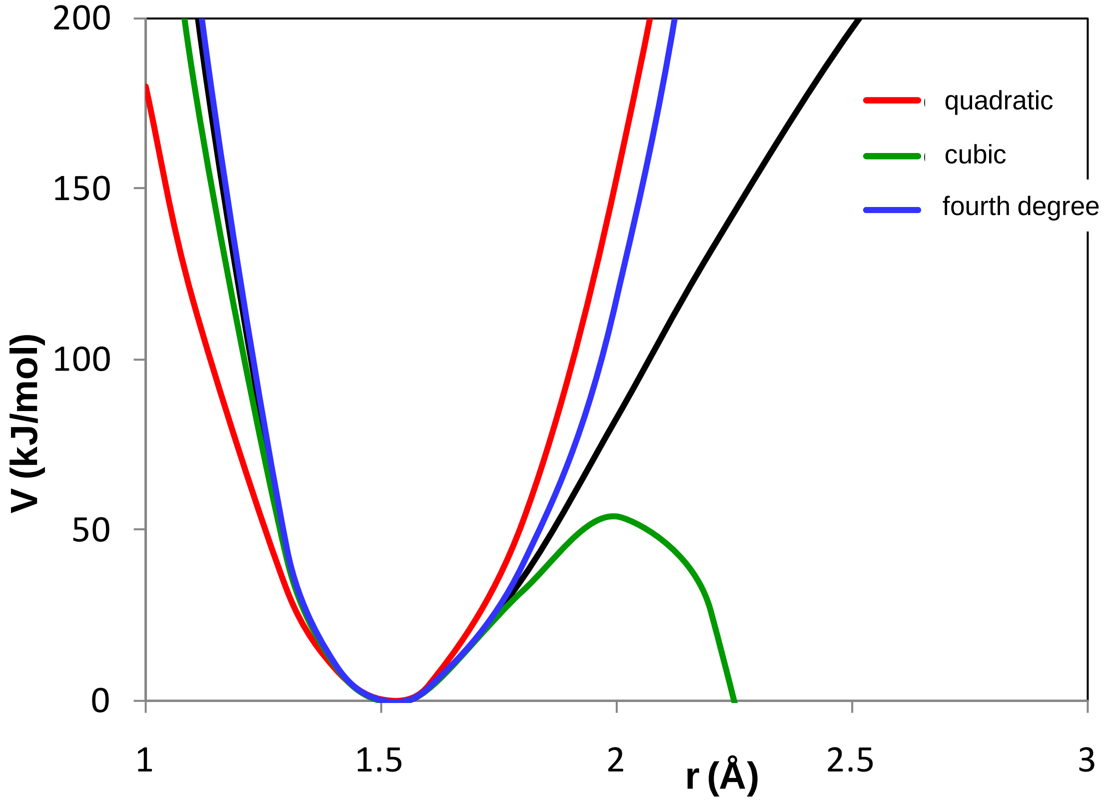
However, the quadratic function wrongly predicts increasing energies as the bond is stretched, being unable to reproduce the dissociation effect.

On the other hand, this function predicts a smaller increase in energy for bond distances that are less than the equilibrium. While the experimental curve tends to infinity when r→0, the quadratic function does not. This function allows structures with bond distances shorter than in real molecules.



2. Energy terms

Different Taylor's expansions compared to a real energy curve for C-C bond dissociation



2. Energy terms

Valence Angle Bending

Small deformations in the bond angle between atoms ijk can be described by a polynomial expansion as:

$$V(\theta) = \frac{1}{2}\left[k_{ijk} + k_{ijk}^{(3)}\left(\theta_{ijk} - \theta_{0,ijk}\right) + k_{ijk}^{(4)}\left(\theta_{ijk} - \theta_{0,ijk}\right)^2\right]\left(\theta_{ijk} - \theta_{0,ijk}\right)^2$$

Where θ_{ijk} is the angle between bonds ij and jk. The force constants depend on the three atoms which are implied in the bonds

Many force fields use a quadratic expansion (OPLS; CHARMM, AMBER, GROMOS), while others such as MM2 or MM3 use up to a 6th order term for certain combinations of atoms.

2. Energy terms

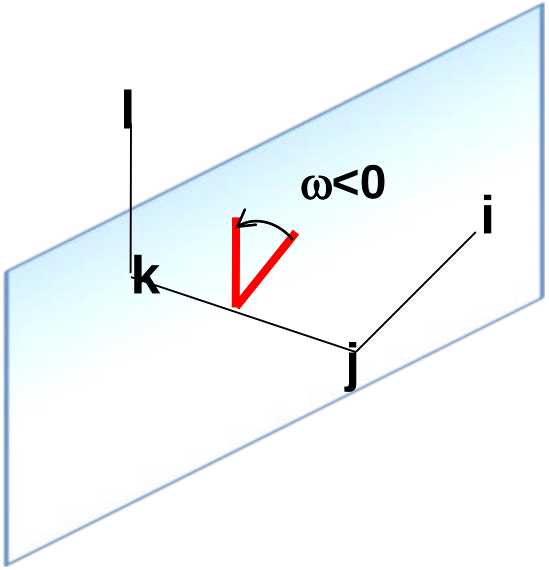
The following table provides some examples of reference values and force constants for important bond angles in the MM2 force field

Angle	θ_0 (grades)	K (kJ·mol^{-1}·grade^{-2})
Csp3-Csp3-Csp3	109.47	0.0414
Csp3-Csp2=Csp2	121.4	0.0506
Csp3-Csp2=O	122.5	0.0423
Csp3-Csp3-H	109.47	0.0331

2. Energy terms

Torsion

Let’s consider four atoms joined in a secuence ijkl. The dihedral or torsion angle associated to this secuence is defined as the angle between bonds ij and kl when they are projected over a plane which divides the bond jk perpendicularly.



The standard is to take the angle as positive if the bond in front of the plane has to be rotated clockwise, and negative if it is rotated anticlockwise

The torsion angle is periodic. The range of values can be defined between $0 \leq \omega \leq 2\pi$ or between $-\pi \leq \omega \leq +\pi$

2. Energy terms

The observed displacements in the torsion angle are much larger than those found for bond distances or angles, so a polynomial expansion around the equilibrium value is not valid. Furthermore, we need a periodic function. Normally the torsion term is modelled by a Fourier's expansion:

$$V(\omega) = \frac{1}{2}\sum_n V_{n,ijkl}\left[1 + \cos\left(n\cdot\omega_{ijkl} - \delta_{n,ijkl}\right)\right]$$

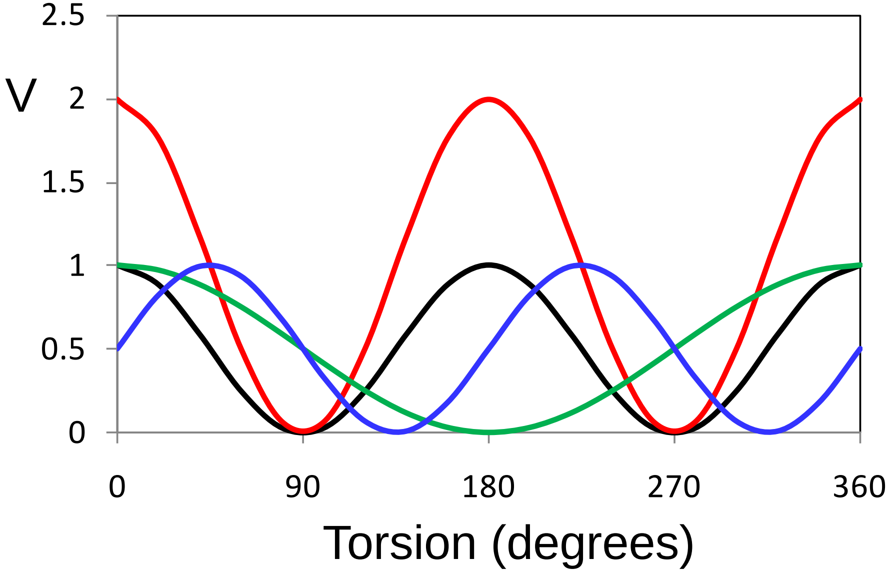
V_n is the force constant associated with rotation, and defines the energetic barrier for it. n gives the peroidicity, while the phase angle δ allows us to displace the minimum energy position.

$V=1/2*[1+\cos(2\cdot\omega)]$

$V=2/2*[1+\cos(2\cdot\omega)]$

$V=1/2*[1+\cos(1\cdot\omega)]$

$V=1/2*[1+\cos(2\cdot\omega - \pi/2)]$



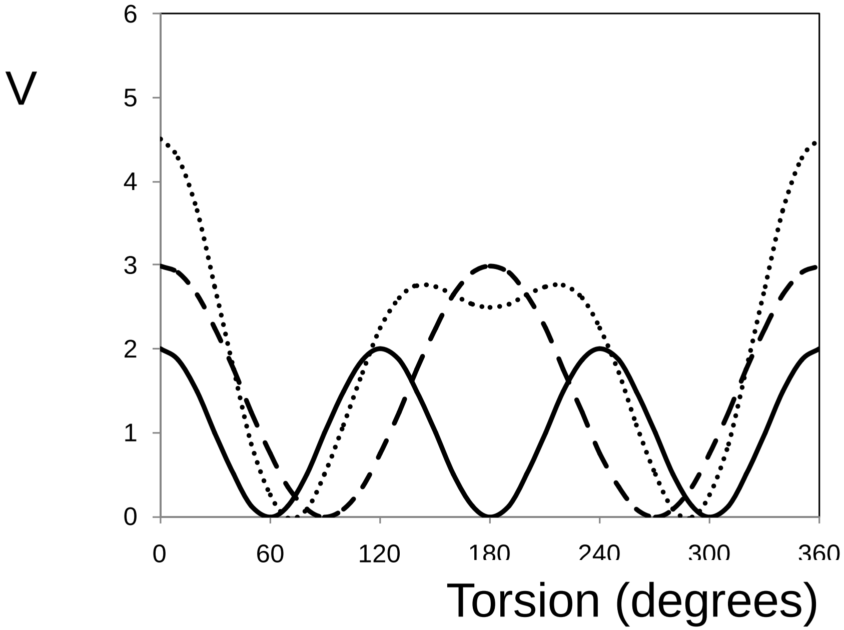
2. Energy terms

These terms can be combined to reproduce more complex behaviors:

$V=2/2*[1+\cos(3\cdot\omega)]$ ——

$V=3/2*[1+\cos(2\cdot\omega)]$ – – ·

$V=1/2*[3*[1+\cos(2\cdot\omega)]+2*[1+\cos(3\cdot\omega)]]$ ········

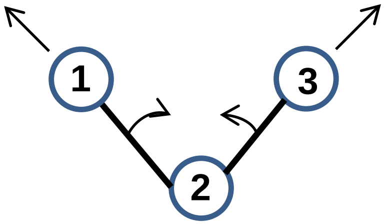


Any periodic function can be fitted with an infinite number of terms. In addition, it is possible to attribute a physical sense to each of them: interaction between bond dipoles, hyperconjugation, steric factors…

2. Energy terms

Crossed terms

The presence of crossed terms in a force field shows the connection between the different internal coordinates. For example, as a bond angle gets smaller, we observe a lengthening of the bonds in order to reduce the repulsion between the atoms involved:



The stretching-bending coupling can be treated with the same kind of expression (as used in MM2 and MM3 force fields):

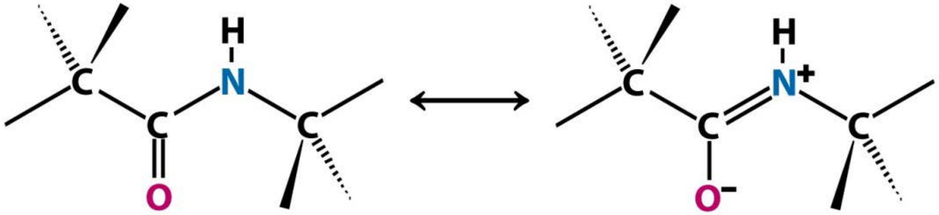
$$V(r_{ij}, r_{jk}, \theta_{ijk}) = \frac{1}{2} k_{ij,jk,ijk} \left[\left(r_{ij} - r_{0,ij} \right) + \left(r_{jk} - r_{0,jk} \right) \right] \left(\theta_{ijk} - \theta_{0,ijk} \right)$$

In general, these terms only appear in force fields which are designed to accurately reproduce molecular properties, and those that are normally restricted to small or medium-sized molecules.

2. Energy Terms

The streching-stretching coupling between C=O y C-N bonds in amides can be very important. This term can be modelled as:

$$V(r_{CN},r_{CO}) = \frac{1}{2}k_{CN,CO}\left(r_{CN} - r_{0,CN}\right)\left(r_{CO} - r_{0,CO}\right)$$

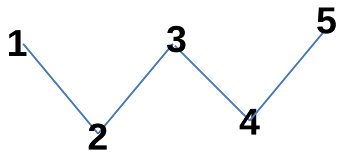


Peptide-bond resonance structures

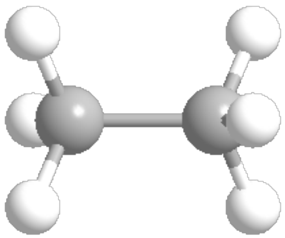
2. Energy terms

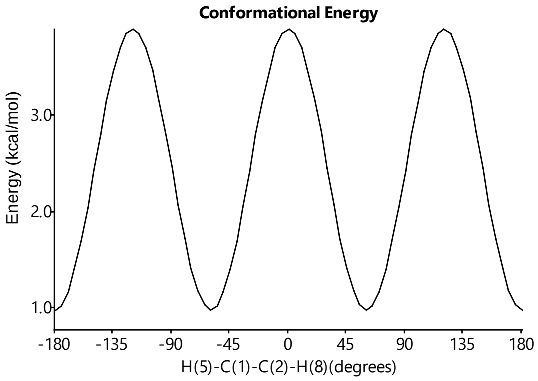
Intermolecular interactions

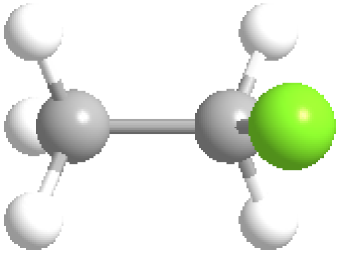
In molecular mechanics, atoms which do not belong to the same molecule, or those that are separated by more than three bonds (1-5 interaction), do interact by means of **intermolecular terms** (van der Waals + electrostatics)

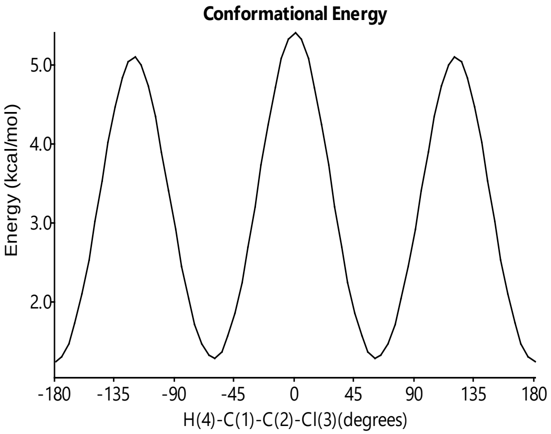


The total or partial interaction between atoms 1-4 is also allowed in certain force fields (usually reduced to a set %). In this way, the treatment of torsion is more extrapolable. For example, the differences between the rotation around the C-C bond in ethane and chloroethane can be attributed to steric effects included in the van der Waals term between the Hs from one carbon and Hs or Cl from the other:









2. Energy terms

1-4 intermolecular interactions are often multiplied by a factor of 0.5 (depending on the force field) simulating the damping of these interactions due to electronic redistributions that can take place between atoms separated only by three bonds.

Van der Waals interactions

The usual form for the van der Waals interaction is the Lennard-Jones potential or 12-6 potential:

$$V(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

Van der Waals parameters are needed for each possible pair of atom types. In order to avoid this, the Lorentz-Berthelot combination rules may be employed so that only 2 parameters are needed for each atom type:

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_{ii} + \sigma_{jj}\right)$$

$$\varepsilon_{ij} = \left(\varepsilon_{ii} \cdot \varepsilon_{jj}\right)^{1/2}$$

One can obtain van der Waals parameters from the packing data in crystals, as well as from the simulation of liquids, in which case these parameters may be adjusted to reproduce the liquids’ structural and thermodynamic properties

2. Energy terms

Electrostatic interactions

The usual way to describe electrostatic interactions is by means of interactions between partial charges, which are assigned to each atom in the molecule. Therefore , for two molecules A and B we will have.

$$V = \sum_{i}^{N_A} \sum_{j}^{N_B} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

As mentioned previously, this electrostatic interaction is calculated for atoms belonging to different molecules, or those separated by 3+ bonds in one molecule.

- The advantage is that with an appropiate charge distribution, one can represent any molecule (dipolar, cuadrupolar…)

- The problem is that atomic charges are not an observable, so many definitions and schemes are possible for their calculation.

3. Force field examples

Force field classification

Force fields can be classified according to various criteria:

According to the terms included in the potential function

- Class I: only quadratic terms are used to describe the tension and angle bond terms (AMBER, OPLS, CVFF, GROMOS, CHARMM)
- Class II: these force fields include an expansion of higher order for tension and angle as well as crossed terms (MM2, MM3, CFF93)
- Class III: these force fields include terms of higher order and more crossed terms than in class II. They also take into account specific effects like hyperconjugation (MM4)

According to the data origin used in the parametrization

- Experimentals
- Quantum
- Hybrids

3. Force field examples

Force field classification

Classification according to the more common field of application

- Organic force fields (MM3, MM4)
- Biological force fields (AMBER, CHARMM, GROMOS)
- Inorganic force fields (YETI, SHAPES)
- Universal force fields (UFF)

3. Force field examples

Force fields for simulating water

There are many force fields to study liquid water, due to its importance. Most of these force fields are pairwise, although there are also some that explicitly include polarization.

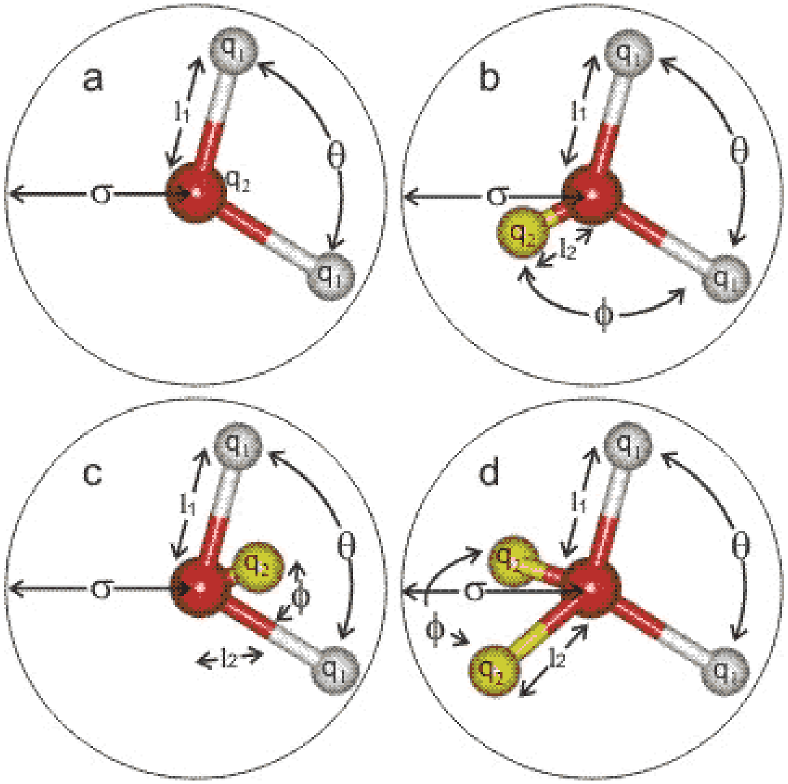
Normally they are parametrized by comparing simulations to the experimental properties of liquid water, but they can also be parametrized using ab initio studies of water clusters.

Many force fields for water are rigid: they do not allow changes in OH distances nor in the HOH angle. In these force fields, water molecules can only translate and rotate.

3. Force field examples

Normally, only one center is considered for van der Waals interactions (the oxygen atom)

Based on the number and the positioning of the point charges, they can be classified in four types:



3. Force field examples

Force fields used for water simulation

	SPC	SPC/E	TIP3P	PPC	TIP4P	TIP5P
Tipo	**a**	**a**	**a**	**b** **(Polarizable)**	**c**	**d**
r(OH),(Å)	**1.0**	**1.0**	**0.9572**	**0.943**	**0.9572**	**0.9572**
HOH (deg)	**109.47**	**109.47**	**104.52**	**106**	**104.52**	**104.52**
φ (deg)	**---**	**---**	**---**	**127**	**52.26**	**109.47**
σ(Å)	**3.166**	**3.166**	**3.15061**	**3.334**	**3.15635**	**3.12**
ε (kJ·mol^{-1})	**0.650**	**0.650**	**0.6364**	**0.6000**	**0.6480**	**0.6694**
q(O)	**-0.82**	**-0.8472**	**-0.834**	**0.0**	**0.0**	**0.0**
q(H)	**0.41**	**0.4238**	**0.417**	**0.517**	**0.52**	**0.2410**
q(M)	**0.0**	**0.0**	**0.0**	**-1.034**	**-1.04**	**-0.2410**
r(OM), Å	**---**	**---**	**---**	**0.106**	**0.15**	**0.7**

3. Force field examples

Force fields used for water simulation

Results obtained for liquid water at 25 ºC and 1 atm (except the maximum density temperature)

	SPC	SPC/E	TIP3P	PPC	TIP4P	TIP5P	Exp
Dipole (D)	**2.27**	**2.35**	**2.35**	**2.52**	**2.18**	**2.29**	**2.85-2.95**
Dielectric Constant	**65**	**71**	**82**	**77**	**53**	**81.5**	**78.4**
Auto Diffusion10^{-5} (cm^2s^{-1})	**3.85**	**2.49**	**5.19**	**2.6**	**3.29**	**2.62**	**2.30**
U ($kJ \cdot mol^{-1}$)	**-41.0**	**-41.5**	**-41.1**	**-43.2**	**-41.8**	**-41.3**	**-41.5**
Temp. of Maximum density (C)	**-45**	**-38**	**-91**	**4**	**-25**	**4**	**3.984**
Expansion coeff. 10^{-4} (ºC^{-1})	**7.3**	**5.14**	**9.2**	**---**	**4.4**	**6.3**	**2.53**

3. Force field examples

MMX force fields (X=2, 3, 4)

These force fields are due to the pioneering work of Allinger and coworkers

They are designed for organic molecules:

- MM2 force field gives good results for energy and geometry.
- MM3 was designed to better reproduce vibrational frequencies
- MM4 force field includes new crossed terms to decribe electronic effects such as hyperconjugation or the explicit treatment of lone pairs.

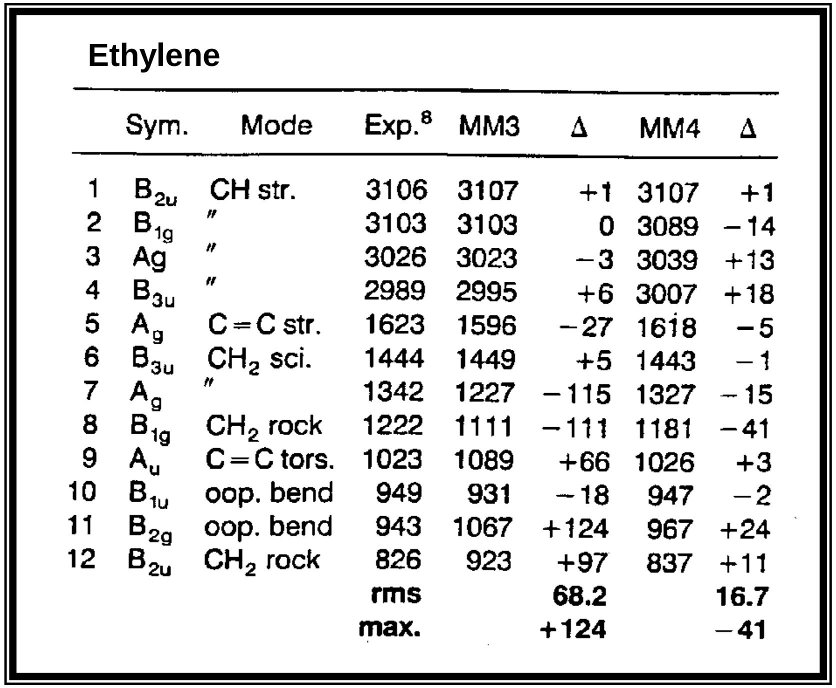
Streching and bending include anharmonic terms until third order in MM2 and until fourth order in MM3.

It includes streching-bending crossed terms

The van der Waals interaction is treated by a Hill potential

MMX are experimental force fields: they use experimental properties to fit the parameters (thermodynamics, geometric and spectroscopic properties)

3. Force field examples



Ethylene

	Sym.	Mode	Exp.[8]	MM3	Δ	MM4	Δ
1	B_{2u}	CH str.	3106	3107	+1	3107	+1
2	B_{1g}	"	3103	3103	0	3089	−14
3	Ag	"	3026	3023	−3	3039	+13
4	B_{3u}	"	2989	2995	+6	3007	+18
5	A_g	C=C str.	1623	1596	−27	1618	−5
6	B_{3u}	CH_2 sci.	1444	1449	+5	1443	−1
7	A_g	"	1342	1227	−115	1327	−15
8	B_{1g}	CH_2 rock	1222	1111	−111	1181	−41
9	A_u	C=C tors.	1023	1089	+66	1026	+3
10	B_{1u}	oop. bend	949	931	−18	947	−2
11	B_{2g}	oop. bend	943	1067	+124	967	+24
12	B_{2u}	CH_2 rock	826	923	+97	837	+11
			rms		68.2		16.7
			max.		+124		−41

Saturated hydrocarbons. Deviation between experimental and MM3/MM4 results

	MM4	MM3
Distances (Å)	0.004	0.004
Angles (°)	1	1
Frequencies (cm^{-1})	24	36

Unsaturated hydrocarbons. Deviation between experimental and MM3/MM4 results

	MM4	MM3
Distances (Å)	0.004	0.005
Angles (°)	1	1.1
Frequencies (cm^{-1})	25-31	38-52

3. Force field examples

AMBER force field (Assisted Model Building and Energy Refinement)

It was first developed in 1984 as a ‘united atom’ version and as an ‘all atom’ version in 1986 for the study of biomolecules.

Stretching and bending terms are harmonic.

The torsion term depends only on the central atom.

Van der Waals interactions are treated with a 12-6 potential.

It included a specific term for hydrogen bonds of the 12-10 type in the first versions, but the later development of better sets of charges made this unnecessary.

3. Force field examples

OPLS force field (Optimized Potential for Liquid Simulations)

It was first developed as a ‘united atom’ version and after as an ‘all atom’ version for the study of liquids (water, alcohol, polar and non-polar solutions…). It was then extended to the study of proteins and all kinds of biomolecules.

It uses the same energy potential as AMBER, and never included an explicit term for hydrogen bonds.

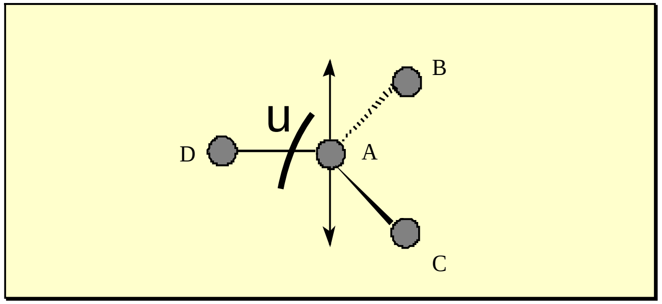
4. Force field examples

CHARMM force field (Chemistry at Harvard Macromolecular Mechanics)

It was first developed as a ‘united atom’ version and after as an ‘all atom’ version for the study of aminoacids.

It uses the same potential energy function as AMBER. The first versions included a 12-10 hydrogen bond term modulated for a set of functions that were independent of hydrogen bonds angles and distances. In more recent versions, hydrogen bonds do not include any special term.

It includes a harmonic term to describe improper angles known as the Urey-Bradley term.



$$V(u) = \frac{1}{2}k(u - u_0)^2$$

4. Force field validation

Which force field should I choose for my problem?

This is a difficult question to answer. It is usually safer to search the bibliography for studies carried out on systems similar to the one we are interested in. However, there are some general rules:

- For organic molecules MMX force fields(X=2, 3,…) and MMFF94 give good results. More generic force fields (as UFF) give worse results

- In general it is difficult to find a force field that gives good results for inorganic complexes

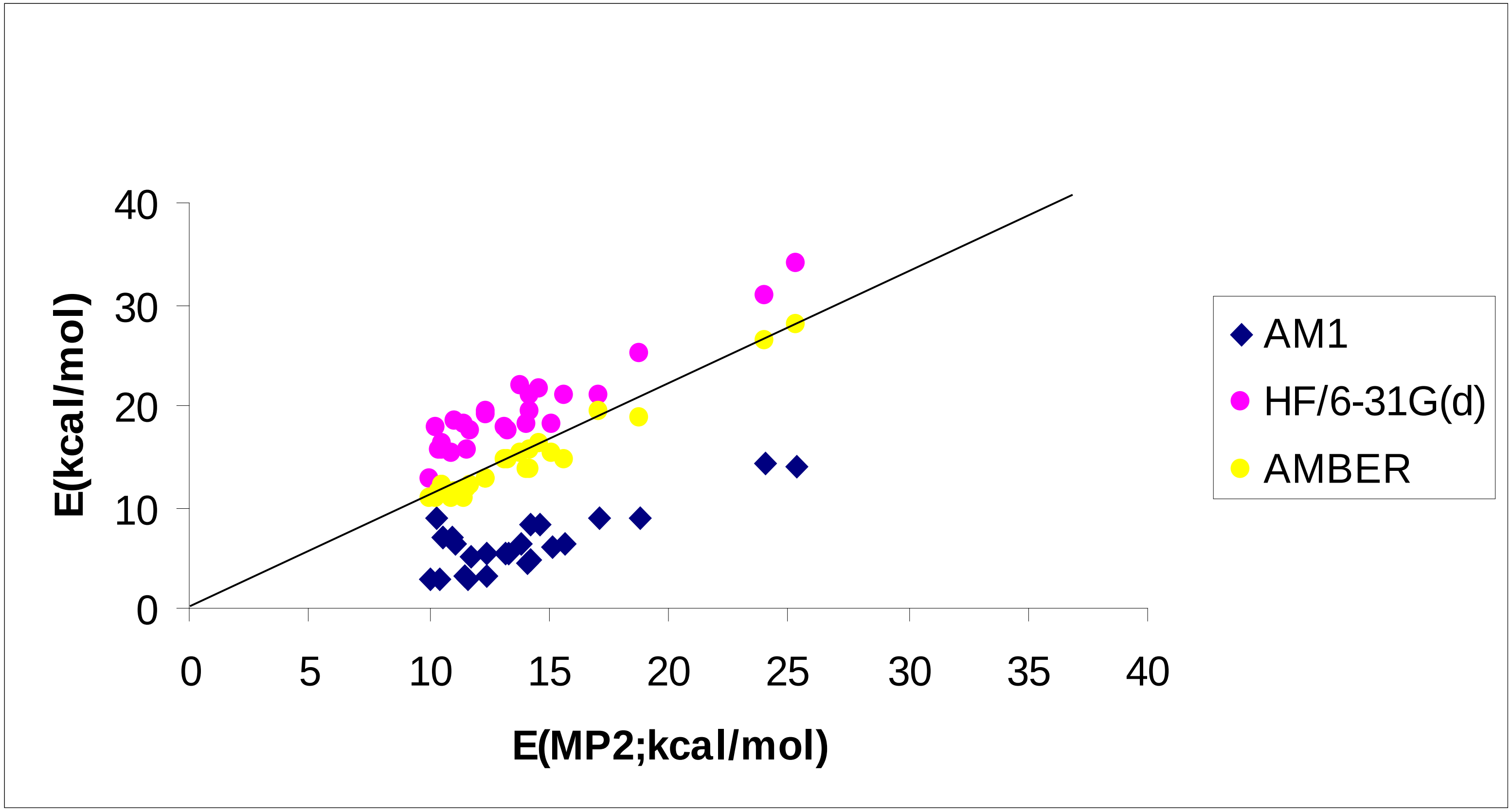
- For biomolecules OPLS, AMBER, CHARMM and GROMOS force fields give results of similar quality

- For specific studies of nucleic acids AMBER and CHARMM force fields seem to be the most appropiate

4. Force field validation

A well designed force field can provide interaction energies and geometries of similar quality to ab initio calculations.

The following graph compares interaction energies between nucleobases obtained at the AM1, HF/6-31G* levels and with a AMBER force field with the results of MP2/6-31G* calculations



Molecular Dynamics

Computational Chemistry
Elective Course
Chemistry Degree
4th year

Contents

1. **Introduction**
2. **The system**
3. **Molecular dynamics**
4. **Practical questions**

Bibliography

M. P. Allen, D. J. Tildesley
Computer Simulation of Liquids
Oxford University Press, New York 1989

A. R. Leach
Molecular Modelling
Longman, London, 1996

D. Frenkel & B. Smit
Understanding Molecular Simulation
Academic Press, San Diego, 1996

J. Andrés & J. Bertrán (eds)
Química Teórica y Computacional
UJI, Castellón, 2007

1. Introduction

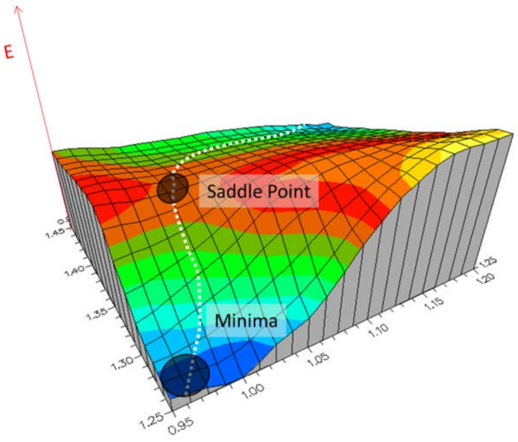
The solution of the quantum or classical Hamiltonian gives possible states (*microstates*) in which the system can be found.

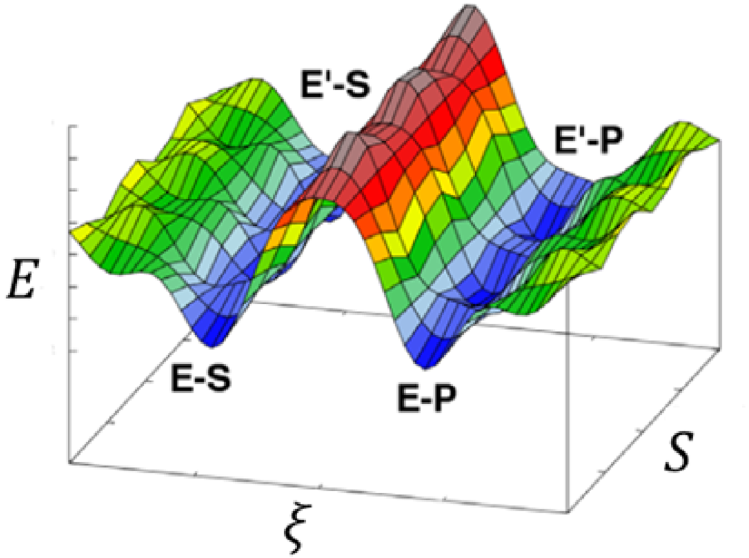
In the case of molecules, the use of the Born-Oppenheimer approximation to solve the molecular Hamiltonian results in the definition of *molecular structures.* This concept can be very useful to study chemical processes (chemical reactions, conformational equilibria…)

However, this strategy is not usually enough to describe chemical processes, except gas phase processes involving a reduced number of atoms.

In any other situation (e.g. reactions in solution), we need to consider that experimental *observables* are an *average* over a huge number of microstates (and structures) that the system can visit during the time it takes for measurements to be carried out.

1. Introduction





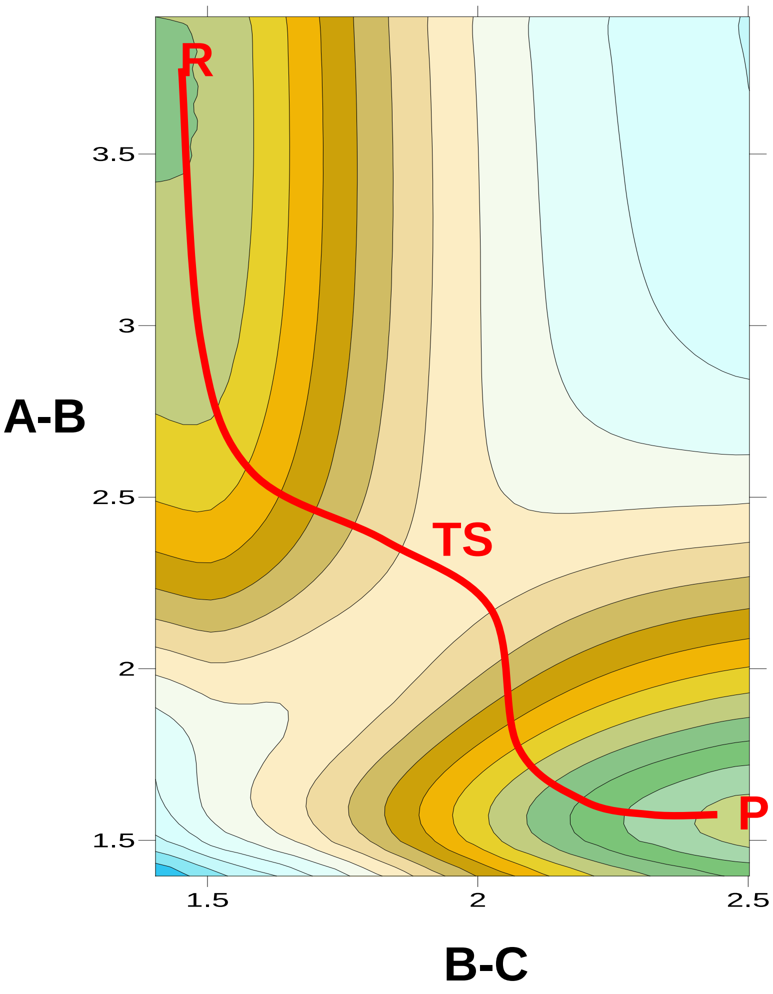
However, this strategy is not usually enough to describe chemical processes, except gas phase processes involving a reduced number of atoms.

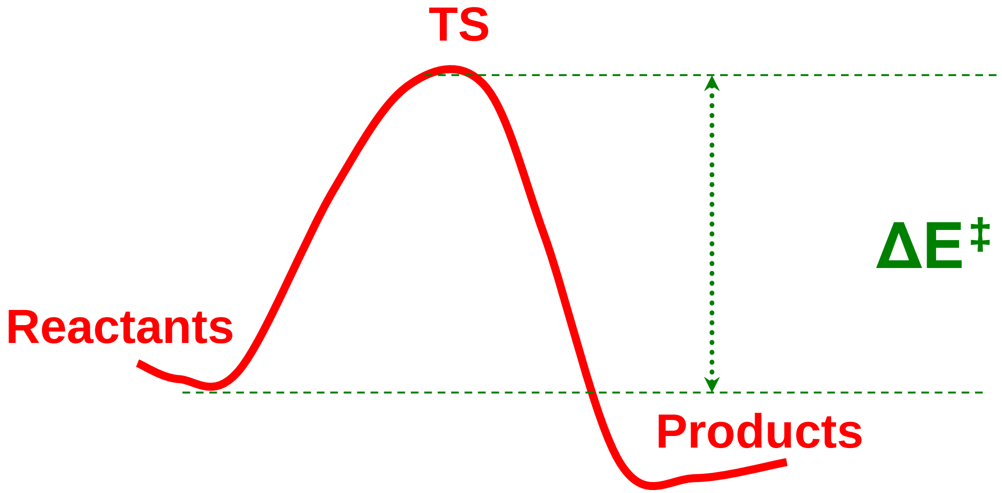
In any other situation (e.g. reactions in solution), we need to consider that experimental *observables* are an *average* over a huge number of microstates (and structures) that the system can visit during the time it takes for measurements to be carried out.

1. Introduction

Potential Energy Surface (PES)

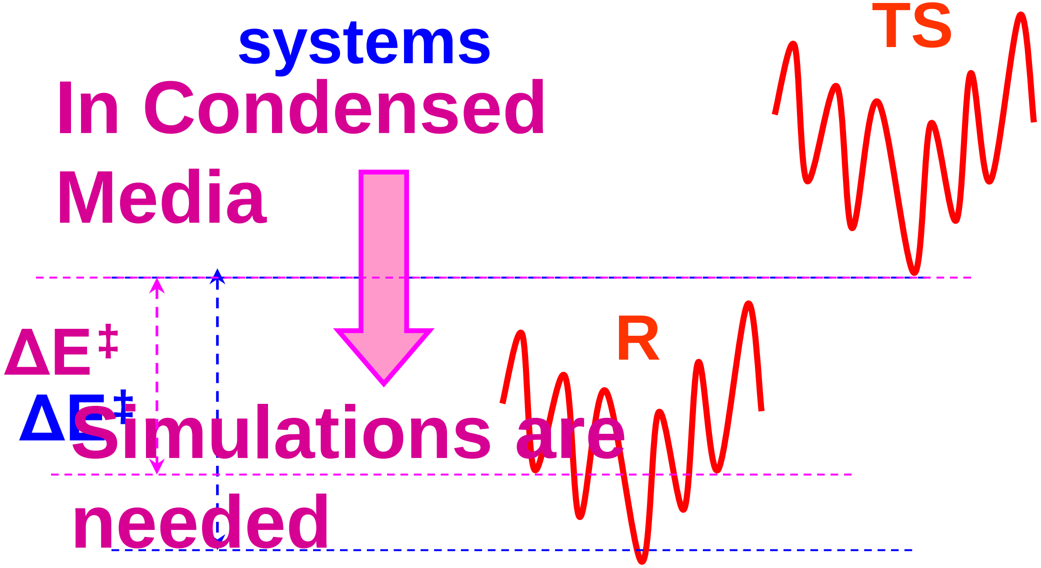
$AB + C \longrightarrow A + BC$





In large systems

In Condensed Media

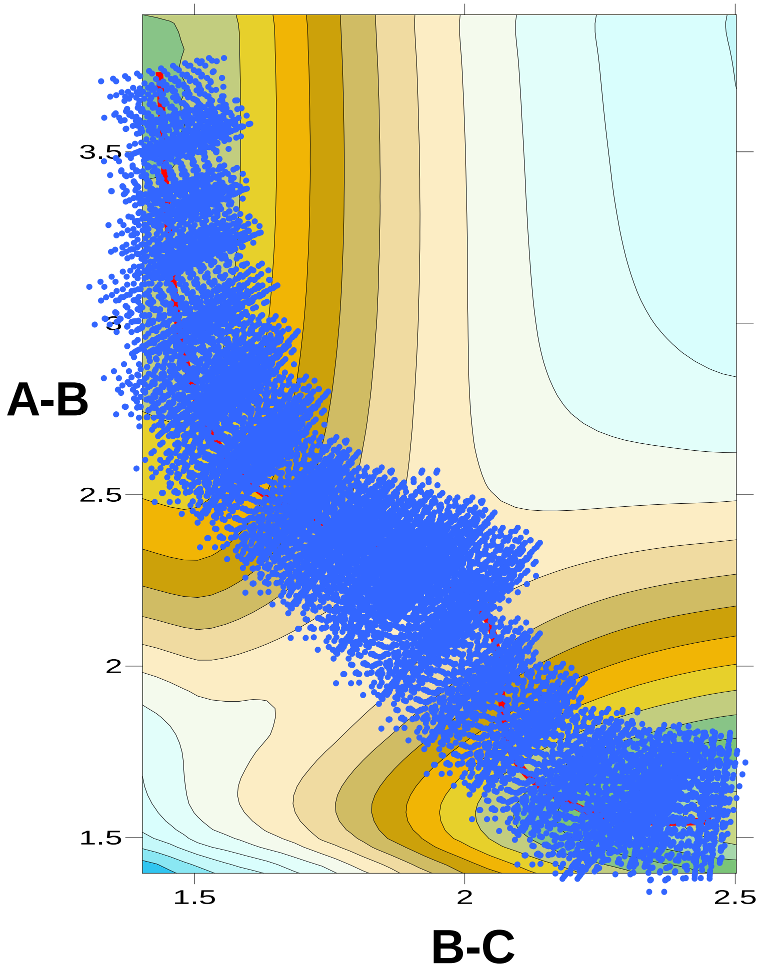


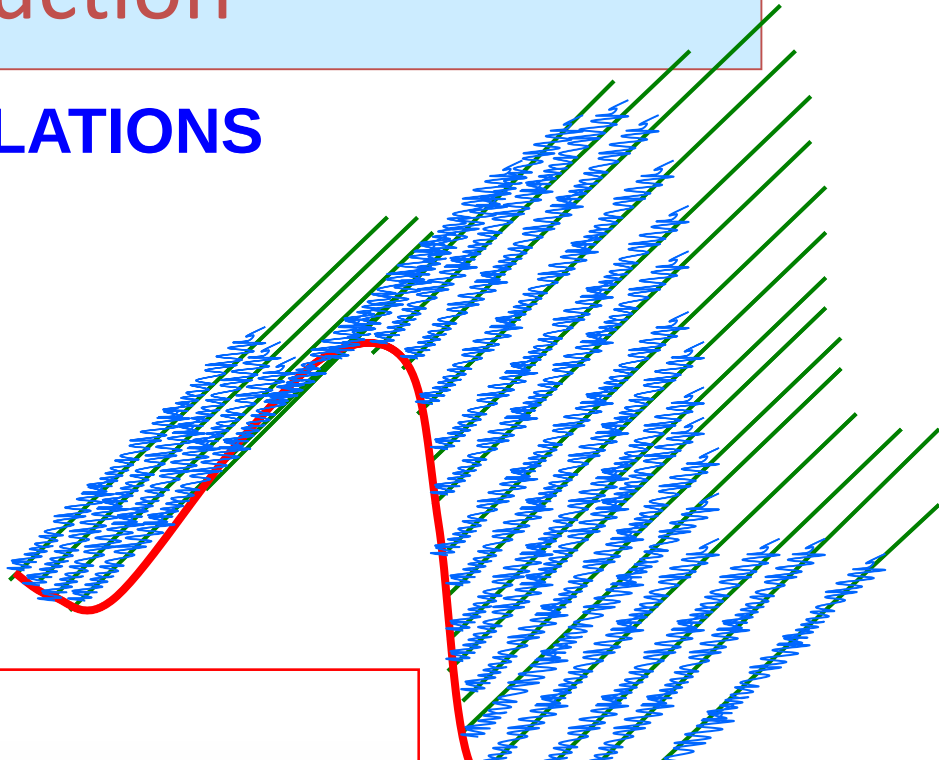
Simulations are needed

1. Introduction

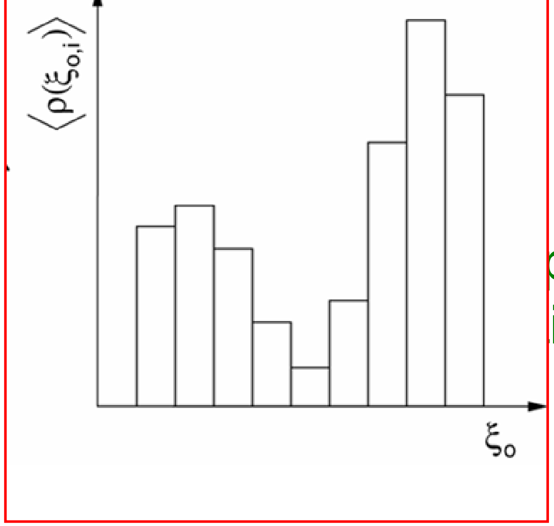
MD SIMULATIONS

AB + C ⟶ A + BC





ζ= d(A-B) – d(B-C)



properties
ined

1. Introduction

Therefore, the solution of the Hamiltonian $\hat{H}(N,V)$ is not enough to correctly describe the system under study:

- We need to consider many microstates in our analysis in order to find average properties. Mechanical properties (internal energy, pressure…) are an average of all the values that this property takes in the microstates that our system visits during measurement. Therefore, the internal energy (U) is the average energy (E) of the visited microstates:

$$U = \langle E \rangle_t = \lim_{t \to \infty} \frac{1}{t} \int_0^t E \, dt'$$

- Not all of the properties can be directly obtained from the Hamiltonian. Non-mechanical properties (temperature, entropy, free energy…) are not defined for just one microstate. Therefore, entropy (S) can be obtained from the number of ways to distribute the system between the possible microstates (W):

$$S = k \cdot \ln W$$

where k is the Boltzmann constant

1. Introduction

Simulation methods are designed to obtain a great number of microstates starting from realistic models of the system in which we are interested. This means the model must contain a large enough number of particles (molecules) and a potential energy function that accounts for both intra- and intermolecular terms.

There are two main simulation methods:

- Molecular dynamics: the microstates are obtained as a time sequence which is determined by an approximate solution of the equations for motion in the system (often using a newtonian treatment).
  The $\mathbf{r}^N$ positions and the velocities (or momenta), $\mathbf{p}^N$, of N particles are both considered, giving access to the both the kinetic and potential energies.

- Monte Carlo: microstates are obtained by random displacements of the coordinates of one or more particles. Microstates obtained in this way do not form a time sequence.
  Only the coordinates of the particles are considered, but not their momenta or velocities.

2. The system

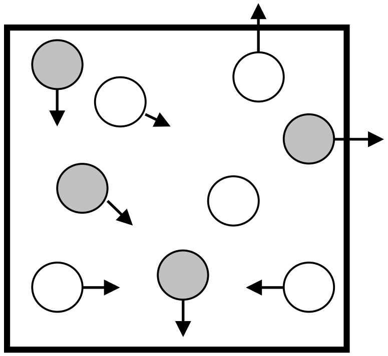
The aim of simulation methods is to study ‘realistic’ systems. Therefore, when choosing the model to best represents the system to be studied, the three following points should be considered:

- The number of molecules or atoms that form the system. This is obviously limited by the computational capacity (time and memory)
- The number of microstates that are going to be generated to obtain the averaged properties of our system, which will be limited by the available calculation time.
- The potential that governs the system behavior (intra and intermolecular interactions)

2. The system

2.1. The boundary

One of the most important problems in a simulation is the number of particles (atoms or molecules) that can be described. Let's consider the case of liquid water: a typical simulation can include about 10^4 molecules, which corresponds to a spherical micro-drop of 40 Å diameter!! This microdrop has nothing to do with a macroscopic quantity of water (around one mole), since most of the molecules in the microdrop will be influenced by surface effects.



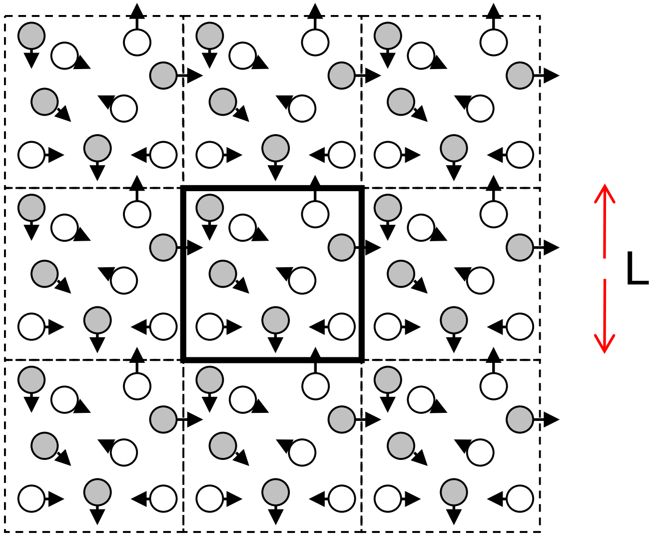
Obviously, we need techniques that deal with 'small' systems while avoiding the boundary effects in such a way that they behave as macroscopic systems. In general these techniques can be divided in two classes:

- Periodic Boundary Conditions
- Non-Periodic Boundary Conditions

2. The system

Periodic Boundary conditions

In this method, the original system or simulation cell is surrounded by identical copies. The number of molecules we describe does not increase since the motion of the copies is exactly the same as that for the molecules of the simulation cell. The advantage is that now all of the molecules in the system are surrounded by more molecules, and therefore surface effects vanish.



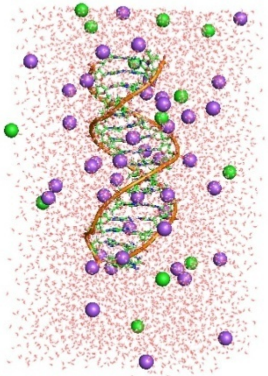
If a molecule leaves the initial cell, another will enter from a neighbouring cell. The system no longer ‘feels’ walls nor artificial limits.

2. The system

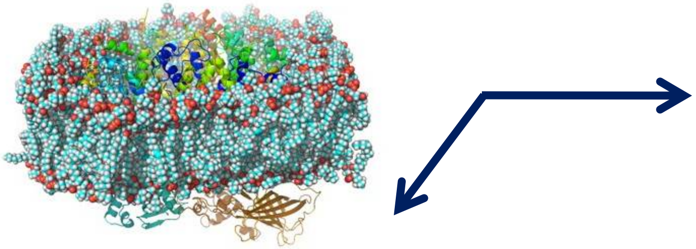
Periodic boundary conditions

The simulation cell can be cubic (such as in the previous figure) or any other geometry adapted to the problem we are studying, as long as it assures the space is completely filled: parallelepiped, truncated octahedron, hexagonal prism, rhombic decahedron.

For example, DNA is often studied using the hexagonal prism:



Furthermore, it is possible to use periodic conditions in only two directions. For example, if we want to study surface or membrane phenomena we apply periodic conditions in just two dimensions:



2. The system

Periodic boundary conditions

Periodic conditions are commonly used in simulations, but they have some limitations:

- We cannot observe fluctuations with a wavelength longer than the box size
- Its use imposes an artificial periodicity in the system, which can favor the appearance of 'crystalline' behavior.

In order to minimize these problems the simulation cell must be as large as possible. The effect of using periodic conditions can be validated by comparing the results of simulations that have been done in cells with different sizes and shapes.

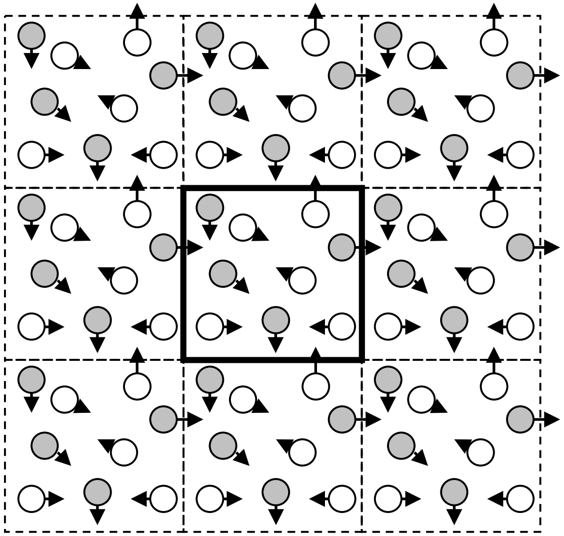
- Some systems do not require the use of periodic conditions, such as the study of molecular aggregates in gas phase.
- In some cases, such as in non-homogeneous systems, the use of periodic conditions can present some difficulties.
- Finally, in some systems, such as macromolecules in solution, the use of periodic conditions may need too many solvent molecules in the simulation cell.

2. The system

2.2. Potential energy truncation

The potential energy of the system can be obtained from an expression which is a function of the relative positions of the particles. In general, it is necessary to evaluate ½N·(N-1) distances between particles.

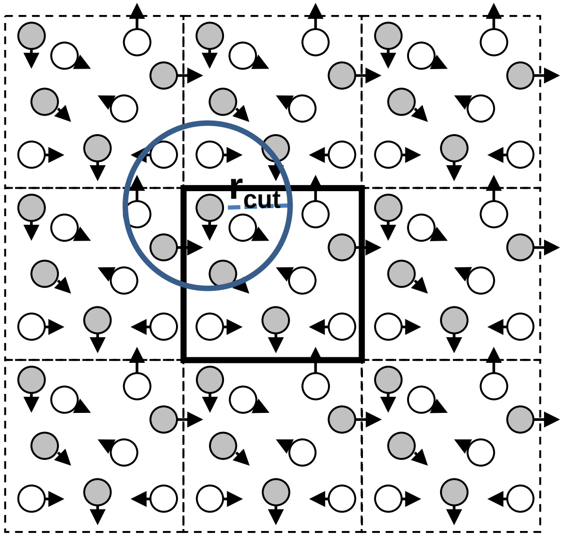
In a big system, or in a simulation employing periodic conditions, we should evaluate the interaction between distant particles, which are mostly irrelevant from a quantitative point of view. For example, the Lennard-Jones potential is < 1% at distances longer than 2.5·σ.



2. The system

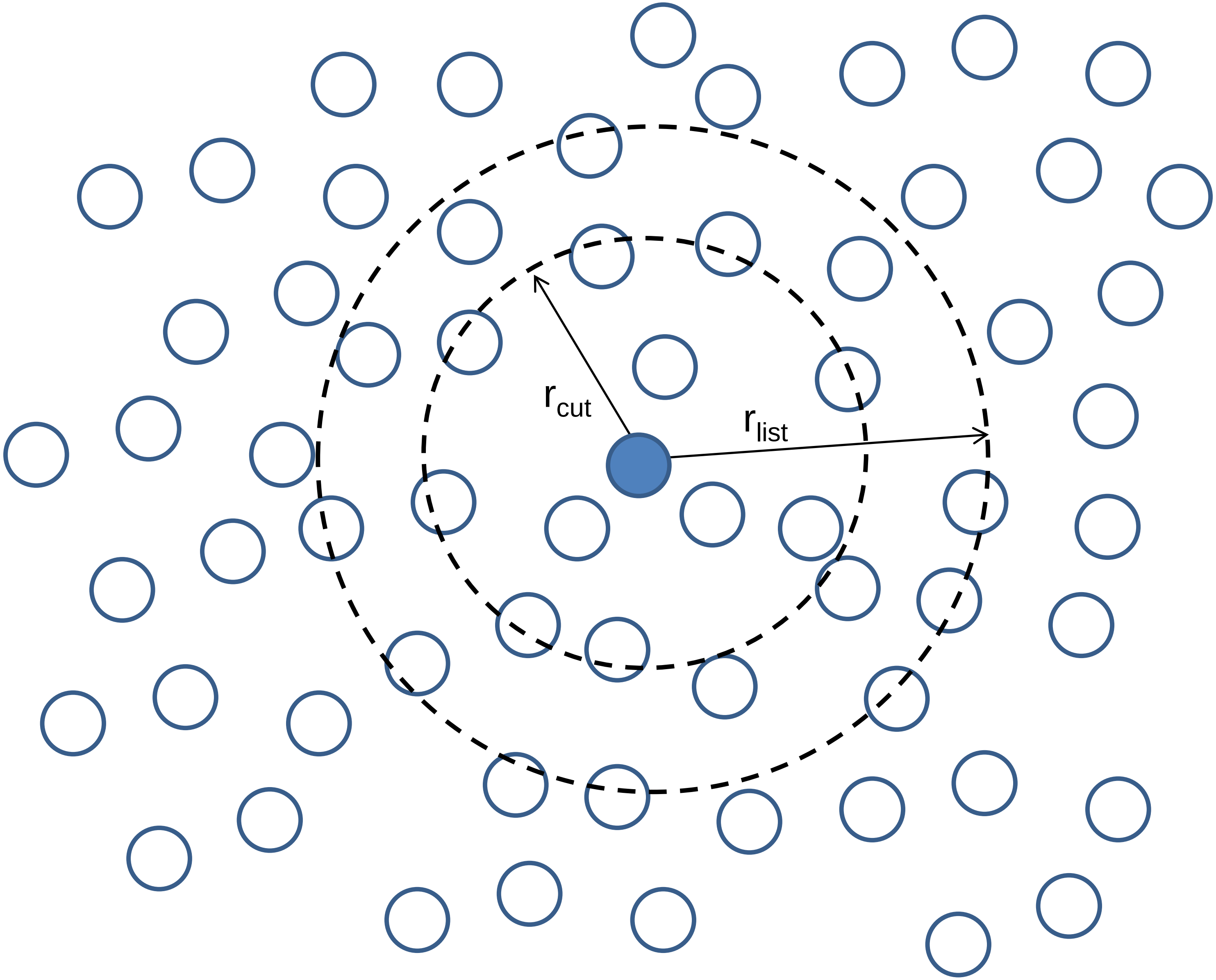
One possibility is the use of a *cutoff* distance: the interaction energy between particles that are at longer distances than a fixed value (r_{cut}) are assumed to be negligible.

Cutoff radii of less than 10 Å are not usually recommended, but they must be smaller than L/2 to avoid interactions between a molecule and its replica.



In order to be computationally efficient, the cutoff distance must be combined with the use of a list of neighbours. This list tell us which particles are found in the cutoff area, or next to it, for each particle. In this way, we only need to evaluate distances between each particle and its neighbours. This list is not updated for each new system configuration, but is typically updated for every 10-20 configurations.

2. The system

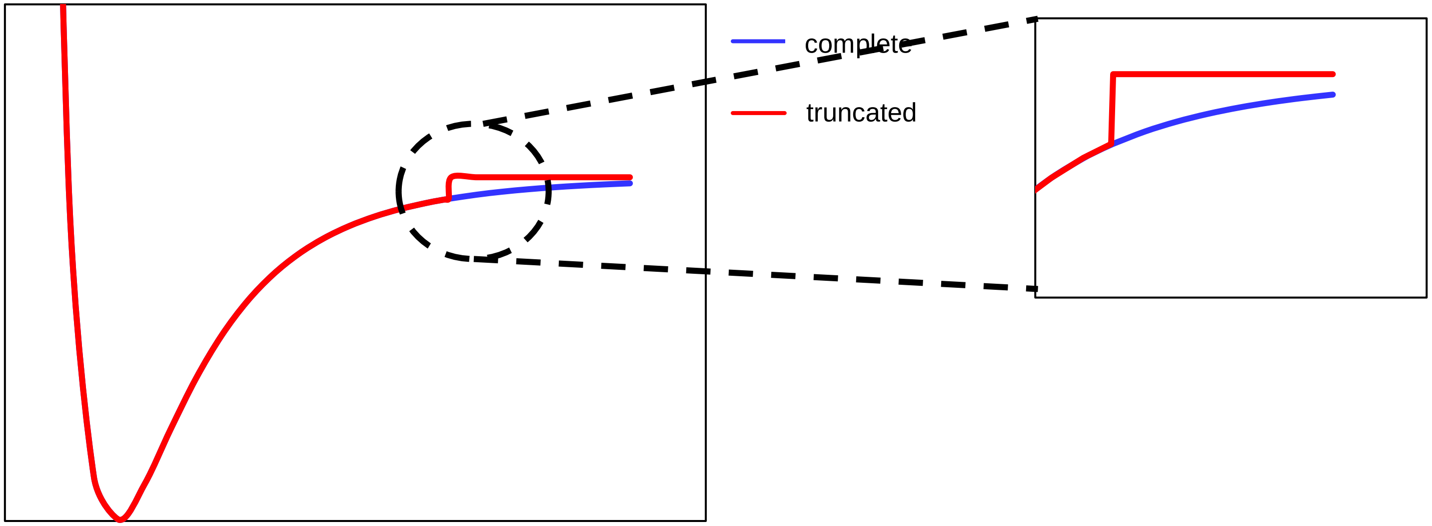


2. The system

Truncation problems

A problem associated to truncation is discontinuity. The interaction energy vanishes when the distance is larger than the cutoff radius, and this causes potential energy ‘jumps’ as the molecules move away from or approach each other during the simulation.

The following image compares a complete Lennard-Jones potential with that obtained after truncation at a certain cutoff radius.



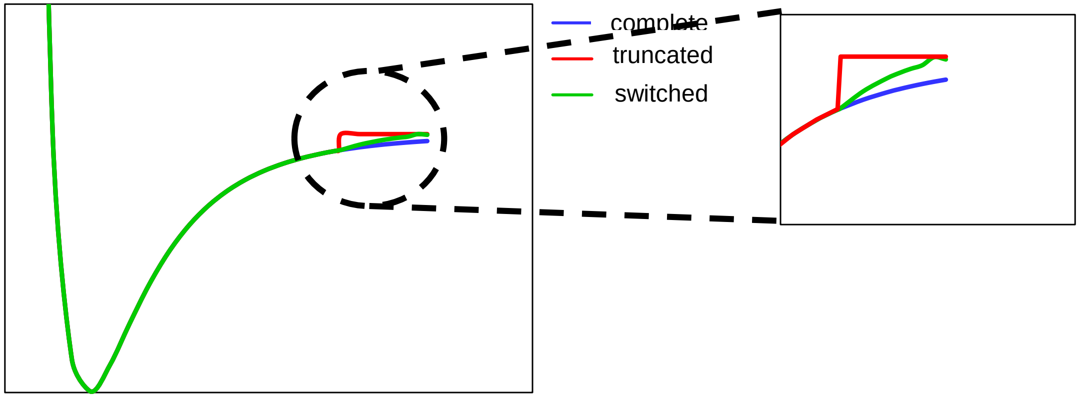
2. The system

Truncation problems

A way to reduce the cutoff radius effect is to multiply the potential energy function by a function of the distance (the *switching function* or S(r)) that takes values between 0 and 1, allowing a smooth transition between the complete value of the potential and the truncated one. An example of a switching function is:

$$S(r)\begin{cases} = 1 & r < r_{lower} \\ = \dfrac{r_{upper} - r}{r_{upper} - r_{lower}} & r_{lower} \leq r \leq r_{upper} \\ = 0 & r > r_{upper} \end{cases}$$

The next picture compares the complete Lennard-Jones potential with the truncated one and the switched one. The latter avoids discontinuities in the potential (but not in its derivatives): it is possible to define other, more sophisticated functions of S(r) to avoid discontinuities in both its first and second derivatives.

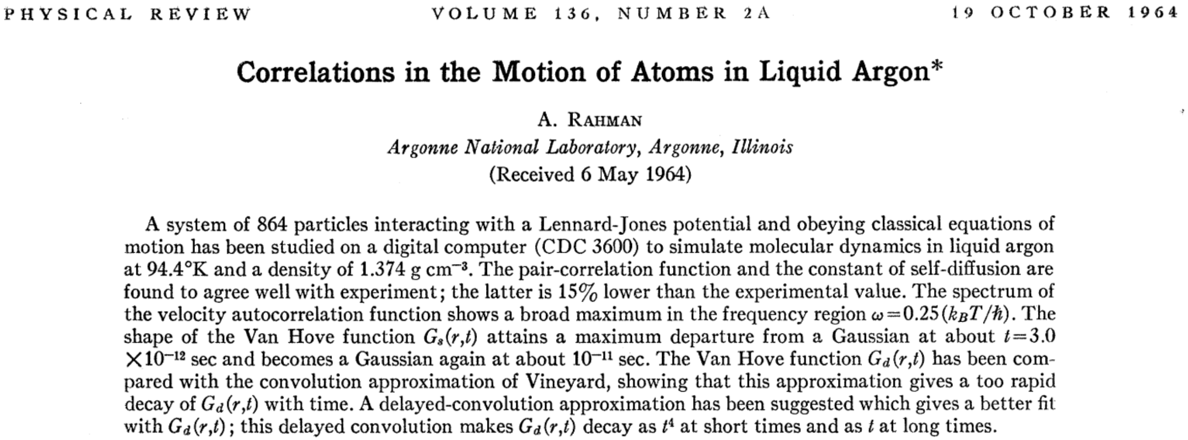


3.Molecular Dynamics

3.1. Introduction

Molecular dynamics simulations (MD) generate configurations of the system as a time sequence. With this purpose, the equations of motion in the system are solved, often in its classical version (Newton equations). It must be considered that this is not a correct approximation to study the motion of very light particles (such as H atoms)

The first MD was carried out by Alder and Wainwright in 1956 for a system made up of rigid spheres. The first MD simulation of a realistic system was made by A. Rahman in 1964: liquid argon was simulated using a Lennard-Jones potential.



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Correlations in the Motion of Atoms in Liquid Argon*

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A system of 864 particles interacting with a Lennard-Jones potential and obeying classical equations of motion has been studied on a digital computer (CDC 3600) to simulate molecular dynamics in liquid argon at 94.4°K and a density of 1.374 g cm^{-3}. The pair-correlation function and the constant of self-diffusion are found to agree well with experiment; the latter is 15% lower than the experimental value. The spectrum of the velocity autocorrelation function shows a broad maximum in the frequency region $\omega=0.25(k_BT/\hbar)$. The shape of the Van Hove function $G_s(r,t)$ attains a maximum departure from a Gaussian at about $t=3.0\times10^{-12}$ sec and becomes a Gaussian again at about 10^{-11} sec. The Van Hove function $G_d(r,t)$ has been compared with the convolution approximation of Vineyard, showing that this approximation gives a too rapid decay of $G_d(r,t)$ with time. A delayed-convolution approximation has been suggested which gives a better fit with $G_d(r,t)$; this delayed convolution makes $G_d(r,t)$ decay as t^4 at short times and as t at long times.

3.Molecular Dynamics

MD simulations are very similar to the process of a real measurement of the system: one prepares the system and measures it during a certain amount of time.

MD programs are based on a very simple algorithm:

1. The coordinates and initial velocities are read
2. The potential energy and forces are calculated
3. The Newton equations are integrated
4. The properties are calculated, and then go back to step 2

To integrate the equations of motion (the heart of an MD program) we need to know the forces that are acting on each particle. Newton equations are often solved in cartesian coordinates, therefore we need the forces as a function of coordinates x, y, z.

3.Molecular Dynamics

3.2. Integrating the equations of motion

Once we know the forces that are acting on each particle, we can now integrate the Newton equations to find the coordinates and velocities that the particles will have as time progresses:

$$m_j \frac{d^2\mathbf{r}_j}{dt^2} = \mathbf{f}_j = -\vec{\nabla}_j V$$

The most effective methods to solve differential equations are those based on finite differences. The general idea is the following: given the particles' coordinates and velocities at a certain time t, we can try to find the coordinates and velocities at a subsequent time (t+Δt) using a Taylor's expansion for coordinates and velocities:

$$\mathbf{r}_j(t+\Delta t) = \mathbf{r}_j(t) + \mathbf{v}_j(t)\Delta t + \frac{\mathbf{f}(t)}{2m_j}\Delta t^2 + \frac{d\mathbf{r}_j^3}{dt^3}\frac{\Delta t^3}{3!} + O(\Delta t^4)$$

$$\mathbf{v}_j(t+\Delta t) = \mathbf{v}_j(t) + \frac{\mathbf{f}(t)}{m_j}\Delta t + \frac{d\mathbf{r}_j^3}{dt^3}\frac{\Delta t^2}{2} + O(\Delta t^3)$$

$$\mathbf{f}_j(t+\Delta t) = \mathbf{f}_j(t) + \frac{d\mathbf{r}_j^3}{dt^3}\Delta t + O(\Delta t^2)$$

where $O(\Delta t^n)$ shows the presence of terms that depend on the powers of Δt that are higher or equal to n.

3.Molecular Dynamics

A simple truncatation of the previous equations at n=2, assuming constant forces during the time step Δt, does not usually provide a good (accurate and stable) integration algorithm. Such an algorithm must fulfill certain requirements:

- It must be fast (although integration is not the rate-determining step in a MD simulation)
- It must allow us to use a time step Δt that is as large as possible. This will allow us to cover a larger simulation time with the same number of simulation steps. In molecular simulations, Δt is often in the order of fs and the simulation time tends to be larger than 10^2 ps (meaning, at least, 10^5-10^6 integration steps)
- It must conserve the total energy: MD produces, in principle, NVE trajectories
- It must be reversible in time

3.Molecular Dynamics

One of the simplest, yet most effective, algorithms is the so called Verlet-algorithm

Let's take a Taylor's expansion for positions at t+Δt and t-Δt:

$$\mathbf{r}_j(t+\Delta t)=\mathbf{r}_j(t)+\mathbf{v}_j(t)\Delta t+\frac{\mathbf{f}(t)}{2m_j}\Delta t^2+\frac{d\mathbf{r}_j^3}{dt^3}\frac{\Delta t^3}{3!}+O(\Delta t^4)$$

$$\mathbf{r}_j(t-\Delta t)=\mathbf{r}_j(t)-\mathbf{v}_j(t)\Delta t+\frac{\mathbf{f}(t)}{2m_j}\Delta t^2-\frac{d\mathbf{r}_j^3}{dt^3}\frac{\Delta t^3}{3!}+O(\Delta t^4)$$

If we add both equations we get:

$$\mathbf{r}_j(t+\Delta t)+\mathbf{r}_j(t-\Delta t)=2\mathbf{r}_j(t)+\frac{\mathbf{f}(t)}{m_j}\Delta t^2+2O(\Delta t^4)$$

Arranging and rejecting terms of an order equal to or higher than Δt^4:

$$\mathbf{r}_j(t+\Delta t)=2\mathbf{r}_j(t)-\mathbf{r}_j(t-\Delta t)+\frac{\mathbf{f}(t)}{m_j}\Delta t^2$$

According to this equation, using the positions of the two preceding steps, we can predict the new ones with an error in the order of Δt^4. Although the algorithm does not directly use the velocities, they can be derived from the relationship:

$$\mathbf{r}_j(t+\Delta t)-\mathbf{r}_j(t-\Delta t)=2\mathbf{v}_j(t)\Delta t+O(\Delta t^3)$$

Rejecting terms in the order of Δt^3

$$\mathbf{v}_j(t)=\frac{\mathbf{r}_j(t+\Delta t)-\mathbf{r}_j(t-\Delta t)}{2\Delta t}$$

3.Molecular Dynamics

3.2. Constant temperature (NVT) dynamics

Newton equations are conservative, meaning that they produce a NVE trajectory. Nevertheless, most of the experimental information is obtained from systems in which the temperature remains constant. There are several strategies to obtain trajectories in the NVT ensemble. We recall that the equipartition principle establishes a relationship between the kinetic translational energies and the temperature. Therefore, an instantaneous temperature (T(t)) simulation could be defined from the velocities:

$$N_f \cdot \frac{1}{2} kT = \sum_{j=1}^{N_f} \frac{1}{2} m_j v_j^2 \quad \Longrightarrow \quad T(t) = \sum_{j=1}^{N_f} \frac{m_j v_j^2}{k \cdot N_f}$$

Where N_f refers to the number of degrees of freedom of the system. This expression suggests that we can obtain a trajectory at the desired temperature (T_0), scaling the particle velocities:

$$v_{\alpha,j}^{new} = v_{\alpha,j} \cdot \left(\frac{T_0}{T(t)} \right)^{1/2} \qquad \alpha = x, y, z$$

3.Molecular Dynamics

A widely-used method is the Langevin equation. This method adds friction and random forces to the real ones, both of which aim to represent the effect of a heating bath on the particles and the molecular collisions that take place. The Langevin equation of motion is given by:

$$m_j \frac{d^2\mathbf{r}_j}{dt^2} = -\vec{\nabla}_j V - m_j \cdot \gamma \cdot \frac{d\mathbf{r}_j}{dt} + \mathbf{R}_j(t)$$

Where γ is a friction parameter (in units of time^{-1}) or damping constant. The random force **R** is a Gaussian distribution defined by the statistical properties:

$$\langle R_j(t) \rangle = 0 \qquad \langle R_j^2(t) \rangle = 2\gamma \cdot m_j \cdot k \cdot T$$

where T the target temperature.

4. Practical questions

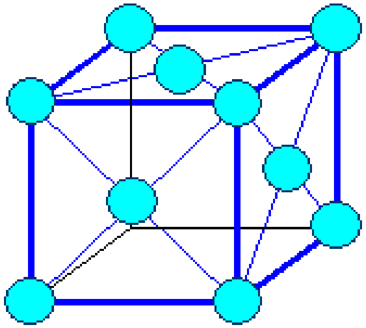
Every simulation has at least 3 steps: initialization, equilibration and production

Initialization

Preparation of the initial configuration for the study, the set of coordinates or coordinates and velocities of the atoms in our system.

If we do not have the configuration from a previous simulation, we will need to estimate the configuration to start with the simulation.

- In homogeneous systems (liquid, gases) we can use a homogeneous distribution of the molecules in the total volume, reproducing the experimental density in the simulation conditions. We can use the coordinates corresponding to a face-centered cubic crystal.



4. Practical questions

- For non-homogeneous systems, such as solutions of proteins, DNA, or solid surfaces, we can use X-ray structures as starting points for the simulations

The initial configuration can be submitted to several optimization cycles in order to relax the forces acting on the system. This step is often essential in molecular dynamic simulations to prevent divergences in the MD algorithm.

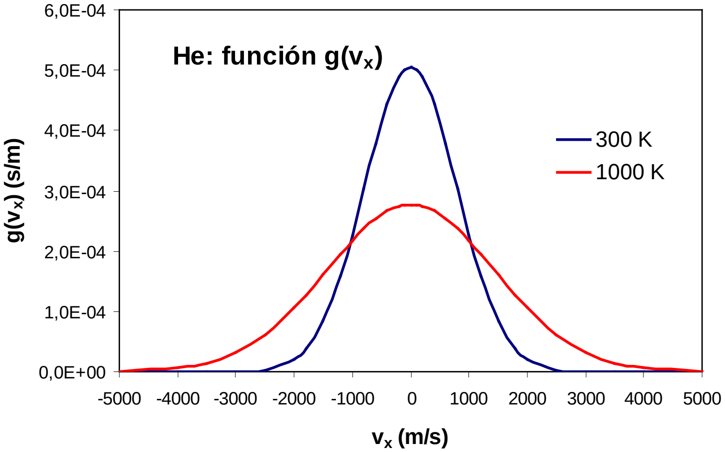
4. Practical questions

Initial velocities can randomly be obtained from a Maxwell-Boltzmann distribution corresponding to the temperature of the study.

$$g(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mv_x^2}{2kT}\right)$$

$$g(v_y) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mv_y^2}{2kT}\right)$$

$$g(v_z) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mv_z^2}{2kT}\right)$$



This Maxwell-Boltzmann distribution is only valid for translation velocities, and not for rotational nor vibrational components. Nevertheless, after a (generally) small simulation time, energy redistribution between molecular degrees of freedom is reached

4. Practical questions

Equilibration

This is the part of the simulation in which the system evolves under certain conditions (number of molecules, temperature, total energy, volume…) until it reaches equilibrium.

Equilibrium is reached when the average properties do not change during the simulation

Production

Once we have reached equilibrium, the system is studied by generating the desired number of configurations (MD or MC) to analyze the desired structural or enegetic properties.

4. Practical questions

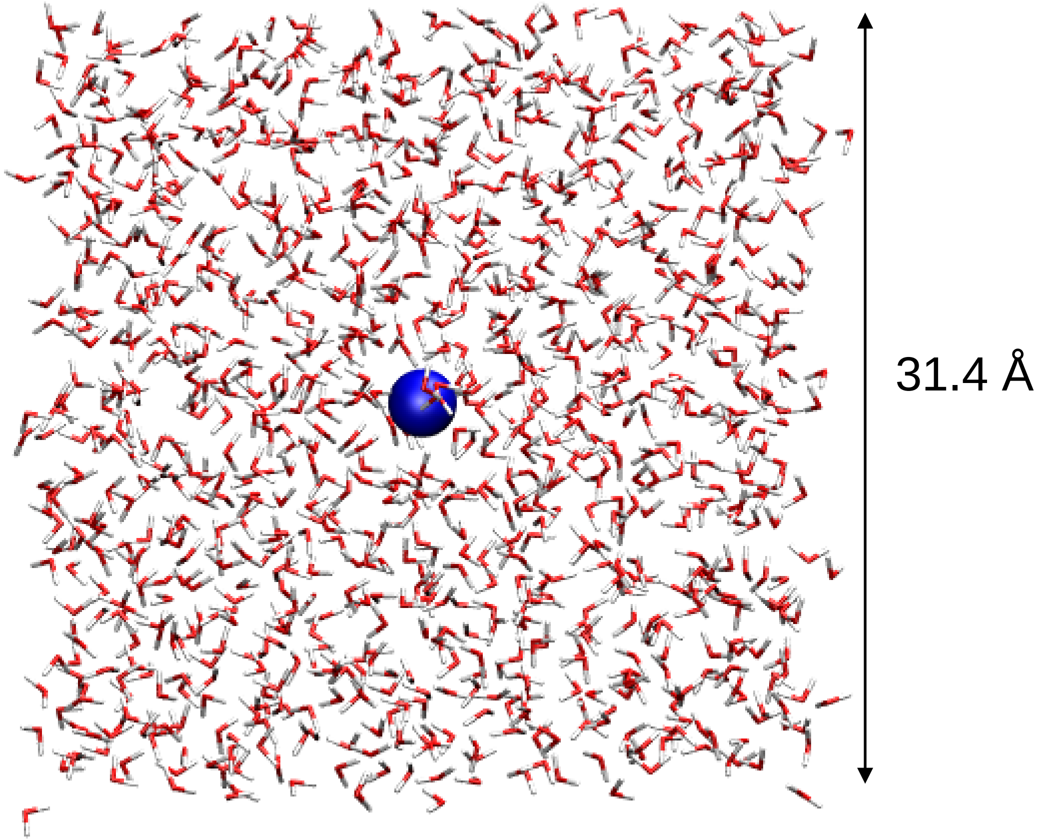
Molecular dynamics example: Na^+ in water

MD from a sodium ion in a box containing 1032 TIP3P water molecules

Na^+ $q=+1$
$\sigma=3.3305$ Å
$\varepsilon= 0.00277$ kJ·mol^{-1}

Periodic boundary conditions

Switched cut-off radius 12 Å

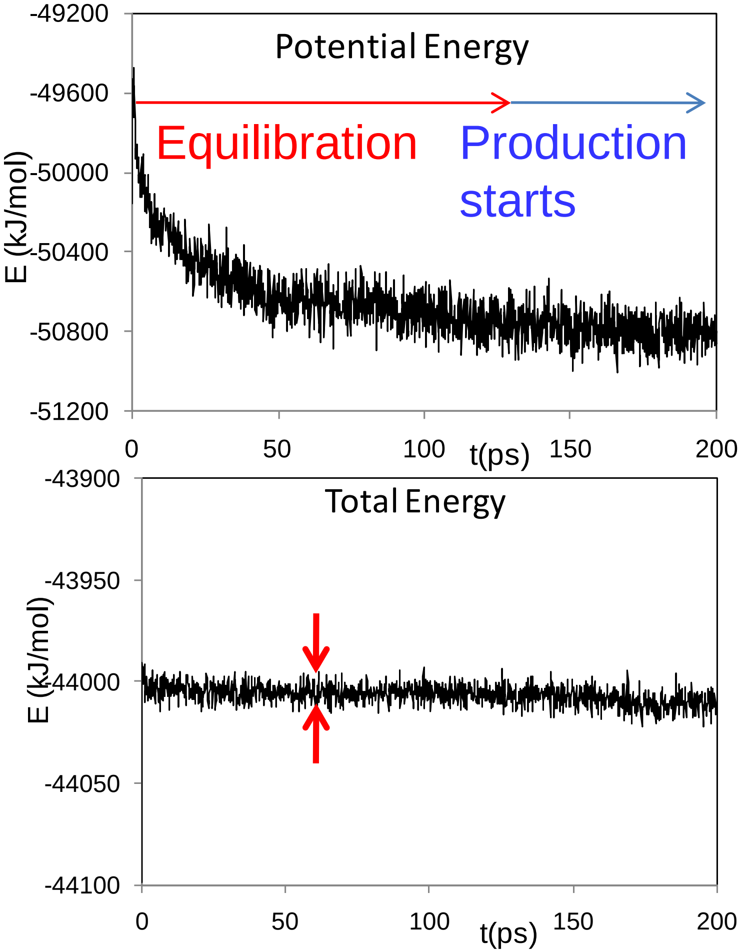


2 simulations were done, NVE and NVT (T=300K)

4. Practical questions

Molecular dynamics example: Na$^+$ in water

NVE



NVT