Theoretical Chemistry

Frédéric Castet

frederic.castet@u-bordeaux.fr

université de BORDEAUX

Summary

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

Download material (lectures & practicals) at the address
http://blake.ism.u-bordeaux1.fr/~castet/doc4.html

THE HARTREE-FOCK-ROOTHAAN METHOD

Douglas Hartree
(1897-1958)

Vladimir Fock
(1898-1974)

Clemens Roothaan
(1918-)

THE HARTREE-FOCK-ROOTHAAN METHOD

Electronic Hamiltonian for a molecule with 2N electrons and P nuclei

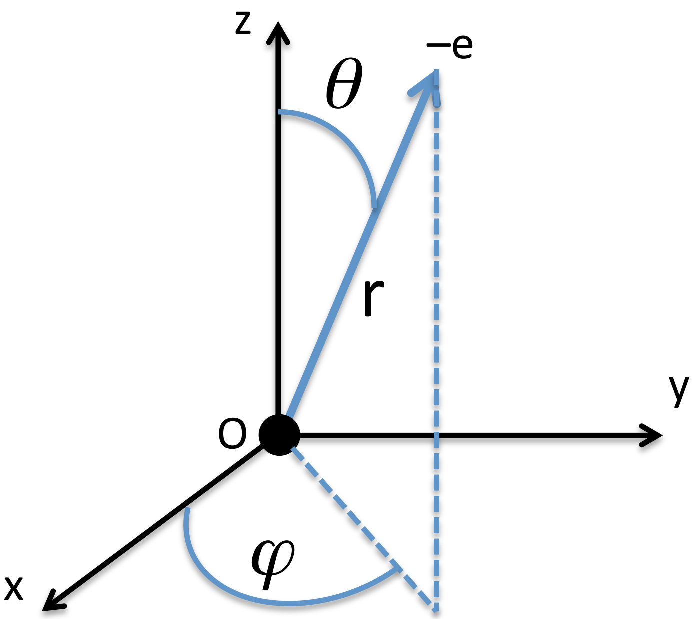
$$\hat{H} = -\sum_{\mu=1}^{2N}\frac{1}{2}\Delta_\mu - \sum_{\mu=1}^{2N}\sum_{A=1}^{P}\frac{Z_A}{r_\mu} + \sum_{\mu<\upsilon}^{2N}\sum_{\upsilon=1}^{2N}\frac{1}{r_{\mu\upsilon}} = \sum_{\mu=1}^{2N}\hat{h}_\mu + \sum_{\mu<\upsilon}^{2N}\sum_{\upsilon=1}^{2N}\frac{1}{r_{\mu\upsilon}}$$

$$\mathbf{r} = \{r, \theta, \varphi\}$$

$$d\mathbf{r} = dV = r^2 \sin\theta \, dr \, d\theta \, d\varphi$$

Single determinant wavefunction

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



Spin-orbitals

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

Spin function α or β

Molecular orbital

HF: search for the best *variational* wavefunction

THE HARTREE-FOCK-ROOTHAAN METHOD

Variational principle

$$\langle \mathrm{E} \rangle = \int \Psi \hat{\mathrm{H}} \Psi \, \mathrm{d}\mathbf{r} \geq \mathrm{E}_{\mathrm{exact}}$$

1. Introduction of variational parameters $\Psi \rightarrow \Psi(\alpha_1 \ldots \alpha_M)$

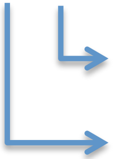
2. Optimization of the parameters

$$\frac{\partial \langle \mathrm{E} \rangle}{\partial \alpha_i} = 0 \quad \forall\, \mathrm{i}$$

Minimization of the total energy

Linear Combination of Atomic Orbitals (Roothaan)

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



Basis set of known atomic functions

Expansion coefficients = ***variational parameters***

HF: search for the best *orbitals*

THE HARTREE-FOCK-ROOTHAAN METHOD

Total energy

$$\langle E \rangle = \int \Psi \hat{H} \Psi \, d\mathbf{r}$$

$$\langle E \rangle = \sum_{i=1}^{N} 2I_i + \sum_{i=1}^{N} \sum_{j=1}^{N} \left(2J_{ij} - K_{ij} \right)$$

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

Sum over N doubly occupied molecular orbitals

HF integrals

$$I_i = \int \phi_i^*(\mathbf{r}_\mu) \hat{h} \phi_i(\mathbf{r}_\mu) d\mathbf{r}_\mu$$

1-electron integrals

$$J_{ij} = \int \frac{\phi_i^*(\mathbf{r}_\mu)\phi_i(\mathbf{r}_\mu)\phi_j^*(\mathbf{r}_\nu)\phi_j(\mathbf{r}_\nu)}{r_{\mu\nu}} d\mathbf{r}_\mu d\mathbf{r}_\nu$$

Coulomb integrals

$$K_{ij} = \int \frac{\phi_i^*(\mathbf{r}_\mu)\phi_i(\mathbf{r}_\nu)\phi_j^*(\mathbf{r}_\nu)\phi_j(\mathbf{r}_\mu)}{r_{\mu\nu}} d\mathbf{r}_\mu d\mathbf{r}_\nu$$

Exchange integrals

THE HARTREE-FOCK-ROOTHAAN METHOD

Roothaan expansion

$$\phi_i(\mathbf{r}) = \sum_{p=1}^{M} C_{pi}\, \underbrace{\chi_p(\mathbf{r})}_{\textit{Atomic basis functions}}$$

Integrals in the AO basis

$$I_i = \int \phi_i^*(\mathbf{r}_\mu)\hat{h}\phi_i(\mathbf{r}_\mu)d\mathbf{r}_\mu = \sum_{p=1}^{M}\sum_{q=1}^{M} C_{pi}C_{qi}h_{pq}$$

$$h_{pq} = \int \chi_p(\mathbf{r}_\mu)\hat{h}\chi_q(\mathbf{r}_\mu)d\mathbf{r}_\mu$$

⇨ **M^2 *integrals***

$$J_{ij} = \int \frac{\phi_i^*(\mathbf{r}_\mu)\phi_i(\mathbf{r}_\mu)\phi_j^*(\mathbf{r}_\nu)\phi_j(\mathbf{r}_\nu)}{r_{\mu\nu}}d\mathbf{r}_\mu d\mathbf{r}_\nu = \sum_{p=1}^{M}\sum_{q=1}^{M}\sum_{r=1}^{M}\sum_{s=1}^{M} C_{pi}C_{qi}C_{rj}C_{sj}\left(pq|rs\right)$$

$$\left(pq|rs\right) = \int \frac{\chi_p(\mathbf{r}_\mu)\chi_q(\mathbf{r}_\mu)\chi_r(\mathbf{r}_\nu)\chi_s(\mathbf{r}_\nu)}{r_{\mu\nu}}d\mathbf{r}_\mu\, d\mathbf{r}_\nu$$

⇨ **M^4 *integrals***

$$\left(pq|rs\right) = \left(qp|rs\right) = \left(pq|sr\right) = \left(qp|sr\right) = \left(rs|pq\right) = \left(sr|pq\right) = \left(rs|qp\right) = \left(sr|qp\right)$$

THE HARTREE-FOCK-ROOTHAAN METHOD

Energy minimization

$$\langle E \rangle = \sum_{i=1}^{N} 2I_i + \sum_{i=1}^{N}\sum_{j=1}^{N}\left(2J_{ij} - K_{ij}\right) \xrightarrow{\textit{Minimisation}} \hat{F}(\mathbf{r})\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

N Fock equations

Fock operator

$$\hat{F}(\mathbf{r}_\mu) = \hat{h}(\mathbf{r}_\mu) + \sum_{i=1}^{N}\left[2\hat{J}_i(\mathbf{r}_\mu) - \hat{K}_i(\mathbf{r}_\mu)\right]$$

1-electron Fock operator

Describes electron μ in the mean electrostatic field of the other electrons

$$\hat{J}_i(\mathbf{r}_\mu)\phi_j(\mathbf{r}_\mu) = \left(\int \frac{\phi_i^*(\mathbf{r}_\nu)\phi_i(\mathbf{r}_\nu)}{r_{\mu\nu}} dV_\nu\right)\phi_j(\mathbf{r}_\mu)$$

Coulomb operator

$$\hat{K}_i(\mathbf{r}_\mu)\phi_j(\mathbf{r}_\mu) = \left(\int \frac{\phi_i^*(\mathbf{r}_\nu)\phi_j(\mathbf{r}_\nu)}{r_{\mu\nu}} dV_\nu\right)\phi_i(\mathbf{r}_\mu)$$

Exchange operator

The Fock operator depends on its own solutions $\phi(\mathrm{r})$

Iterative process until self-consistence

THE HARTREE-FOCK-ROOTHAAN METHOD

Matrix form of the Fock equations

$$\left.\begin{aligned}&\hat{\mathrm{F}}(\mathbf{r})\phi_i(\mathbf{r})=\varepsilon_i\phi_i(\mathbf{r})\\ &\textit{with}\;\;\phi_i(\mathbf{r})=\sum_{p=1}^{M}C_{pi}\chi_p(\mathbf{r})\end{aligned}\right\}\xrightarrow{\textit{Method of Linear Variations}}\mathbf{FC}=\varepsilon\mathbf{SC}$$

W. Ritz, J. Reine Angew. Math. **135**, 1 (1909).
See A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*, McGraw-Hill, New York, 1989.

Overlap matrix S

Dimension M x M

Elements $S_{pq}=\int\chi_p^*(\mathbf{r}_\nu)\chi_q(\mathbf{r}_\nu)d\mathbf{r}_\nu$

Fock matrix F

Dimension M x M

Elements $F_{pq}=\int\chi_p^*(\mathbf{r}_\nu)\hat{\mathrm{F}}(\mathbf{r}_\nu)\chi_q(\mathbf{r}_\nu)d\mathbf{r}_\nu=h_{pq}+\sum_r\sum_s D_{rs}\left[\left(pq|rs\right)-\left(ps|rq\right)\right]$

First-order density matrix D

Dimension M x M

Elements $D_{pq}=\sum_i n_iC_{pi}C_{qi}$

THE HARTREE-FOCK-ROOTHAAN METHOD

General solution of the HF matrix equations for non orthogonal basis sets

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

One seeks to obtain an eigenvalue equation of the form

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\varepsilon$$

Löwdin orthogonalization

P. O. Löwdin *J. Chem. Phys*. **1950**, *18*, 365

$$\mathbf{F} \times \mathbf{S}^{-1/2} \times \mathbf{S}^{1/2} \times \mathbf{C} = \mathbf{S}^{1/2} \times \mathbf{S}^{1/2}\mathbf{C}\varepsilon$$

By multiplying by $S^{-1/2}$ on each side

$$\underbrace{\mathbf{S}^{-1/2} \times \mathbf{F} \times \mathbf{S}^{-1/2}}_{\mathbf{F}'} \times \underbrace{\mathbf{S}^{1/2} \times \mathbf{C}}_{\mathbf{C}'} = \underbrace{\mathbf{S}^{1/2}\mathbf{C}}_{\mathbf{C}'}\varepsilon$$

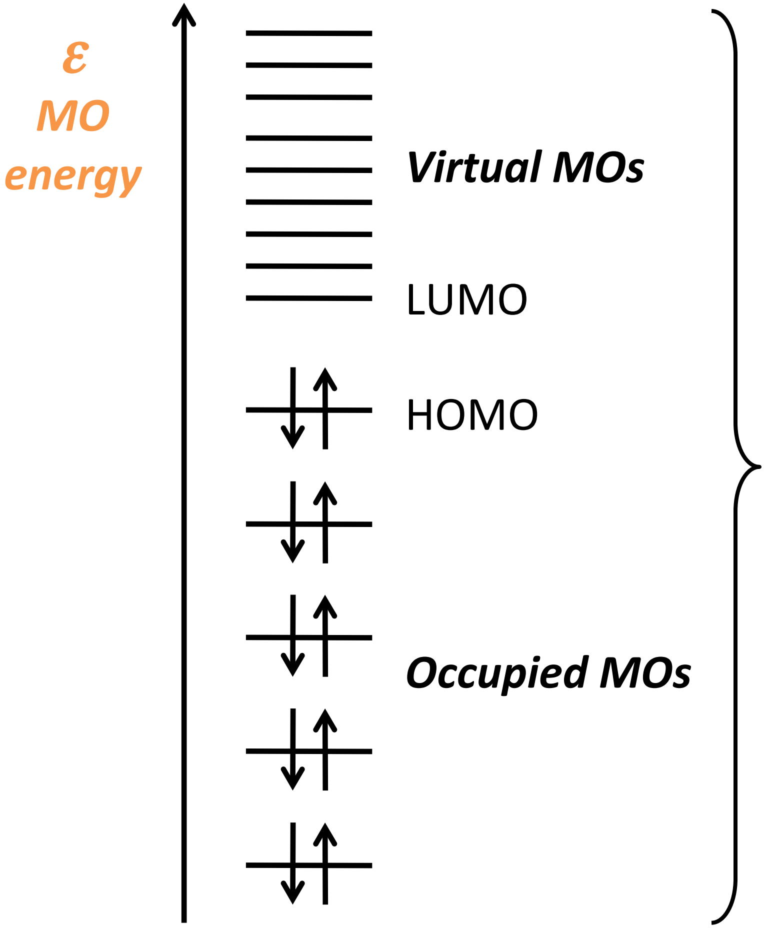
$$\Rightarrow \mathbf{F}'\mathbf{C}' = \mathbf{C}'\varepsilon$$

$\mathbf{C}'$ = *eigenvectors of* $\mathbf{F}'$

$$\mathbf{C} = \mathbf{S}^{-1/2}\mathbf{C}'$$

THE HARTREE-FOCK-ROOTHAAN METHOD

Solution of the HF equations



ε
MO
energy

Virtual MOs

LUMO

HOMO

Occupied MOs

M basis functions
$\Rightarrow$ *M MOs*

Koopmans theorem: IP ≈ – ε

ELECTRON DENSITY AND RELATED PROPERTIES

Total electron density

$$\rho(\mathbf{r}) = \sum_{i=1}^{M} n_i \phi_i^*(\mathbf{r})\phi_i(\mathbf{r})$$

$$\int_{\text{space}} \rho(\mathbf{r})d\mathbf{r} = \sum_{i=1}^{M} n_i \int_{\text{space}} \phi_i^*(\mathbf{r})\phi_i(\mathbf{r})d\mathbf{r} = \sum_{i=1}^{M} n_i = N$$

Mulliken AO populations

$$\rho(\mathbf{r}) = \sum_{i=1}^{M} n_i \sum_{p=1}^{M}\sum_{q=1}^{M} C_{pi}C_{qi}\chi_p(\mathbf{r})\chi_q(\mathbf{r}) = \sum_{p=1}^{M}\sum_{q=1}^{M} D_{pq}\chi_p(\mathbf{r})\chi_q(\mathbf{r}) \quad \textit{with} \quad D_{pq} = \sum_{i=1}^{M} n_i C_{pi}C_{qi}$$

$$\int_{\text{space}} \rho(\mathbf{r})d\mathbf{r} = N = \sum_{p=1}^{M}\sum_{q=1}^{M} D_{pq}S_{pq} = \sum_{p=1}^{M}\left(D_{pp} + \sum_{q\neq p}^{M} D_{pq}S_{pq}\right) = \sum_{p=1}^{M}\left(Q_p\right)$$

$$Q_p = D_{pp} + \sum_{q\neq p}^{M} D_{pq}S_{pq}$$ ***Electron population in χ_p***

Mulliken atomic charges

$$n_A = \sum_{p\in A} Q_p \quad \Rightarrow \quad \delta_A = Z_A - n_A$$ ***Net charge on atom A***

ELECTRON DENSITY AND RELATED PROPERTIES

Dipole moment

$$\vec{\mu} = \int \Psi \hat{\vec{\mu}} \Psi d\mathbf{r} = \int \Psi \left(\hat{\vec{\mu}}_{\mathrm{elec}} + \hat{\vec{\mu}}_{\mathrm{nuc}} \right) \Psi d\mathbf{r}$$

with $\hat{\vec{\mu}}_{\mathrm{elec}} = \sum_{i} -e\mathbf{r}_i$ *and* $\hat{\vec{\mu}}_{\mathrm{nuc}} = \sum_{A} eZ_A \vec{R}_A$

$$\vec{\mu}_{\mathrm{nuc}} = \sum_{A} \int \phi_i^*(\mathbf{r})\; eZ_A \vec{R}_A \phi_i^*(\mathbf{r}) d\mathbf{r} = \sum_{A} eZ_A \vec{R}_A$$

$$\vec{\mu}_{\mathrm{elec}} = -2e \sum_{i=1}^{\mathrm{occ}} \int \phi_i^*(\mathbf{r})\; \mathbf{r}\; \phi_i^*(\mathbf{r}) d\mathbf{r}$$

$$\vec{\mu}_{\mathrm{elec}} = -2e \sum_{i=1}^{\mathrm{occ}} C_{pi} C_{qi} \sum_{p=1}^{M} \sum_{q=1}^{M} \int \chi_p(\mathbf{r})\; \mathbf{r}\; \chi_q(\mathbf{r}) d\mathbf{r}$$

$$= -e \sum_{p=1}^{M} \sum_{q=1}^{M} D_{pq} \underbrace{\int \chi_p(\mathbf{r})\; \mathbf{r}\; \chi_q(\mathbf{r}) d\mathbf{r}}_{\textbf{\textit{Dipole integrals}}}$$

VARIOUS TYPES OF BASIS SETS

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

Atomic basis functions

Slater-type orbitals (STO)

$$\chi^{STO}_{\alpha,n,l,m}(r,\theta,\varphi) = NY_{l,m}(\theta,\varphi)r^{n-1}e^{-\alpha r}$$

STO are not efficient for evaluating the 3- and 4-center integrals

Gaussian-type orbitals (GTO)

$$\chi^{GTO}_{\alpha,n,l,m}(r,\theta,\varphi) = NY_{l,m}(\theta,\varphi)r^{2n-2-l}e^{-\alpha r^2}$$

The use of GTO ensures analytical solutions for all integrals appearing in the HF method

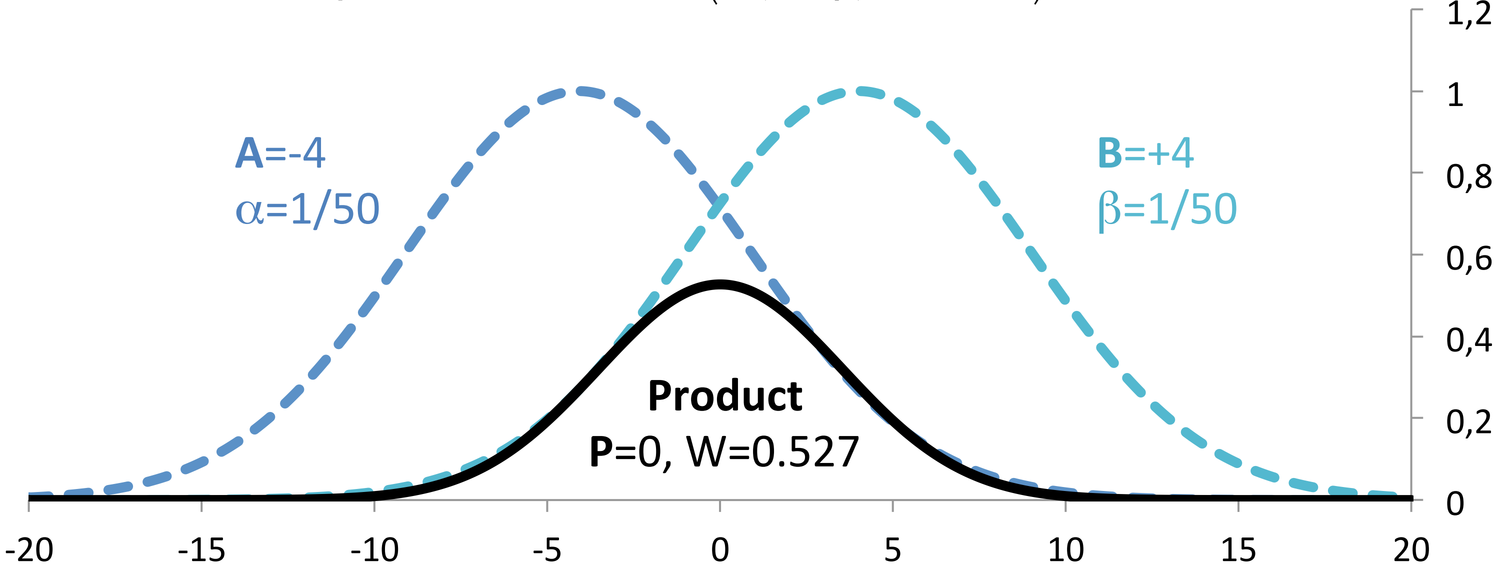
PRACTICAL INTEREST OF GAUSSIAN FUNCTIONS

Product of 2 Gaussian functions

The product of two Gaussian functions centered on A and B respectively is a Gaussian centered on the barycenter P of A and B

$$\exp\left(-\alpha(\mathbf{r}-\mathbf{A})^2\right)\times\exp\left(-\beta(\mathbf{r}-\mathbf{B})^2\right)=\mathrm{W}\exp\left(-(\alpha+\beta)(\mathbf{r}-\mathbf{P})^2\right)$$

$$\text{with}\quad \mathbf{P}=\frac{\alpha\mathbf{A}+\beta\mathbf{B}}{\alpha+\beta}\qquad\text{and}\quad \mathrm{W}=\exp\left(-\frac{\alpha\beta}{(\alpha+\beta)}\left(\mathbf{A}-\mathbf{B}\right)^2\right)$$



GAUSSIAN VS. SLATER FUNCTIONS: EXAMPLE OF HELIUM

He atom using a single STO

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}} 1s(\mathbf{r}_1)1s(\mathbf{r}_2)\left[\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)\right]$$

What is the best (variational) STO to describe the ground state of He?

$$1s(\mathbf{r}) = \frac{\alpha^{3/2}}{\pi^{1/2}}\exp(-\alpha\ r) \quad \Leftarrow \quad \alpha\,?$$

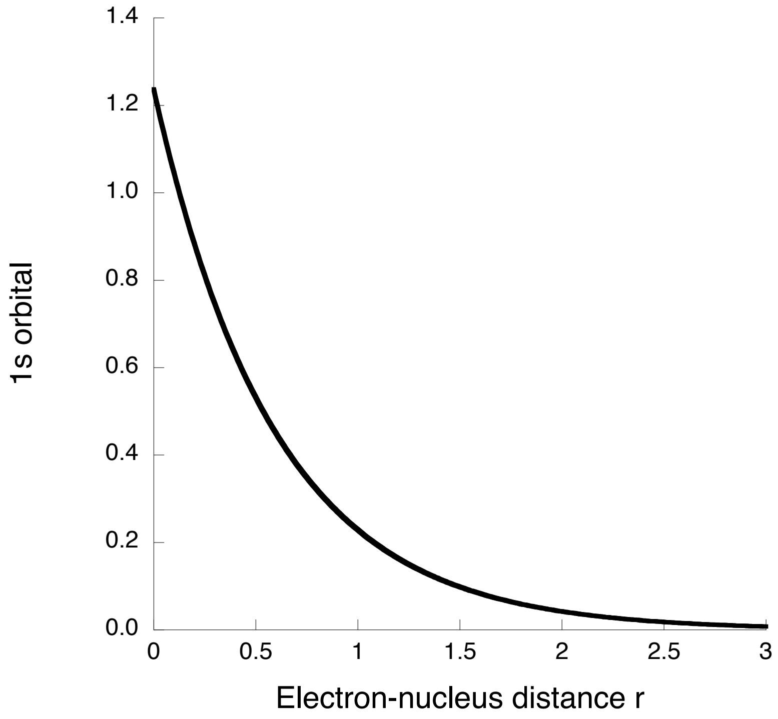
Total energy

$$\langle E\rangle = 2I + J = 2\underbrace{\int 1s(\mathbf{r})\hat{h}1s(\mathbf{r})d\mathbf{r}}_{\alpha^2/2-2\alpha} + \underbrace{(1s1s|1s1s)}_{5\alpha/8}$$

$$\langle E\rangle = \alpha^2 - \frac{27}{8}\alpha$$

$$\frac{d\langle E\rangle}{d\alpha} = 0 \Rightarrow \alpha = \frac{27}{16} = 1.6875$$

$$\langle E\rangle = -2.84766 \text{ a.u.}$$



GAUSSIAN VS. SLATER FUNCTIONS: EXAMPLE OF HELIUM

He atom using a single GTO

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{2}}1s(\mathbf{r}_1)1s(\mathbf{r}_2)\left[\alpha(\sigma_1)\beta(\sigma_2)-\beta(\sigma_1)\alpha(\sigma_2)\right]$$

What is the best (variational) GTO to describe the ground state of He?

$$1s(\mathbf{r})=\left(\frac{2\alpha}{\pi}\right)^{3/4}\exp(-\alpha r^2)\quad\Leftarrow\quad\alpha\,?$$

Total energy

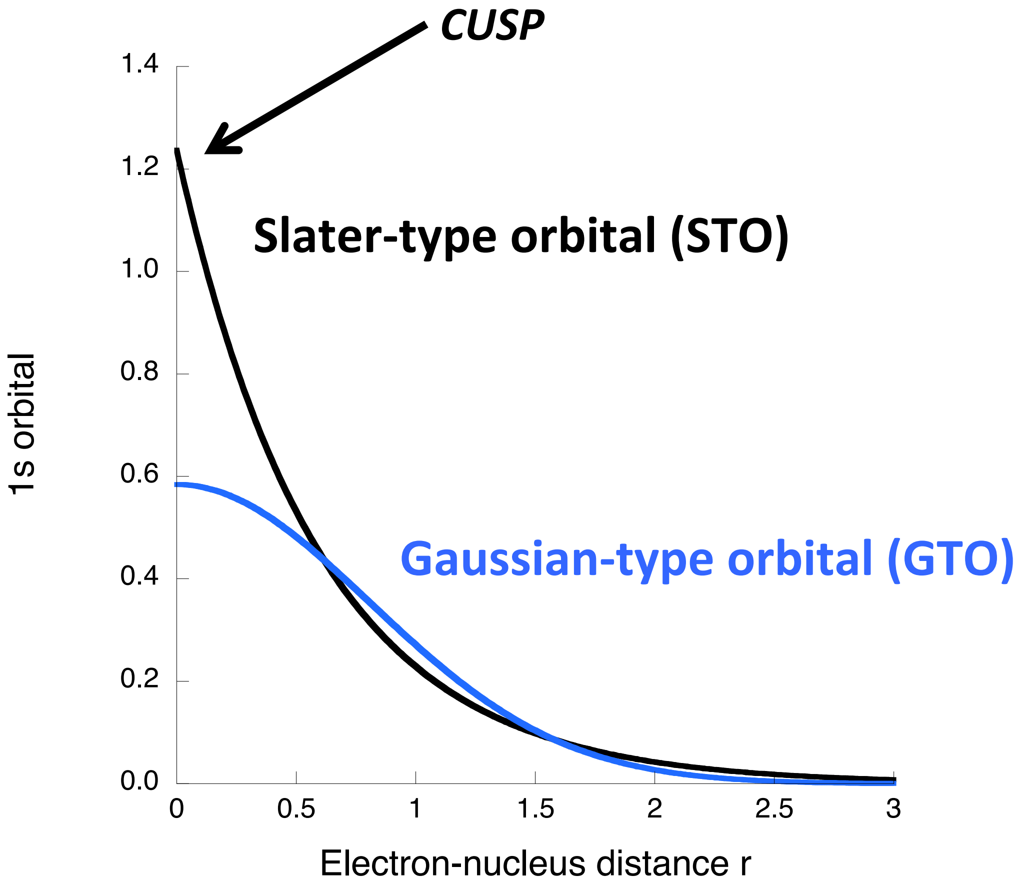
$$\langle E\rangle=2I+J=2\int 1s(\mathbf{r})\hat{h}1s(\mathbf{r})d\mathbf{r}+\left(1s1s|1s1s\right)$$

$$\langle E\rangle=3\alpha-\left[8-\sqrt{2}\right]\sqrt{\frac{2\alpha}{\pi}}$$

$$\frac{d\langle E\rangle}{d\alpha}=0\Rightarrow\alpha=0.766996$$

$\langle E\rangle=-2.300987\text{ a.u.}$ ⇒ $\langle E\rangle_{\mathrm{GTO}}>>\langle E\rangle_{\mathrm{STO}}$ ***GTO much less efficient than STO!***

GAUSSIAN VS. SLATER FUNCTIONS: EXAMPLE OF HELIUM



CONTRACTED GAUSSIAN BASIS SETS

Use of *contracted* Gaussian functions

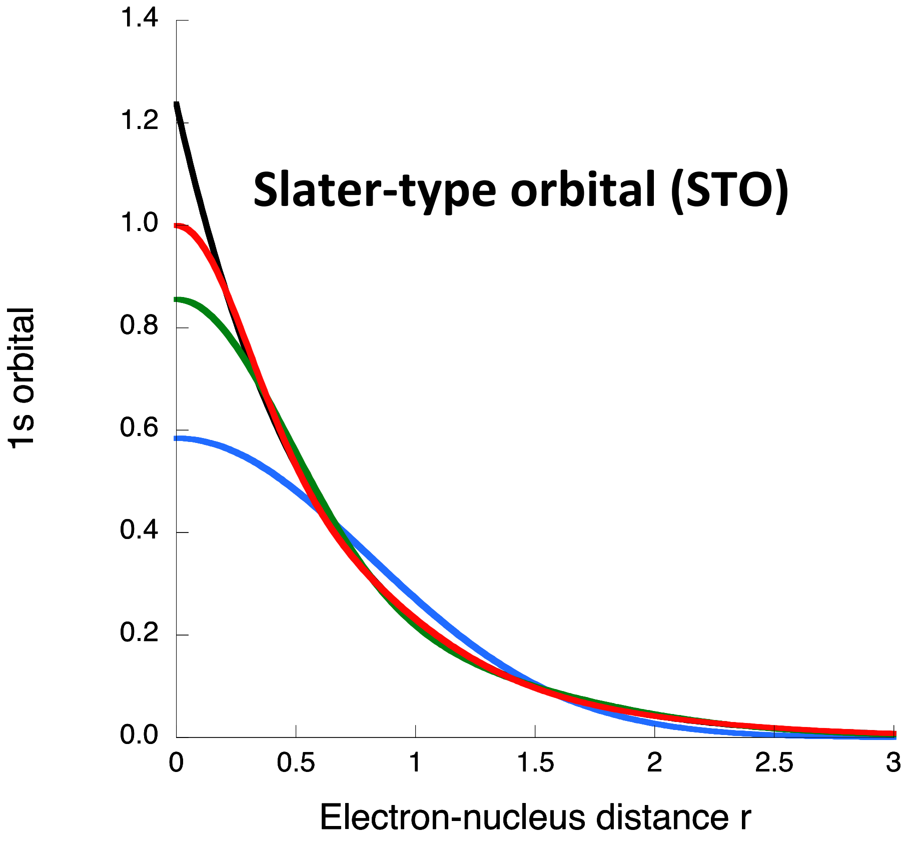
$$1s(\mathbf{r}) = \sum_{i=1}^{X} a_i \chi_i^G \qquad \chi_i^G = \left(\frac{2\alpha_i}{\pi}\right)^{3/4} \exp(-\alpha_i r^2)$$

STO-2G

Slater exponents α	*Contraction coefficients*
0.2432879285D+01	0.4301284983D+00
0.4330512863D+00	0.6789135305D+00

STO-3G

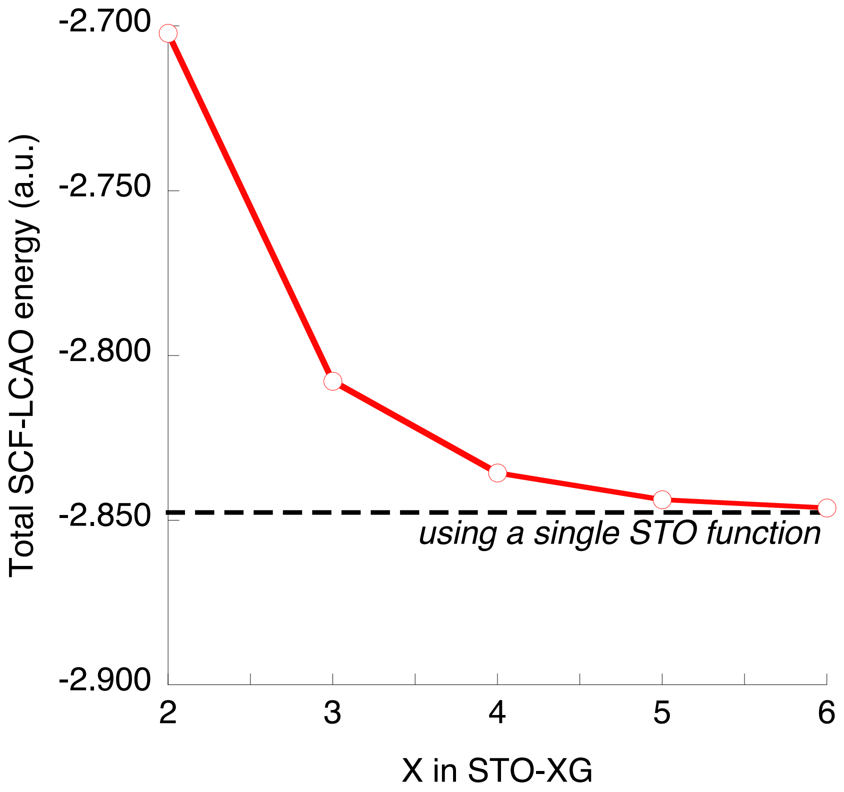
Slater exponents α	*Contraction coefficients*
0.6362421394D+01	0.1543289673D+00
0.1158922999D+01	0.5353281423D+00
0.3136497915D+00	0.4446345422D+00



CONTRACTED GAUSSIAN BASIS SETS

Use of *contracted* Gaussian functions

Influence of the number of Gaussian contractions on the total energy



PRACTICAL EXERCISE

SCF-LCAO CALCULATION OF THE GROUND STATE OF THE HELIUM ATOM

Connect to the workstation bacon with your login and password

```
ssh -Y tp00@bacon.ism.u-bordeaux1.fr
```

Create a new directory named TP1

```
mkdir TP1
```

Go to the directory TP1

```
cd TP1
```

Copy the input file (data) used by the helium code

```
cp /home/tp/Helium/Test/data .
```

Modify the data file as you need and save

```
kwrite data
```

Run the helium calculation

```
/home/tp/Helium/Src/helium < data > results
```

Open the result file (results) and note the relevant information

```
kwrite results
```

LOGIN AND PASSWORDS

CHOOSE YOUR LOGIN AND PASSWORD IN THE LIST

tp00 --> E9gLwpeP
tp01 --> wclzHhR7
tp02 --> Ookl9DMz
tp03 --> ypCp7Faf
tp04 --> HVg09F7X
tp05 --> NH8l0c6q
tp06 --> FgMy9xkx
tp07 --> YP5IeeTc
tp08 --> iYEWXZB4
tp09 --> I7DGJSg5
tp10 --> z4PiqfQy