



Preliminaries

Material:

- Book: J. Kohanoff, *Electronic Structure Calculations for Solids and Molecules: Theory and Computational Methods*, Cambridge.
- G.A. de Wijs, Notes on “Density Functional Theory” (on theochem site).
- These lecture notes (on theochem site: <https://www.theochem.ru.nl>).

Additional material:

- P.E.S. Wormer & A. van der Avoird, Dictaat Moleculaire Quantummechanica, Nijmegen (on theochem site).
- G.C. Groenenboom, Notes on “Undetermined Multiplier Method of Lagrange” and “Lecture Notes on Group Theory” (on theochem site).

Planning:

- 7 hoorcolleges: Hartree-Fock (3), Density Functional Theory & extensions (3), intro to post-HF (1).
- 7 werkcolleges: with exercises.
- 4 practica: to learn to use quantum chemical software to solve simple problems. Returns in exam.
Compulsory assignments. Practica are in weeks 4, 5, 6, 7.



Preliminaries

Examination:

- written exam: Counts for 3/4. Calculators without formula memory allowed. Resit.
- written report: On (final) assignments of computer training. Counts for 1/4. Practical sessions with tutor(s) only planned in Q2.



Towards Hartree-Fock: The Hamiltonian

The Hamiltonian for N electrons and m nuclei with Coulomb interactions in atomic (Hartree) units (fixed nuclei):

$$\hat{H} = \sum_{i=1}^N \underbrace{\left\{ -\frac{1}{2} \nabla_i^2 + \sum_{\nu=1}^m \frac{-Z_\nu}{|\mathbf{r}_i - \mathbf{R}_\nu|} \right\}}_{\hat{h}(i)} + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \underbrace{\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{g}(i,j)} + \frac{1}{2} \sum_{\nu=1}^m \sum_{\mu \neq \nu}^m \frac{Z_\nu Z_\mu}{|\mathbf{R}_\mu - \mathbf{R}_\nu|}$$

Notation: vector are boldface, e.g., \mathbf{r}_i and \mathbf{R}_ν .

- $\hat{h}(i)$: One-electron operator, $\sum_i \hat{h}(i)$: core Hamiltonian,
 - kinetic energy: $-\frac{1}{2} \begin{pmatrix} \partial/\partial x_i \\ \partial/\partial y_i \\ \partial/\partial z_i \end{pmatrix} \cdot \begin{pmatrix} \partial/\partial x_i \\ \partial/\partial y_i \\ \partial/\partial z_i \end{pmatrix} = -\frac{1}{2} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right)$
 - attraction between electron i and m nuclei with charges Z_ν .
- $\hat{g}(i,j)$: Electron-electron repulsion operator. Note the prefactor 1/2 (each pair is counted twice!).
- **Nuclear repulsion.**

In Born-Oppenheimer approximation ("fast & light" electrons decouple from "heavy & slow" nuclei) consider this as constant. Nuclei then move on potential energy surface given by ground state of \hat{H} .



Towards Hartree-Fock: Wave function & Pauli

Each electron is described by spatial and spin coordinates:

- the spatial part: a function of $\mathbf{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$, e.g. " $\phi(\mathbf{r})$ " or " $\phi(\mathbf{r}_i)$ ".
- the spin part: the two eigenfunctions of \hat{s}_z are a complete set, we call them $|\alpha\rangle$ and $|\beta\rangle$.
- the most general mixture, for a one-electron spin-orbital:

$$\psi(\mathbf{r}, s) = \phi_\alpha(\mathbf{r})\alpha(s) + \phi_\beta(\mathbf{r})\beta(s)$$

[we will use only pure spin orbitals in Hartree-Fock (HF)]

Pauli (loosely formulated):

*The wave function for Bosons (Fermions) is symmetric (anti-symmetric) for particle interchange.
Hence the probability distributions are indistinguishable upon particle exchange.*

Electrons are Fermions, so: $\Psi(1, \dots, i, \dots, j, \dots, N) = -\Psi(1, \dots, j, \dots, i, \dots, N)$.



Towards Hartree-Fock: Hartree

Assume each electron feels average(mean) field of the others:

$$\hat{h}_{(i)}^{\text{eff}}(\mathbf{r}) = \hat{h}_{(i)}(\mathbf{r}) + V_{(i)}^{\text{eff}}(\mathbf{r}) = -\frac{1}{2}\nabla_i^2 + \sum_{\nu=1}^m \frac{-Z_{\nu}}{|\mathbf{r}_i - \mathbf{R}_{\nu}|} + V_{(i)}^{\text{eff}}(\mathbf{r}) \quad (1)$$

You can solve:

$$\hat{h}_{(i)}^{\text{eff}}(\mathbf{r})\psi_{(i)}^n(\mathbf{r}) = \epsilon_{(i)}^n\psi_{(i)}^n(\mathbf{r})$$

Now you put an up and a down spin in each of the N lowest levels... well, not really... we get different, non-orthogonal orbitals for each new integer value of i .

Next the problem has to bite in its tail: each electron i yields a charge density $|\psi_i(\mathbf{r})|^2$. In total:

$$\rho_{(\text{except } i)}(\mathbf{r}) = \sum_{j \neq (i)}^N \rho_j(\mathbf{r}) = \sum_{j \neq (i)}^N |\psi_j(\mathbf{r})|^2 \quad \text{so that} \quad V_{(i)}^{\text{eff}}(\mathbf{r}) = \sum_{j \neq (i)}^N \int \frac{|\psi_j(\tilde{\mathbf{r}})|^2}{|\mathbf{r} - \tilde{\mathbf{r}}|} d\tilde{\mathbf{r}}$$

Now we return to (1) and keep repeating until the orbitals do not change anymore: we have attained the "self-consistent field" $V_{(i)}(\mathbf{r})$.

Better: self-consistent field theory satisfying Pauli by construction, **Hartree-Fock**.



Towards Hartree-Fock: The Plan

Minimize (Rayleigh-Ritz):

$$E = \min \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

In words:

Change the wave function $|\Psi\rangle$ until the expectation value of the energy is minimal.

Alternatively:

$$E = \min \langle \Psi | H | \Psi \rangle \quad \text{while} \quad \langle \Psi | \Psi \rangle = 1$$

In HF we write a specific Ansatz for $|\Psi\rangle$: a *Slater determinant* of molecular orbitals (here denoted ψ_i or ϕ_i). This is an *approximation*.

To get a useful method (on computer) we expand the molecular orbitals in a basis of (in chemistry usually “atomic”) orbitals. Carrying out the constrained minimization yields the Roothaan equations: these constitute a *self-consistent theory* that has to be solved *self-consistently*.

HF yields an exact description of *exchange* (Pauli is “happy”) but lacks any *electron correlation*.



Towards Hartree-Fock: Permutations

We need to consider permutations, as they are needed to describe the anti-symmetry of the wave function. Consider the example of Wormer & van der Avoird ($N = 5$). It is:

$$1 \rightarrow 3 \rightarrow 2 \rightarrow 5 \rightarrow 1 \text{ and } 4 \rightarrow 4.$$

It is one loop, that can be denoted \hat{P}_{1325} . You can see that it can be considered a series of pair permutations (reading from right to left) and moving 5 along the “chain”:

$$\hat{P}_{1325} = \hat{P}_{13}\hat{P}_{23}\hat{P}_{25}$$

Any permutation can be written as a product of pair permutations. The number of pair permutations is not unique. The **parity**, i.e. an **odd** or an **even** number of permutations, is unique.

Important properties:

$$\hat{P}^{-1} = \hat{P}^\dagger \text{ and } \hat{P}_{ij}^{-1} = \hat{P}_{ij}^\dagger = \hat{P}_{ij} = \hat{P}_{ji}$$



Towards Hartree-Fock: Permutations

Help page:

Route 1:

$$1 \rightarrow 3 \rightarrow 2 \rightarrow 5 \rightarrow 1 \text{ and } 4 \rightarrow 4.$$

Route 2:

$$\hat{P}_{1325} = \hat{P}_{13}\hat{P}_{32}\hat{P}_{25} = \hat{P}_{13}\hat{P}_{23}\hat{P}_{25}$$

	1	2	3	4	5
	A	B	C	D	E
\hat{P}_{1325}	E	C	A	D	B
	A	B	C	D	E
\hat{P}_{25}	A	E	C	D	B
\hat{P}_{23}	A	C	E	D	B
\hat{P}_{13}	E	C	A	D	B

Adjoint operator:

$$\langle O\phi|\psi\rangle = \langle\phi|O^\dagger\psi\rangle \quad , \quad \langle O^\dagger\phi|\psi\rangle = \langle\phi|O\psi\rangle$$



Towards Hartree-Fock: Anti-symmetrizer

$$\hat{A} = \frac{1}{N!} \sum_{P \in S_N} (-1)^p \hat{P}$$

The sum is over all \hat{P} that are part of the permutation group S_N . The group has $N!$ elements. p is the parity of \hat{P} .

Properties:

$$\begin{aligned} \text{(i)} : \hat{A}^\dagger &= \hat{A} \quad , \quad \text{(ii)} : \hat{P}\hat{A} = \hat{A}\hat{P} = (-1)^p \hat{A} \\ \text{(iii)} : \hat{A}^2 &= \hat{A} \quad , \quad \text{(iv)} : [\hat{A}, \hat{H}] = 0 \end{aligned}$$

Proof of (ii):

$$\hat{P}\hat{A} = \frac{1}{N!} \sum_Q (-1)^q \hat{P}\hat{Q} = \frac{1}{N!} \sum_Q (-1)^{r-p} \hat{R} = (-1)^p \frac{1}{N!} \sum_Q (-1)^r \hat{R} = (-1)^p \hat{A}$$

\hat{A} makes an arbitrary function (ϕ) an antisymmetric function ($\psi = \hat{A}\phi$):

$$\begin{aligned} P_{ij}\psi(1, \dots, N) &= P_{ij}\hat{A}\phi(1, \dots, N) = (-1)^1 \hat{A}\phi(1, \dots, N) = -\psi(1, \dots, N) \\ \text{so: } \psi(1, \dots, j, \dots, i, \dots, N) &= -\psi(1, \dots, i, \dots, j, \dots, N) \quad \text{Pauli!} \end{aligned}$$

Towards Hartree-Fock: Slater determinant

In Hartree-Fock one approximates the wave function as a single Slater determinant of single-electron (molecular) *spin*-orbitals:

$$\Phi(1, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \dots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \dots & \psi_N(2) \\ \vdots & \vdots & & \vdots \\ \psi_1(N) & \psi_2(N) & \dots & \psi_N(N) \end{vmatrix} = \sqrt{N!} \hat{A} \psi_1(1) \psi_2(2) \dots \psi_N(N) = \sqrt{N!} \hat{A} \prod_i^N \psi_i(i)$$

where our *molecular* orbitals are orthonormal (space & spin degrees of freedom):

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

Check normalisation of the wave function:

$$\begin{aligned} \langle \Phi | \Phi \rangle &= N! \langle \hat{A} \psi_1(1) \dots \psi_N(N) | \hat{A} | \psi_1(1) \dots \psi_N(N) \rangle \\ &= N! \langle \psi_1(1) \dots \psi_N(N) | \hat{A}^\dagger \hat{A} | \psi_1(1) \dots \psi_N(N) \rangle \\ &= \sum_{P \in S_N} (-1)^P \langle \psi_1(1) \dots \psi_N(N) | P \psi_1(1) \dots \psi_N(N) \rangle = 1 \end{aligned}$$



Towards Hartree-Fock: Slater determinant

Are both expressions identical?

$$\Phi(1, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \dots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \dots & \psi_N(2) \\ \vdots & \vdots & & \vdots \\ \psi_1(N) & \psi_2(N) & \dots & \psi_N(N) \end{vmatrix}$$
$$\stackrel{??}{=} \frac{\sqrt{N!}}{N!} \sum_{P \in S_N} (-1)^P \hat{P} \psi_1(1) \psi_2(2) \dots \psi_N(N)$$

- The prefactors are okay...
- Expand the determinant row-by-row. The first row puts particle 1 in all N possible orbitals. The second row puts particle 2 in the remaining $N - 1$ orbitals, etc., yielding all $N!$ permutations.
- Swapping two particles is swapping two rows in the determinant which yields a minus, hence Pauli is happy. All terms in the sum are connected by a series of pair permutations (swaps) and Pauli has swaps change sign. Hence the signs in the sum are unique, and identical in both expressions.



Towards Hartree-Fock: the one-electron operator

Start similar as with normalisation, but we also use $[\hat{A}, \sum_i \hat{h}(i)] = 0$.

$$\begin{aligned}\langle \Phi | \sum_i \hat{h}(i) | \Phi \rangle &= \sum_{P \in S_N} (-1)^P \langle \psi_1(1) \dots \psi_N(N) | \sum_i \hat{h}(i) | P \psi_1(1) \dots \psi_N(N) \rangle \\ &= \sum_i \sum_{P \in S_N} (-1)^P \langle \psi_1(1) | \psi_{1'}(1) \rangle \dots \langle \psi_i(i) | \hat{h}(i) | \psi_{i'}(i) \rangle \dots \langle \psi_N(N) | \psi_{N'}(N) \rangle\end{aligned}$$

Here i' labels the orbital in which particle i sits after permutation P .

For a non-vanishing contribution, $1' = 1, 2' = 2, \dots, (i-1)' = i-1, (i+1)' = i+1, \dots, N' = N$, hence, $i' = i$ and $p = 0$.

$$\langle \Phi | \sum_i \hat{h}(i) | \Phi \rangle = \sum_i \langle \psi_i(i) | \hat{h}(i) | \psi_i(i) \rangle = \sum_i \langle \psi_i(1) | \hat{h}(1) | \psi_i(1) \rangle$$

The integration variable is a dummy and can be relabeled.



Towards Hartree-Fock: the one-electron operator

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$$\begin{aligned}\langle \Phi | \sum_i^N \hat{h}(i) | \Phi \rangle &= N! \langle \hat{A} \psi_1(1) \dots \psi_N(N) | \sum_i^N \hat{h}(i) | \hat{A} \psi_1(1) \dots \psi_N(N) \rangle \\ &= N! \langle \psi_1(1) \dots \psi_N(N) | \hat{A}^\dagger \sum_i^N \hat{h}(i) | \hat{A} \psi_1(1) \dots \psi_N(N) \rangle \\ &= N! \langle \psi_1(1) \dots \psi_N(N) | \hat{A} \sum_i^N \hat{h}(i) | \hat{A} \psi_1(1) \dots \psi_N(N) \rangle \\ &= N! \langle \psi_1(1) \dots \psi_N(N) | \sum_i^N \hat{h}(i) | \hat{A} \hat{A} \psi_1(1) \dots \psi_N(N) \rangle \\ &= N! \langle \psi_1(1) \dots \psi_N(N) | \sum_i^N \hat{h}(i) | \hat{A} \psi_1(1) \dots \psi_N(N) \rangle\end{aligned}$$

Properties:

$$\begin{aligned}\text{(i)} : \hat{A}^\dagger &= \hat{A} \quad , \quad \text{(ii)} : \hat{P} \hat{A} = \hat{A} \hat{P} = (-1)^p \hat{A} \\ \text{(iii)} : \hat{A}^2 &= \hat{A} \quad , \quad \text{(iv)} : [\hat{A}, \hat{H}] = 0\end{aligned}$$



Towards Hartree-Fock: the two-electron operator

$$\begin{aligned}\langle \Phi | \frac{1}{2} \sum_i^N \sum_{j \neq i}^N \hat{g}(i, j) | \Phi \rangle &= \frac{1}{2} \sum_{P \in S_N} (-1)^P \langle \psi_1(1) \dots \psi_N(N) | \sum_i^N \sum_{j \neq i}^N \hat{g}(i, j) | P \psi_1(1) \dots \psi_N(N) \rangle \\&= \frac{1}{2} \sum_i^N \sum_{j \neq i}^N \sum_{P \in S_N} (-1)^P \langle \psi_1(1) | \psi_{1'}(1) \rangle \dots \langle \psi_i(i) \psi_j(j) | \hat{g}(i, j) | \psi_{i'}(i) \psi_{j'}(j) \rangle \dots \langle \psi_N(N) | \psi_{N'}(N) \rangle \\&= \frac{1}{2} \sum_i^N \sum_{j \neq i}^N \langle \psi_i(i) \psi_j(j) | \hat{g}(i, j) | \psi_i(i) \psi_j(j) \rangle - \langle \psi_i(i) \psi_j(j) | \hat{g}(i, j) | \psi_j(i) \psi_i(j) \rangle \\&= \frac{1}{2} \sum_i^N \sum_j^N \langle \psi_i(1) \psi_j(2) | \hat{g}(1, 2) | \psi_i(1) \psi_j(2) \rangle - \langle \psi_i(1) \psi_j(2) | \hat{g}(1, 2) | \psi_j(1) \psi_i(2) \rangle \\&= \frac{1}{2} \sum_i^N \sum_j^N J_{ij} - K_{ij} \quad J_{ij}: \text{Coulomb integrals, } K_{ij}: \text{exchange integrals}\end{aligned}$$

Note: The added self-terms for $i = j$ cancel. Exchange integral has minus.



Towards Hartree-Fock: the two-electron operator

Make integrals explicit ($d\tau = d\mathbf{r}ds$):

$$J_{ij} = \langle \psi_i(1)\psi_j(2) | \hat{g}(1,2) | \psi_i(1)\psi_j(2) \rangle = \iint \frac{\overbrace{\psi_i^*(1)\psi_i(1)}^{|\psi_i(1)|^2} \overbrace{\psi_j^*(2)\psi_j(2)}^{|\psi_j(2)|^2}}{|\mathbf{r}_1 - \mathbf{r}_2|} d\tau_1 d\tau_2$$

This is the energy of a charge density $\rho_i(1) = |\psi_i(1)|^2$ (if spin were integrated out, here for a *single* spin channel) in the potential due to charge density $\rho_j(2)$.

$$K_{ij} = \langle \psi_i(1)\psi_j(2) | \hat{g}(1,2) | \psi_j(1)\psi_i(2) \rangle = \iint \frac{\psi_i^*(1)\psi_j(1)\psi_j^*(2)\psi_i(2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\tau_1 d\tau_2$$

This has no classical interpretation. It's a pure quantum effect, arising from Pauli exchange.

Again note that the artificial self-terms in the summations cancel: $J_{ii} = K_{ii}$.



Towards Hartree-Fock: integrate spin

Closed shell: each spatial orbital combines with both spin orbitals.

$$|\psi_{(2k-1)}(1)\rangle = |\phi_k(1)\rangle |\alpha(1)\rangle \text{ and } |\psi_{(2k)}(1)\rangle = |\phi_k(1)\rangle |\beta(1)\rangle, \quad k = 1, \dots, \frac{N}{2}$$

In one-electron terms: summation over k taking two orbitals together:

$$\begin{aligned} \langle \Phi | \sum_i^N \hat{h}(i) | \Phi \rangle &= \sum_i^N \langle \psi_i(1) | \hat{h}(1) | \psi_i(1) \rangle \\ &= \sum_k^{N/2} \langle \phi_k(1) | \hat{h}(1) | \phi_k(1) \rangle (\langle \alpha | \alpha \rangle + \langle \beta | \beta \rangle) = 2 \sum_k^{N/2} \langle \phi_k(1) | \hat{h}(1) | \phi_k(1) \rangle \end{aligned}$$

In two-electron terms: summation over k, l taking 2×2 orbitals together:

$$|\phi_k(1)\rangle |\alpha(1)\rangle, |\phi_k(1)\rangle |\beta(1)\rangle, |\phi_l(1)\rangle |\alpha(1)\rangle, |\phi_l(1)\rangle |\beta(1)\rangle$$

All 4 Coulomb integrals survive and yield the same spatial integral.

Only those exchange integrals survive that have identical spin functions. These have the same spatial integral.



Towards Hartree-Fock: integrate spin

$$|\phi_k(1)\rangle |\alpha(1)\rangle, |\phi_k(1)\rangle |\beta(1)\rangle, |\phi_l(1)\rangle |\alpha(1)\rangle, |\phi_l(1)\rangle |\beta(1)\rangle$$

All 4 Coulomb integrals survive and yield the same spatial integral.

Only those exchange integrals survive that have identical spin functions. These have the same spatial integral. Note the *minus*.

$$\begin{aligned}\langle \Phi | \frac{1}{2} \sum_i^N \sum_{j \neq i}^N \hat{g}(i, j) | \Phi \rangle &= \frac{1}{2} \sum_i^N \sum_j^N \langle \psi_i(1) \psi_j(2) | \hat{g}(1, 2) | \psi_i(1) \psi_j(2) \rangle - \langle \psi_i(1) \psi_j(2) | \hat{g}(1, 2) | \psi_j(1) \psi_i(2) \rangle \\ &= \sum_k^{N/2} \sum_l^{N/2} 2 \langle \phi_k(1) \phi_l(2) | \hat{g}(1, 2) | \phi_k(1) \phi_l(2) \rangle - \langle \phi_k(1) \phi_l(2) | \hat{g}(1, 2) | \phi_l(1) \phi_k(2) \rangle \\ &= \sum_k^{N/2} \sum_l^{N/2} 2 J_{kl} - K_{kl}\end{aligned}$$

J_{kl} and K_{kl} **redefined**, with **only** integrals on spatial orbitals.



Towards Hartree-Fock: integrate spin

Let's be a bit more specific:

The Coulomb terms for kl :

$$\begin{aligned} & \langle \phi_k(1)\phi_l(2) | \hat{g}(1,2) | \phi_k(1)\phi_l(2) \rangle \\ & \left(\langle \alpha(1) | \alpha(1) \rangle \langle \alpha(2) | \alpha(2) \rangle + \langle \alpha(1) | \alpha(1) \rangle \langle \beta(2) | \beta(2) \rangle \right. \\ & + \langle \beta(1) | \beta(1) \rangle \langle \alpha(2) | \alpha(2) \rangle + \langle \beta(1) | \beta(1) \rangle \langle \beta(2) | \beta(2) \rangle \Big) \\ & = (1 + 1 + 1 + 1) \langle \phi_k(1)\phi_l(2) | \hat{g}(1,2) | \phi_k(1)\phi_l(2) \rangle \end{aligned}$$

The exchange terms for kl :

$$\begin{aligned} & \langle \phi_k(1)\phi_l(2) | \hat{g}(1,2) | \phi_l(1)\phi_k(2) \rangle \\ & \left(\langle \alpha(1) | \alpha(1) \rangle \langle \alpha(2) | \alpha(2) \rangle + \langle \alpha(1) | \beta(1) \rangle \langle \beta(2) | \alpha(2) \rangle \right. \\ & + \langle \beta(1) | \alpha(1) \rangle \langle \alpha(2) | \beta(2) \rangle + \langle \beta(1) | \beta(1) \rangle \langle \beta(2) | \beta(2) \rangle \Big) \\ & = (1 + 0 + 0 + 1) \langle \phi_k(1)\phi_l(2) | \hat{g}(1,2) | \phi_l(1)\phi_k(2) \rangle \end{aligned}$$



Towards Hartree-Fock: some remarks

There is a “shorthand” notation for Slater determinants. It just denotes the orbitals whereover the particles are distributed where β spin gets a bar, e.g.:

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix} = |\phi_1\bar{\phi}_2|$$

There are several flavours of Hartree-Fock:

- **restricted closed-shell** What we do here, one spatial molecular orbital for two spin orbitals (with α and β spin). $N/2$ is integer.
- **restricted open-shell** Also a single Slater determinant, with identical molecular orbitals for both spins, except for the unpaired electrons (only single spin function(s)).
- **unrestricted** Also for open shell, but with different spatial orbitals for α and β spin in the Slater determinant. As it is open shell, the number of α orbitals is different from the number of β orbitals.

