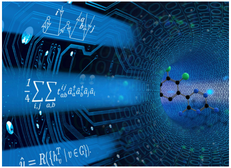
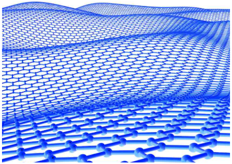
# Hartree–Fock theory in first quantization





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# Recap

First quantization

- Hamiltonian is a differential operator

$$H = -\frac{1}{2}\sum_{i=1}^{N}\Delta_{r_i} - \sum_{i=1}^{N}\sum_{j=1}^{N_{\mathrm{nuc}}}\frac{Z_j}{|r_i - R_j|} + \sum_{j>i}^{N}\frac{1}{|r_i - r_j|}$$

- We see a solution that is anti-symmetric

$$\Psi(x_1, ..., x_N) = \mathrm{sgn}(\pi)\Psi(x_{\pi(1)}, ..., x_{\pi(N)}) \quad \text{for } \pi \in S_n$$

- Idea: Let's use an anti-symmetric product ansatz

$$\Psi[i_1, ..., i_N](x_1, ..., x_N) = \frac{1}{\sqrt{N!}}\phi_{i_1} \wedge ... \wedge \phi_{i_N}(x_1, ..., x_N)$$

given $\{\phi_i\}_{i=1}^{K}$ and $i_1 < ... < i_N$.
... still, this scales as $\binom{K}{N} \Rightarrow$ We cannot diagonalize this!

# Atomic orbitals

For a given molecule, we have a set of basis functions

$$\{\phi_1, ..., \phi_K \mid \phi_i \in L^2(X) \text{ and } \langle \phi_i, \phi_j \rangle_x = \delta_{i,j}\}$$

where

$$\langle \phi_i, \phi_j \rangle_x = \int_X \phi_i^*(x)\phi_j(x)\, dx = \sum_{\sigma \in \{\pm 1/2\}} \int_{\mathbb{R}^3} \phi_i^*(r,\sigma)\phi_j(r,\sigma)\, dr$$

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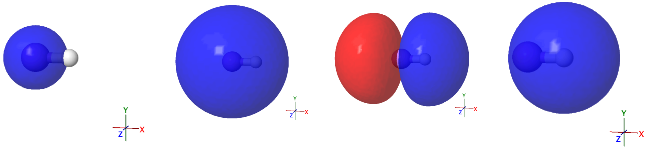

# Atomic orbitals

For a given molecule, we have a set of basis functions

$$\{\phi_1, ..., \phi_K\}$$

We can build $N$-particle functions (Slater determinants)

$$\Phi[i_1, ..., i_N] = \frac{1}{\sqrt{N!}} \phi_{i_1} \wedge ... \wedge \phi_{i_N}$$

that form a basis for our numerics.

Are they "any good"? Does

$$\langle \Phi[i_1, ..., i_N], H\Phi[i_1, ..., i_N] \rangle$$

mean anything?

# Hartree–Fock – one body part

One body term:

$$h = \sum_{i=1}^{N} h_i = \sum_{i=1}^{N} -\frac{1}{2}\Delta_{r_i} + V_{\mathrm{ext}}(r_i) = \sum_{i=1}^{N} -\frac{1}{2}\Delta_{r_i} - \sum_{j=1}^{M} \frac{Z_j}{\|r_i - R_j\|}$$

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Let $\Psi = \Phi[j_1, ..., j_N]$ be a Slater determinant. Then

$$\langle \Psi, h\Psi \rangle = \sum_{i=1}^{N} \langle \Psi, h_i \Psi \rangle = N \left\langle \Psi, -\frac{1}{2}\Delta_{r_1} + V_{\mathrm{ext}}(r_1)\Psi \right\rangle$$

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Look at $N = 2$ example:

$$\begin{aligned}
&\langle \phi_1 \wedge \phi_2, \Delta_{r_2} \phi_1 \wedge \phi_2 \rangle_{x_1, x_2} \\
&\text{“definition”} && = \int_{X \times X} \phi_1^* \wedge \phi_2^*(x_1, x_2) \Delta_{r_2} \phi_1 \wedge \phi_2(x_1, x_2) dx_1 dx_2 \\
&\text{“renaming”} && = \int_{X \times X} \phi_1^* \wedge \phi_2^*(x_2, x_1) \Delta_{r_1} \phi_1 \wedge \phi_2(x_2, x_1) dx_1 dx_2 \\
&\text{“anti} - \text{sym.”} && = \int_{X \times X} \phi_1^* \wedge \phi_2^*(x_1, x_2) \Delta_{r_1} \phi_1 \wedge \phi_2(x_1, x_2) dx_1 dx_2 \\
& && = \langle \phi_1 \wedge \phi_2, \Delta_{r_1} \phi_1 \wedge \phi_2 \rangle
\end{aligned}$$

# Revisiting inner product structure

Recall

$$\Psi(x_1, ..., x_N) = \frac{1}{\sqrt{N!}} \sum_{\pi \in S_{\{i_1,...,i_N\}}} \mathrm{sgn}(\pi) \prod_{i=1}^{N} \phi_{\pi(j_i)}(x_1, ..., x_N)$$

and

$$\langle \Psi, \Psi \rangle = \frac{1}{N!} \sum_{\pi,\pi'} \mathrm{sgn}(\pi)\mathrm{sgn}(\pi') \prod_{i=1}^{N} \left\langle \phi_{\pi(i)}, \phi_{\pi'(i)} \right\rangle_{x_i}$$

where

$$\langle \phi_k, \phi_j \rangle_x = \int_X \phi_k^*(x)\phi_j(x)dx$$

NOTE

$$\langle \phi_i\phi_j, \phi_k\phi_l \rangle_{x_1,x_1} = \int_{X\times X} \phi_i^*(x_1)\phi_j^*(x_2)\phi_k(x_1)\phi_l(x_2)dx_1dx_2$$

# Calculations

$$\left\langle \Psi, \left(-\frac{1}{2}\Delta_{r_1} + V_{\mathrm{ext}}(r_1)\right)\Psi \right\rangle$$

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Two body term:

$$H_I = \sum_{i<j} g(i,j) = \sum_{i<j} \frac{1}{\|r_i - r_j\|}$$

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Again, let $\Psi = \Phi[j_1, ..., j_N]$ be a Slater determinant. Then

$$\langle \Psi, H_I \Psi \rangle = \binom{N}{2} \left\langle \Psi, \frac{1}{\|r_1 - r_2\|} \Psi \right\rangle$$

# Application to the integral expression

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&\quad \times \prod_{i=3}^{N} \left\langle \phi_{\pi(i)}\phi_{\pi'(i)} \right\rangle_{x_i} \\
&= \frac{1}{N!}\sum_{\pi,\pi'} \mathrm{sgn}(\pi)\mathrm{sgn}(\pi') \left\langle \phi_{\pi(1)}\phi_{\pi(2)}, \frac{1}{\|r - r'\|}\phi_{\pi'(1)}\phi_{\pi'(2)} \right\rangle_{x,x'} \\
&\quad \times \prod_{i=3}^{N} \delta_{\pi(i),\pi'(i)}
\end{aligned}
$$

# Observations

Note that

$$\prod_{i=3}^{N} \delta_{\pi(i),\pi'(i)}$$

ensures that $\pi$ and $\pi'$ are the same except for potentially the first two indices:

$$\pi(1) = \pi'(1) = i \quad \text{and} \quad \pi(1) = \pi'(1) = j \tag{1}$$

or

$$\pi(1) = \pi'(2) = i \quad \text{and} \quad \pi(2) = \pi'(1) = j \tag{2}$$

where $i, j \in \{1, ..., N\}$.

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- In case of Eq. (1) we have that

$$\mathrm{sgn}(\pi) = \mathrm{sgn}(\pi') \quad \Rightarrow \quad \mathrm{sgn}(\pi)\mathrm{sgn}(\pi') = 1$$

- In case of Eq. (2) we have that

$$\mathrm{sgn}(\pi) = -\mathrm{sgn}(\pi') \quad \Rightarrow \quad \mathrm{sgn}(\pi)\mathrm{sgn}(\pi') = -1$$

Thus

$$
\begin{aligned}
&\left\langle \Psi, \frac{1}{\|r_1 - r_2\|}\Psi \right\rangle \\
&= \frac{1}{N!}\sum_{\pi,\pi'} \mathrm{sgn}(\pi)\mathrm{sgn}(\pi') \left\langle \phi_{\pi(1)}\phi_{\pi(2)}, \frac{1}{\|r - r'\|}\phi_{\pi'(1)}\phi_{\pi'(2)} \right\rangle_{x,x'} \\
&\qquad \times \prod_{i=3}^{N} \delta_{\pi(i),\pi'(i)} \\
&= \frac{(N-2)!}{N!} \sum_{i \neq j = 1}^{N} \left\langle \phi_i\phi_j, \frac{1}{\|r - r'\|}\phi_i\phi_j \right\rangle_{x,x'} - \left\langle \phi_i\phi_j, \frac{1}{\|r - r'\|}\phi_j\phi_i \right\rangle_{x,x'} \\
&= \frac{1}{N(N-1)} \sum_{i \neq j = 1}^{N} \left\langle \phi_i\phi_j, \frac{1}{\|r - r'\|}\phi_i\phi_j \right\rangle_{x,x'} - \left\langle \phi_i\phi_j, \frac{1}{\|r - r'\|}\phi_j\phi_i \right\rangle_{x,x'}
\end{aligned}
$$

# The full two-body part

$$
\begin{aligned}
&\langle \Psi, H_I \Psi \rangle \\
&= \sum_{k<l} \left\langle \Psi, \frac{1}{\|r_k - r_l\|} \Psi \right\rangle \\
&= \frac{1}{N(N-1)} \sum_{k<l} \sum_{i \neq j = 1}^{N} \left\langle \phi_i \phi_j, \frac{1}{\|r - r'\|} \phi_i \phi_j \right\rangle_{x,x'} - \left\langle \phi_i \phi_j, \frac{1}{\|r - r'\|} \phi_j \phi_i \right\rangle \\
&= \frac{1}{2} \sum_{i \neq j = 1}^{N} \left\langle \phi_i \phi_j, \frac{1}{\|r - r'\|} \phi_i \phi_j \right\rangle_{x,x'} - \left\langle \phi_i \phi_j, \frac{1}{\|r - r'\|} \phi_j \phi_i \right\rangle_{x,x'} \\
&= \frac{1}{2} \sum_{i,j = 1}^{N} \left\langle \phi_i \phi_j, \frac{1}{\|r - r'\|} \phi_i \phi_j \right\rangle_{x,x'} - \left\langle \phi_i \phi_j, \frac{1}{\|r - r'\|} \phi_j \phi_i \right\rangle_{x,x'}
\end{aligned}
$$

where we used

$$
\sum_{k<l=1}^{N} 1 = \sum_{i=1}^{N-1} N - i = \frac{N(N-1)}{2}
$$

# Putting it all together

$$
\begin{aligned}
\mathcal{E}_{\mathrm{HF}}(\{\phi_i\}_{i=1}^N) &= \sum_{i=1}^N \int_X \frac{1}{2}|\nabla_r \phi_i(x)|^2 + V_{\mathrm{ext}}(r)|\phi_i(x)| dx \\
&+ \frac{1}{2}\sum_{i,j} \int_{X\times X} \frac{|\phi_i(x)|^2|\phi_j(x')|^2}{\|r-r'\|} dx dx' \\
&- \frac{1}{2}\sum_{i,j} \int_{X\times X} \frac{\phi_i^*(x)\phi_j^*(x')\phi_j(x)\phi_i(x')}{\|r-r'\|} dx dx' \\
&= \sum_{i=1}^N \langle i||i\rangle - \frac{1}{2}\sum_{i,j} \langle ij||ij\rangle - \langle ij||ji\rangle
\end{aligned}
$$

# Putting it all together

$$\mathcal{E}_{\mathrm{HF}}(\{\phi_i\}_{i=1}^N) = \sum_{i=1}^N \int_X \frac{1}{2}|\nabla_r \phi_i(x)|^2 + V_{\mathrm{ext}}(r)|\phi_i(x)| dx$$

$$+ \frac{1}{2}\sum_{i,j} \int_{X\times X} \frac{|\phi_i(x)|^2 |\phi_j(x')|^2}{\|r - r'\|} dx dx'$$

$$- \frac{1}{2}\sum_{i,j} \int_{X\times X} \frac{\phi_i^*(x)\phi_j^*(x')\phi_j(x)\phi_i(x')}{\|r - r'\|} dx dx'$$

$$= \sum_{i=1}^N \langle i||i\rangle - \frac{1}{2}\sum_{i,j} \langle ij||ij\rangle - \langle ij||ji\rangle$$

Question: Can we find $\{\xi_i\}_{i=1}^N$ that minimize $\mathcal{E}_{\mathrm{HF}}$?

$$E_{\mathrm{HF}} := \min_{\{\phi_i\}_{i=1}^N,\ \langle \phi_i, \phi_j\rangle = \delta_{i,j}} \mathcal{E}_{\mathrm{HF}}(\{\phi_i\}_{i=1}^N)$$

# Molecular orbitals

What if we make the following ansatz (LCAO):

$$\xi_i = \sum_{j=1}^{K} C_{j,i}\phi_j$$

Two options!

- Direct minimization of $\mathcal{E}_{\mathrm{HF}}$
- First order optimality condition (finding a stationary point)
  $\rightarrow$ self-consistent field (SCF) equations
  $\rightarrow$ Roothan-Hall Equations

# Direct minimization – I

Substituting the LCAO into $\mathcal{E}_{\mathrm{HF}}$ yields

$$
\begin{aligned}
\mathcal{E}_{\mathrm{HF}}(C) = & \sum_{i=1}^{N} \frac{1}{2} \sum_{j,k=1}^{K} C_{i,j}^{*} C_{i,k} \langle \nabla\phi_j, \nabla\phi_k \rangle \\
& - \sum_{i=1}^{N} \sum_{j,k=1}^{K} C_{i,j}^{*} C_{i,k} \langle \phi_j, V_{\mathrm{ext}} \phi_k \rangle \\
& + \frac{1}{2} \sum_{i_1=1}^{N} \sum_{j_1,k_1=1}^{K} \sum_{i_2=1}^{N} \sum_{j_2,k_2=1}^{K} C_{i_1,j_1}^{*} C_{i_1,k_1} C_{i_2,j_2}^{*} C_{i_2,k_2} \langle\langle j_1 k_1 || j_2 k_2 \rangle\rangle \\
& - \frac{1}{2} \sum_{i_1=1}^{N} \sum_{j_1,k_1=1}^{K} \sum_{i_2=1}^{N} \sum_{j_2,k_2=1}^{K} C_{i_1,j_1}^{*} C_{i_1,k_1} C_{i_2,j_2}^{*} C_{i_2,k_2} \langle\langle j_1 j_2 || k_1 k_2 \rangle\rangle
\end{aligned}
$$

# Direct minimization – II

Introducing the tensors

$$
\begin{aligned}
A_{j,k} &= \langle \nabla\phi_j, \nabla\phi_k \rangle \\
B_{j,i} &= \langle \phi_j, V\phi_k \rangle \\
F_H(j_1, k_1, j_2, k_2) &= \langle\langle j_1 k_1 || j_2 k_2 \rangle\rangle \\
F_F(j_1, j_2, k_1, k_2) &= \langle\langle j_1 j_2 || k_1 k_2 \rangle\rangle
\end{aligned}
$$

we find

$$
\begin{aligned}
\mathcal{E}_{\mathrm{HF}}(C) = \mathrm{Tr}\left( C^\dagger (\frac{1}{2}A - B) C \right) \\
+ \frac{1}{2} \sum_{i_1=1}^{N} \sum_{j_1,k_1=1}^{K} \sum_{i_2=1}^{N} \sum_{j_2,k_2=1}^{K} C^*_{i_1,j_1} C_{i_1,k_1} C^*_{i_2,j_2} C_{i_2,k_2} F_H(j_1, k_1, j_2, k_2) \\
- \frac{1}{2} \sum_{i_1=1}^{N} \sum_{j_1,k_1=1}^{K} \sum_{i_2=1}^{N} \sum_{j_2,k_2=1}^{K} C^*_{i_1,j_1} C_{i_1,k_1} C^*_{i_2,j_2} C_{i_2,k_2} F_F(j_1, j_2, k_1, k_2)
\end{aligned}
$$

# Roothaan–Hall Equations

Starting point is the HF energy functional

$$\mathcal{E}_{\mathrm{HF}}(\{\phi_i\}_{i=1}^N) = \sum_{i=1}^N \langle i||i\rangle + \frac{1}{2}\sum_{i,j}\langle ij||ij\rangle - \langle ij||ji\rangle$$

Seeking stationary points yields the (generalized) non-linear eigenvalue problem

$$F[\{\phi_i\}_{i=1}^N]\phi_i = \sum_j \phi_j \lambda_{j,i}$$

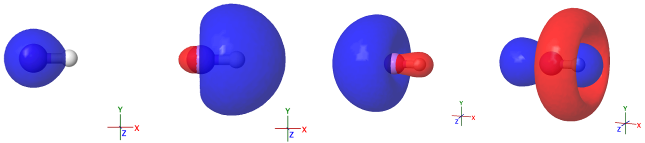
where

$$\begin{aligned} F_{j,i} &= -\frac{1}{2}\langle \phi_j, \nabla \phi_i\rangle + \langle \phi_j, V_{\mathrm{ext}}\phi_i\rangle \\ &+ \int_{X\times X} \frac{\sum_{i=1}^N |\phi_i(x')|^2}{|r-r'|}\phi_j(x)\phi_i(x)\ dx\ dx' \\ &- \int_{X\times X} \frac{\sum_{i=1}^N \phi_i^*(x')\phi_i(x)}{|r-r'|}\phi_j(x)\phi_i(x)\ dx\ dx' \end{aligned}$$

# Molecular orbitals

Either approach yields optimized single-particle functions:

The molecular orbitals




Question: What about spin?

# Spin symmetries (Fukutome)

There are eight spin symmetry classes

$\mathbb{C}$ generalized HF:

$$F = \begin{pmatrix} F_{\alpha,\alpha} & F_{\alpha,\beta} \\ F_{\beta,\alpha} & F_{\beta,\beta} \end{pmatrix}$$

paired unrestricted HF

$$F = \begin{pmatrix} F_{\alpha,\alpha} & 0 \\ 0 & F^*_{\alpha,\alpha} \end{pmatrix}$$

paired generalized HF

$$F = \begin{pmatrix} F_{\alpha,\alpha} & F_{\alpha,\beta} \\ -F^*_{\alpha,\beta} & F^*_{\alpha,\alpha} \end{pmatrix}$$

$\mathbb{R}$ generalized HF:

$$F = \begin{pmatrix} F^*_{\alpha,\alpha} & F^*_{\alpha,\beta} \\ F^*_{\beta,\alpha} & F^*_{\beta,\beta} \end{pmatrix} = \begin{pmatrix} F_{\alpha,\alpha} & F_{\alpha,\beta} \\ F_{\beta,\alpha} & F_{\beta,\beta} \end{pmatrix}$$

$\mathbb{C}$ unrestricted HF:

$$F = \begin{pmatrix} F_{\alpha,\alpha} & 0 \\ 0 & F_{\beta,\beta} \end{pmatrix}$$

$\mathbb{R}$ unrestricted HF

$$F = \begin{pmatrix} F_{\alpha,\alpha} & 0 \\ 0 & F_{\beta,\beta} \end{pmatrix}$$

$\mathbb{C}$ restricted Hartree–Fock:

$$F = \begin{pmatrix} F_R & 0 \\ 0 & F_R \end{pmatrix}$$

with $F_{\alpha,\alpha} = F_{\beta,\beta} = F_R \in \mathbb{C}^{K \times K}$

$\mathbb{R}$ restricted HF

$$F = \begin{pmatrix} F_R & 0 \\ 0 & F_R \end{pmatrix}$$

with $F_{\alpha,\alpha} = F_{\beta,\beta} = F_R \in \mathbb{R}^{K \times K}$