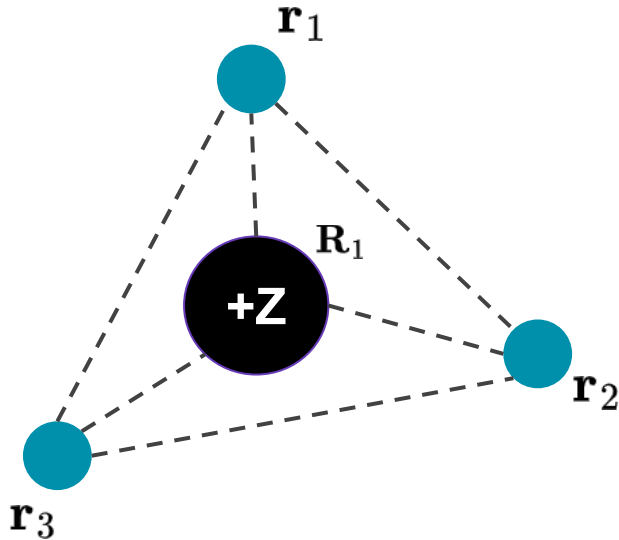# The Hartree (without Fock) method & simplified notation

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The electronic Schrödinger equation (SE)

$$\widehat{H}\Psi = E\Psi$$

- The Born-Oppenheimer approximation allow us to treat only electrons quantum mechanically. We can therefore replace the full Schrödinger equation with electronic one.

- The solution to the electronic Schrödinger equation provide us with the wavefunction that contain all information of our system.

- The SE is in principle impossible to solve, the **Hartree method** tries to deal with this fact.
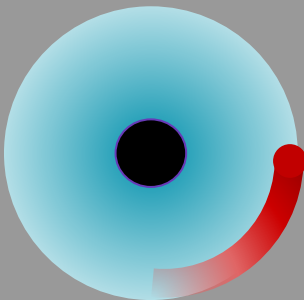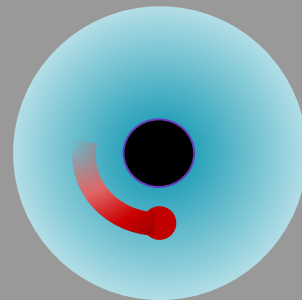
The general idea

We would like to turn the complex many-electron problem into a set of one-electron problems where the effect of the other electrons are treated implicitly by way of an effective field.
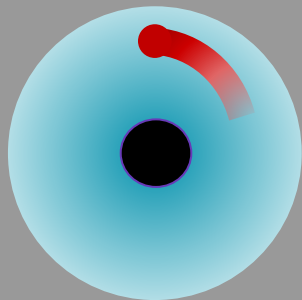
Independent electron approximation
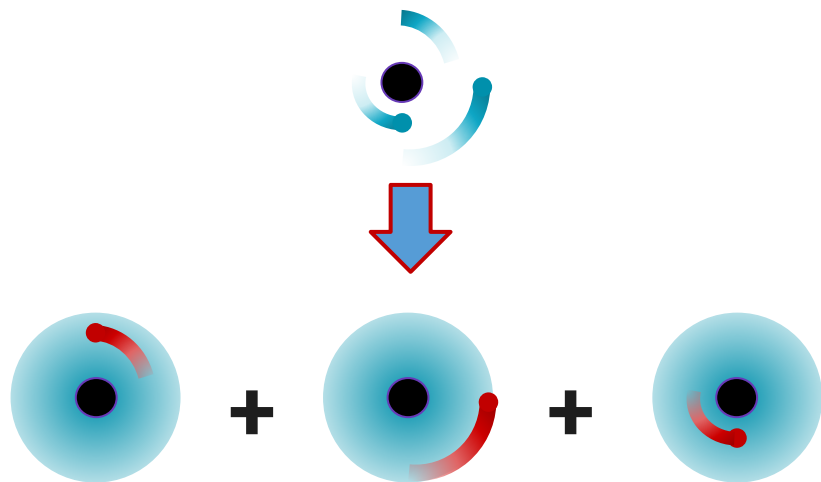
- In the Hartree approach we make the anzats that electrons can be considered to move in their own independent orbits around the nuclei, so-called *orbitals*. This simply enforce the separation from the start.

- Mathematically we can write this as:

$$\Psi(\mathbf{r}_1, \mathbf{r}_1, \cdots, \mathbf{r}_N) = \chi_1(\mathbf{r}_1)\chi_2(\mathbf{r}_2) \cdots \chi_N(\mathbf{r}_N)$$

The right-hand side of the equation is called a **Hartree-product**.

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Energy of a Hartree-product

- We will make use of energy minimization to find the best orbitals to approximate the SE equation.

- The energy of a Hartree-product can be obtained from following integral:

$$E = \int \int \cdots \int \overline{\chi}_1(\mathbf{r}_1) \overline{\chi}_2(\mathbf{r}_2) \cdots \overline{\chi}_N(\mathbf{r}_N) \widehat{H} \chi_1(\mathbf{r}_1) \chi_2(\mathbf{r}_2) \cdots \chi_N(\mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

the overline symbol refer to complex-conjugate.

- We can save some ink by using the following condensed notation:

$$E = \left\langle 12 \cdots N \left| \widehat{H} \right| 12 \cdots N \right\rangle$$

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Let r_{ij} and h_i be defined from the following expressions:

$$\widehat{V}_{ee} = \sum_{j=1}^{N} \sum_{i=1}^{N} \frac{1}{|\mathbf{r_j} - \mathbf{r_i}|} = \sum_{i=1}^{N} \sum_{j=1}^{N} r_{ij}^{-1} \qquad \text{"Two-electron operators"}$$

$$\widehat{T}_e + \widehat{V}_{Ne} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_{j=1}^{M} \sum_{i=1}^{N} \frac{Z_j}{|\mathbf{R_j} - \mathbf{r_i}|} = \sum_{i=1}^{N} h_i \qquad \text{"One-electron operators"}$$

This allow to write the energy as:

$$E = \left\langle 12 \cdots N \left| \sum_{i=1}^{N} h(i) + \sum_{i=1}^{N} \sum_{j=1}^{N} r_{ij}^{-1} \right| 12 \cdots N \right\rangle =$$

$$= \sum_{i=1}^{N} \left\langle 12 \cdots N \left| h(i) \right| 12 \cdots N \right\rangle + \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle 12 \cdots N \left| r_{ij}^{-1} \right| 12 \cdots N \right\rangle$$

This looks quite horrible at first! Please keep calm, we will sort it out.

Let us look at some of the terms...

We can actually simply things a lot by combining simple rules for integration with the orthonormality of the orbitals.

$$\int\int[f(x)+g(y)]dxdy = \int f(x)dx + \int g(y)dy$$

and

$$\int\int f(x)g(y)dxdy = \int f(x)dx \int g(y)dy$$

+

$$\langle i|i\rangle = 1$$

$$\langle i|j\rangle = 0 \ (i \neq j)$$

For example, we can write terms involving the one-electron opeteros h_i as:

$$\langle 12\cdots N|h(i)|12\cdots N\rangle = \langle 1|1\rangle\langle 2|2\rangle\cdots\langle i|h(i)|i\rangle\cdots\langle N-1|N-1\rangle\langle N|N\rangle = \langle i|h(i)|i\rangle$$

We can actually simply things a lot by combining simple rules for integration with the orthonormality of the orbitals.

$$\int \int [f(x) + g(y)] dxdy = \int f(x)dx + \int g(y)dy$$

and

$$\int \int f(x)g(y)dxdy = \int f(x)dx \int g(y)dy$$

+

$$\langle i|i \rangle = 1$$

$$\langle i|j \rangle = 0 \ (i \neq j)$$

A two-electron integral in a similar way...

$$\left\langle 12 \cdots N \left| r_{ij}^{-1} \right| 12 \cdots N \right\rangle = \langle 1|1 \rangle \langle 2|2 \rangle \cdots \left\langle ij \left| r_{ij}^{-1} \right| ij \right\rangle \cdots \langle N-1|N-1 \rangle \langle N|N \rangle = \left\langle ij \left| r_{ij}^{-1} \right| ij \right\rangle$$

! Note that we are left with a double integral that cannot be simplified further. We can see why this is so by comparing to:

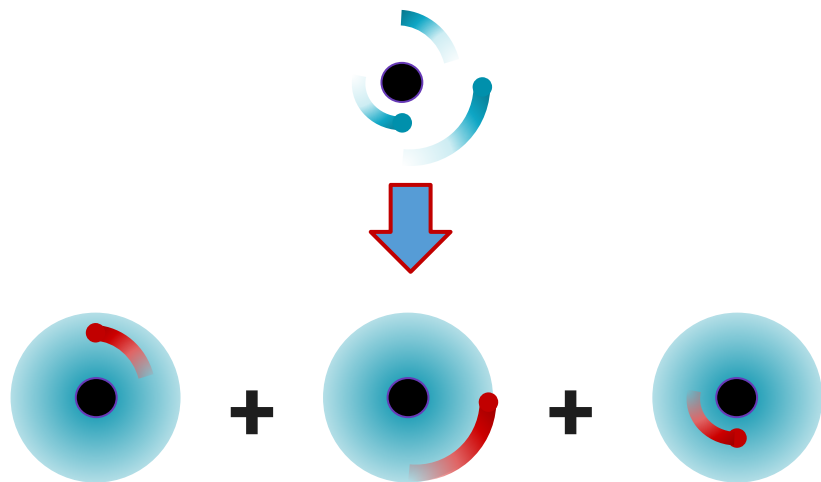$$\frac{1}{|x-y|} \neq f(x)g(y)$$

Energy of a Hartree-product, revisited

- Using the one- and two-electron operators, and the simplifications shown on the previous two slides, we can write the energy of a Hartree-product as:

$$E = \sum_{i=1}^{N} \langle i \,|h(i)|\, i \rangle + \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle ij \left| r_{ij}^{-1} \right| ij \right\rangle$$

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Minimizing the energy of a Hartree-product

- In the SE, the true ground-state *wavefunction* is the one that minimize the energy.

- We follow in that spirit and look for the set of *orbitals* that minimize the energy of the Hartree-product by trying to solve:

$$\frac{\partial E}{\partial \chi_{\mathrm{i}}} = 0$$

The Hartree-equation

$$f_i \chi_i = \varepsilon \chi_i$$

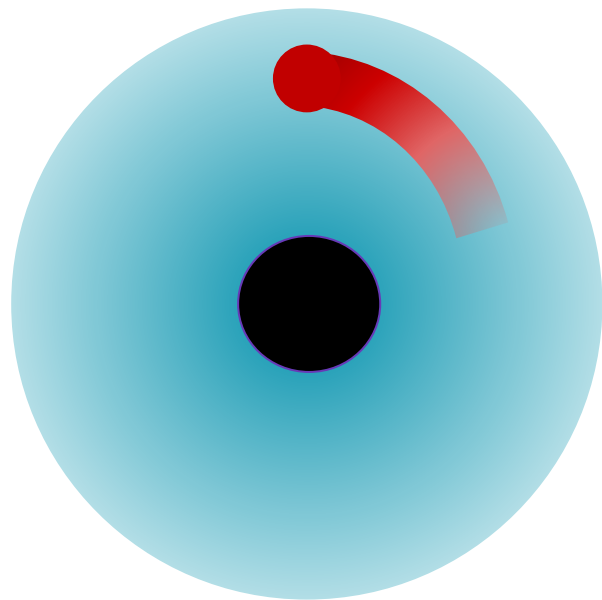**Hartree-operator**

Sum over all other electrons

$$f_i = h_i + \sum_{j=1; j\neq i}^{N} \mathbf{J}_j(\mathbf{r}_i)$$

Kinetic energy + Nuclear attraction

Effective field from another electron

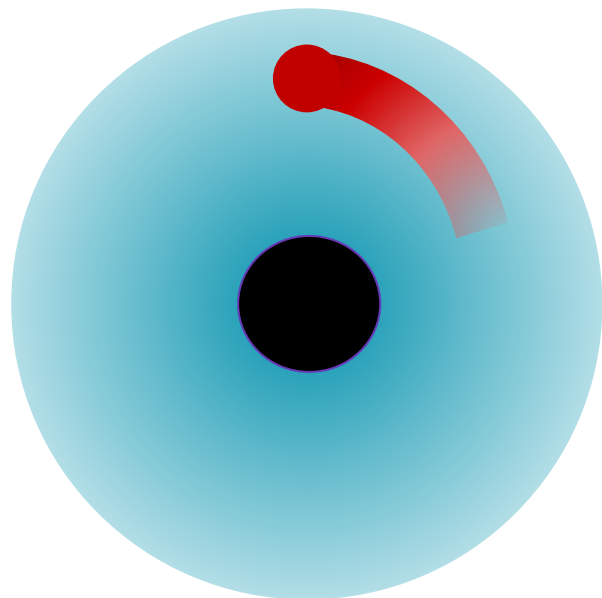$$\mathbf{J}_j(1) = \int \overline{\chi}_j(2) r_{12}^{-1} \chi_j(2) d\mathbf{r}_2$$

Interpretation of **J**

$$\mathbf{J}_j(1) = \int \overline{\chi}_{\mathrm{j}}(2) r_{12}^{-1} \chi_j(2) d\mathbf{r}_2$$

- **J** is called the Coulomb operator.

- $\overline{\chi}_{\mathrm{j}}\chi_{\mathrm{j}} = |\chi_{\mathrm{j}}|^2$ correspond to the electron density of a second electron occupying orbital j.

- We can therefore interpret the **J** as a measure of the average electrostatic repulsion from a second electron.

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Self consistent field

$$\mathbf{J}_j(1) = \int \overline{\chi}_j(2) r_{12}^{-1} \chi_j(2) d\mathbf{r}_2$$

- Since the operator **J** depend on the orbitals we cannot solve: $f_i \chi_i = \varepsilon \chi_i$ without first having to know the orbitals.

- We solve the catch 22 by using an interactive process:
  a. Guess all χ_i
  b. Compute all f_i
  c. Solve to find a new set of χ_i
  d. Iterate b and c until χ_i stops changing

  We have reached the so-called ***self-consistent field*** situation.

- The resulting orbitals, and the corresponding Hartree-product represent our best approximation to the Schrödinger equation.

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Summary

- The Hartree method provide an approximation to the Schrödinger equation.
- The derivation of the method start from the electronic Schrödinger equation.
- We make the *independent electron approximation* and write the wavefunction as a *Hartree-product* of *orbitals*.
- We find a simple expression for the total energy of a Hartree-product and minimize it the respect to the orbitals.
- This leads to a the *Hartree-equation* which describe the motion of each electrons moving in the effective field of the other electrons.
- The effective field is described by Coulomb operator **J**.
- We solve the Hartree-equation using an iterative process called *self-consistent field*.

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