

The Hartree-Fock method

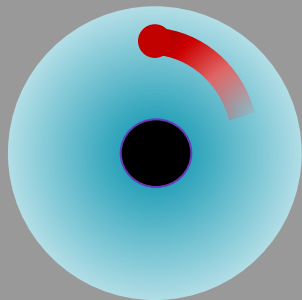
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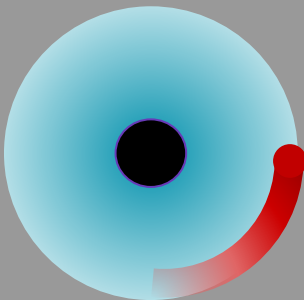
The general idea (The same as for the Hartree method)



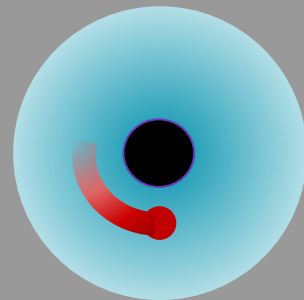
We would like to turn the complex many-electron problem into a set of one-electron problems where the effect of the other electrons are treated implicitly by way of an effective field.



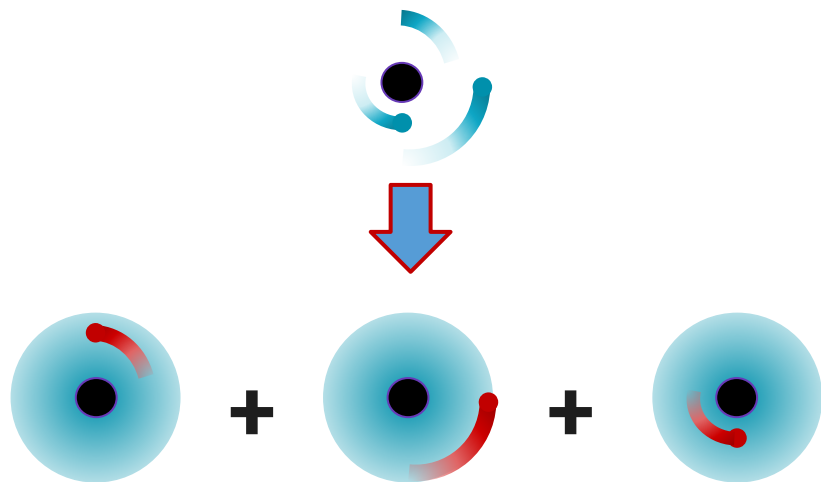
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Why do we need Fock?



- In the Hartree approach we made use of a Hartree-product :

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

- While successful in separating the problem into a coupled set of equations describing the motion of each electron individually. It suffers from poor accuracy and flawed physics!
- The Hartree-Fock approach addresses both these shortcomings.

The Slater determinant

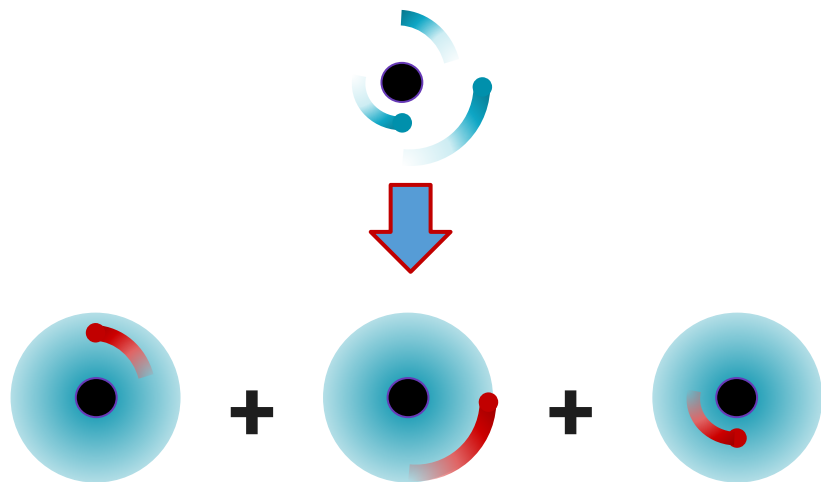
One problem with the Hartree approach is that the Hartree-product does not fulfill the requirement that a wavefunction should be antisymmetric.

- Antisymmetry requires that the wavefunction change sign if two electrons are interchanged.
- By using a so-called Slater-determinant (equation at the bottom of the slide) instead of the Hartree-product we can comply with antisymmetry and still keep the independent electron approximation.

$$\Psi_{\text{SD}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{r}_1) & \chi_2(\mathbf{r}_1) & \cdots & \chi_N(\mathbf{r}_1) \\ \chi_1(\mathbf{r}_2) & \chi_2(\mathbf{r}_2) & \cdots & \chi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{r}_N) & \chi_2(\mathbf{r}_N) & \cdots & \chi_N(\mathbf{r}_N) \end{vmatrix}$$

The mathematical properties of a determinant are such that replacing any two rows leads to a change of sign. This corresponds to interchanging two electrons. The determinant therefore build in the antisymmetry.

Minimizing the energy of a Slater-determinant



- 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 Slater-determinant:

$$\frac{\partial E}{\partial \chi_i} = 0$$

$$\langle \Psi_{\text{SD}} | \hat{H} | \Psi_{\text{SD}} \rangle$$

We plug in the Slater-determinant into the standard energy expression for a quantum system.



Integration rules

$$\begin{aligned} \int \int [f(x) + g(y)] dx dy &= \int f(x) dx + \int g(y) dy \\ \int \int f(x) g(y) dx dy &= \int f(x) dx \int g(y) dy \end{aligned}$$



orthonormality

$$\begin{aligned} \langle i | i \rangle &= 1 \\ \langle i | j \rangle &= 0 \quad (i \neq j) \end{aligned}$$

We simplify.



$$\frac{\partial E}{\partial \chi_i} = 0$$

We take the derivative with respect to the orbitals to find the “best” orbitals.



The Hartree-Fock equation

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

We arrive at a SE-like equation.

The Hartree-Fock equation

$$f_i \chi_i = \epsilon \chi_i$$

Sum over all other electrons

Hartree-Fock operator

$$f_i = h_i + \sum_{j=1}^N [\mathbf{J}_j(\mathbf{r}_i) - \mathbf{K}_j(\mathbf{r}_i)]$$

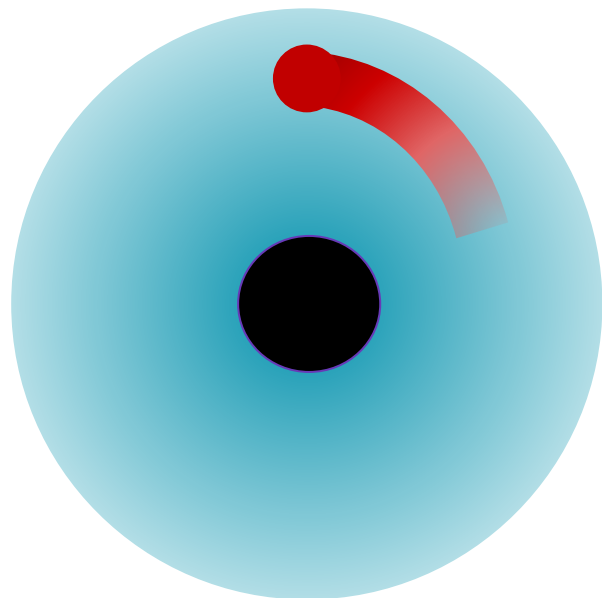
Kinetic energy + Nuclear attraction

Effective field from another electron

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

$$\mathbf{K}_j(1) \chi_i(1) = \left[\int \chi_j^*(2) r_{12}^{-1} \chi_i(2) d\mathbf{r}_2 \right] \chi_j(1)$$

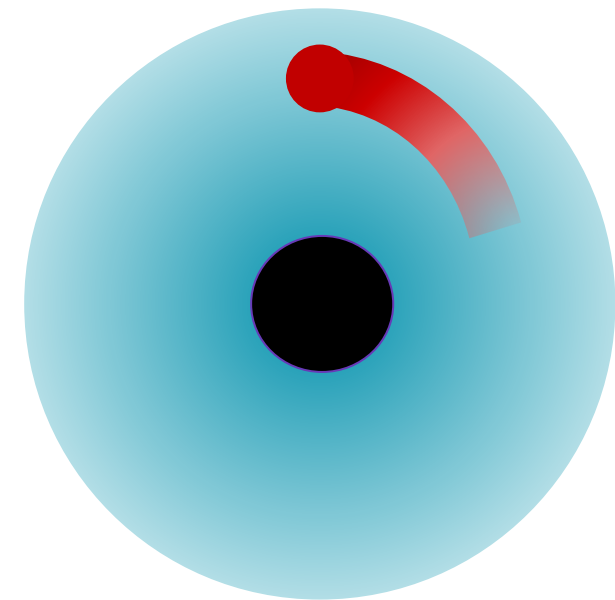
Interpretation of \mathbf{J} (Same as for the Hartree-method)



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

- \mathbf{J} is called the Coulomb operator.
- $\bar{\chi}_j \chi_j = |\chi_j|^2$ correspond to the electron density of a second electron occupying orbital j .
- We can therefore interpret the \mathbf{J} as a measure of the average electrostatic repulsion from a second electron.

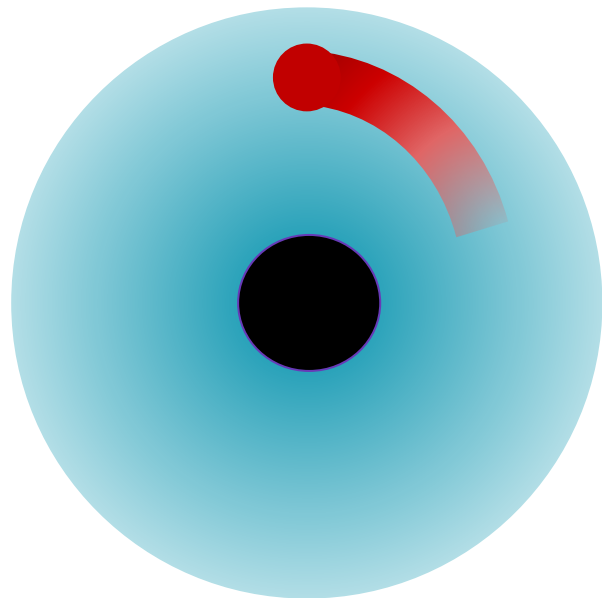
Interpretation of **K** (new in the Hartree-Fock method)



- **K** is called the Exchange operator.
- **K** has no classical counterpart.
- It appears with a negative sign in the Hartree-Fock operator and it therefore acts to reduce repulsion.

$$\mathbf{K}_j(1)\chi_i(1) = \left[\int \chi_j^*(2) r_{12}^{-1} \chi_i(2) d\mathbf{r}_2 \right] \chi_j(1)$$

Self consistent field



- Since the operator \mathbf{J} and \mathbf{K} 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 changingWe have reached the so-called **self-consistent field** situation.
- The resulting orbitals, and the corresponding Slater-determinant correspond to our best approximation to the Schrödinger equation.

Summary

- The Hartree-Fock 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 *Slater-determinant* of *orbitals*.
- We find a simple expression for the total energy of a Slater-determinant and minimize it the respect to the orbitals.
- This leads to the *Hartree-Fock equation* which describe the motion of each electrons moving in the effective field of the other electrons.
- The effective field is described by the *Coulomb operator J* , and the *Exchange operator K* .
- We solve the Hartree-equation using an iterative process called *self-consistent field*.