CHEM3023: Spins, Atoms and Molecules

Lecture 5

The Hartree-Fock method

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Learning outcomes

- Be able to use the variational principle in quantum calculations
- Be able to construct Fock operators for molecules
- Be able to explain the stages of a Hartree-Fock calculation

So far:

- We wanted to construct the simplest possible electronic wavefunction, so we chose to use products of spin orbitals (one-electron wavefunctions)

- The requirement of antisymmetry forced us to use sums of products: these can be represented as a Slater determinant

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

- Spin orbitals have a spatial part and a spin part (either "up" or "down")

$$\chi^{\uparrow}(\mathbf{x}) = \psi(\mathbf{r})\alpha(\omega)$$

Spin **Spatial** **Spin**
orbital **orbital** **function**

$$\chi^{\downarrow}(\mathbf{x}) = \psi(\mathbf{r})\beta(\omega)$$

- We now need a way to calculate the best possible spatial orbitals

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Finding the optimum orbitals

- How do we decide what are the "best" orbitals for a molecule?

- We need a guiding principle

- This is the variational principle: It can be applied to any approximate wavefunction.

- It forms the basis of many computational techniques

- To understand the variational principle we need the following two results for the (exact) eigenfunctions of any Hermitian operator:

    1) The are orthogonal (this is shown at the appendix)

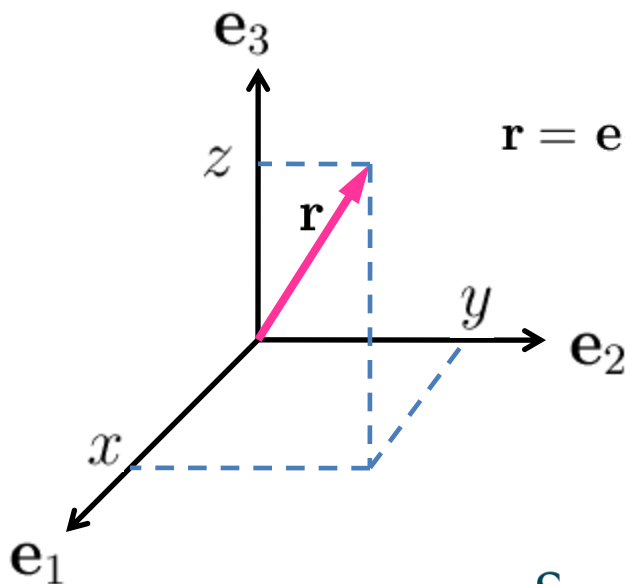   2) They form a complete set of functions (next slide)

The eigenfunctions of a Hermitian operator form a complete set

I.e. **Any function** (so, also any wavefunction) can be written exactly as a linear combination of the eigenfunctions of a Hermitian operator

$$|\Psi\rangle = \sum_n |f_n\rangle c_n$$

Some random function

eigenfunction of Hermitian operator

expansion coefficient

- Proof is beyond this course

- We can understand this result by analogy with ordinary 3D space where any vector **r** can be expanded as a linear combination of the unit vectors along the x, y, z axes

$$\mathbf{r} = \mathbf{e}_1 x + \mathbf{e}_2 y + \mathbf{e}_3 z = \sum_{n=1}^{3} \mathbf{e}_n x_n$$

$$\text{where} \quad x_1 = x, \quad x_2 = y, \quad x_3 = z$$

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The variational principle

$|\Phi\rangle$ is an **approximate** ground state eigenfunction for the Hamiltonian $\hat{H}$

As usual, its energy is given by

$$E_0^{\mathrm{approx.}} = \frac{\langle\Phi|\hat{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle} \qquad (1)$$

The exact wavefunctions are the eigenfunctions:

$$\hat{H}|\Psi_i\rangle = E_i|\Psi_i\rangle$$

Remember that these are a complete set and so we can use them to expand our approximate wavefunction

$$|\Phi\rangle = \sum_i c_i|\Psi_i\rangle$$

Next, substitute this expansion into (1)

The variational principle (continued)

The numerator becomes:

$$\langle \Phi | \hat{H} | \Phi \rangle = \langle \left(\sum_i c_i \Psi_i \right) | \hat{H} | \left(\sum_j c_j \Psi_j \right) \rangle$$

$$= \sum_i \sum_j c_i^* c_j \langle \Psi_i | \hat{H} | \Psi_j \rangle = \sum_i \sum_j c_i^* c_j \langle \Psi_i | E_j | \Psi_j \rangle$$

$$= \sum_i \sum_j c_i^* c_j E_j \langle \Psi_i | \Psi_j \rangle = \sum_i \sum_j c_i^* c_j E_j \delta_{ij} = \sum_i |c_i|^2 E_i \quad (2)$$

In a similar way, the denominator becomes:

$$\langle \Phi | \Phi \rangle = \sum_i |c_i|^2 \quad (3)$$

The variational principle (continued)

By combining (2) and (3) we obtain a relation for $E_0^{\mathrm{approx.}}$:

$$E_0^{\mathrm{approx.}} = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \frac{\sum_i E_i |c_i|^2}{\sum_j |c_j|^2} \geq \frac{\sum_i E_0 |c_i|^2}{\sum_j |c_j|^2} = \frac{E_0 \sum_i |c_i|^2}{\sum_j |c_j|^2} = E_0$$

by definition, the ground state energy is the lowest

$$\ldots E_3 \geq E_2 \geq E_1 \geq E_0$$

Therefore: $E_0^{\mathrm{approx.}} \geq E_0$ **for all approximate wavefunctions**

- The exact ground state energy is lower than any approximation

- Therefore any change to an approximate wavefunction that lowers the energy is an improvement

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The Hartree-Fock equations

Starting from the energy of a Slater determinant wavefunction:

$$E_{SD} = 2 \sum_{i=1}^{N_{elec}/2} h_i + \sum_{i=1}^{N_{elec}/2} \sum_{j=1}^{N_{elec}/2} (2J_{ij} - K_{ij})$$

It can be shown (see e.g. Szabo & Ostlund – or ask me outside the lectures) that the energy of the Slater determinant is minimised when the molecular orbitals are solutions of the following eigenvalue equation:

$$\hat{f} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

This is the Fock operator

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The Fock operator

$$\hat{f}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

Is built from three operators:

- Core Hamiltonian
- Coulomb
- Exchange

$$\hat{J}_i(\mathbf{r}_1)\psi_k(\mathbf{r}_1) = \left[\int \psi_i^*(\mathbf{r}_2)\frac{1}{r_{12}}\psi_i(\mathbf{r}_2)d\mathbf{r}_2\right]\psi_k(\mathbf{r}_1)$$

Coulomb operator

$$\hat{f} = \hat{h} + \sum_{i=1}^{N_{elec}/2}\left(2\hat{J}_i - \hat{K}_i\right)$$
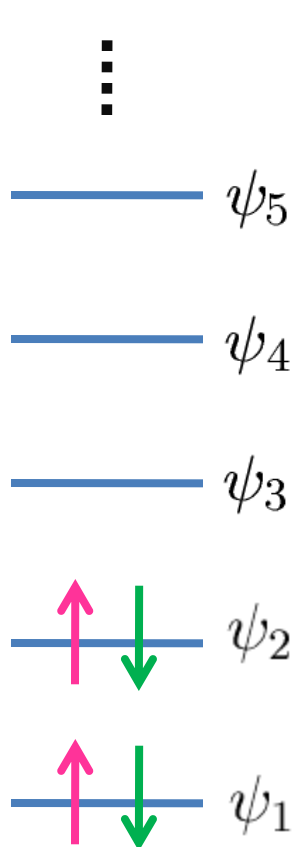
Core Hamiltonian operator

Exchange operator

$$\hat{K}_i(\mathbf{r}_1)\psi_k(\mathbf{r}_1) = \left[\int \psi_i^*(\mathbf{r}_2)\frac{1}{r_{12}}\psi_k(\mathbf{r}_2)d\mathbf{r}_2\right]\psi_i(\mathbf{r}_1)$$

this is not a typo!

$$\hat{h} = -\frac{1}{2}\nabla^2 + \sum_{I=1}^{N_{nuc}}\frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$

Fock operator example with 4 electrons

Fock operator

$$\hat{f} = \hat{h} + 2\hat{J}_1 - \hat{K}_1 + 2\hat{J}_2 - \hat{K}_2$$
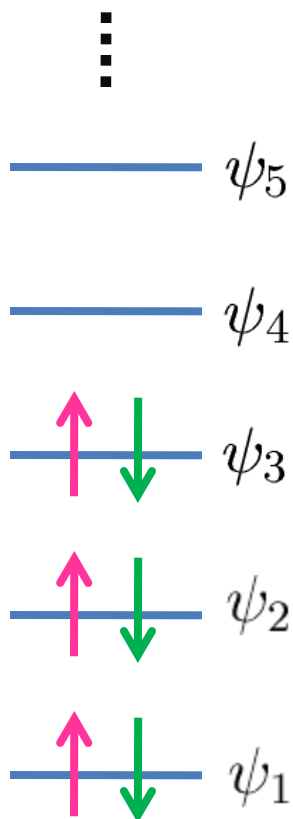
ψ_5

Acting on occupied orbitals

$$\hat{f}\psi_1(\mathbf{r}) = \hat{h}\psi_1(\mathbf{r}) + 2\hat{J}_1\psi_1(\mathbf{r}) - \hat{K}_1\psi_1(\mathbf{r}) + 2\hat{J}_2\psi_1(\mathbf{r}) - \hat{K}_2\psi_1(\mathbf{r})$$

ψ_4

$$= \hat{h}\psi_1(\mathbf{r}) + \hat{J}_1\psi_1(\mathbf{r}) + 2\hat{J}_2\psi_1(\mathbf{r}) - \hat{K}_2\psi_1(\mathbf{r})$$

ψ_3

Cancellation of self-interaction for electron 1

ψ_2

Acting on unoccupied (virtual) orbitals

$$\hat{f}\psi_3(\mathbf{r}) = \hat{h}\psi_3(\mathbf{r}) + 2\hat{J}_1\psi_3(\mathbf{r}) - \hat{K}_1\psi_3(\mathbf{r}) + 2\hat{J}_2\psi_3(\mathbf{r}) - \hat{K}_2\psi_3(\mathbf{r})$$

ψ_1

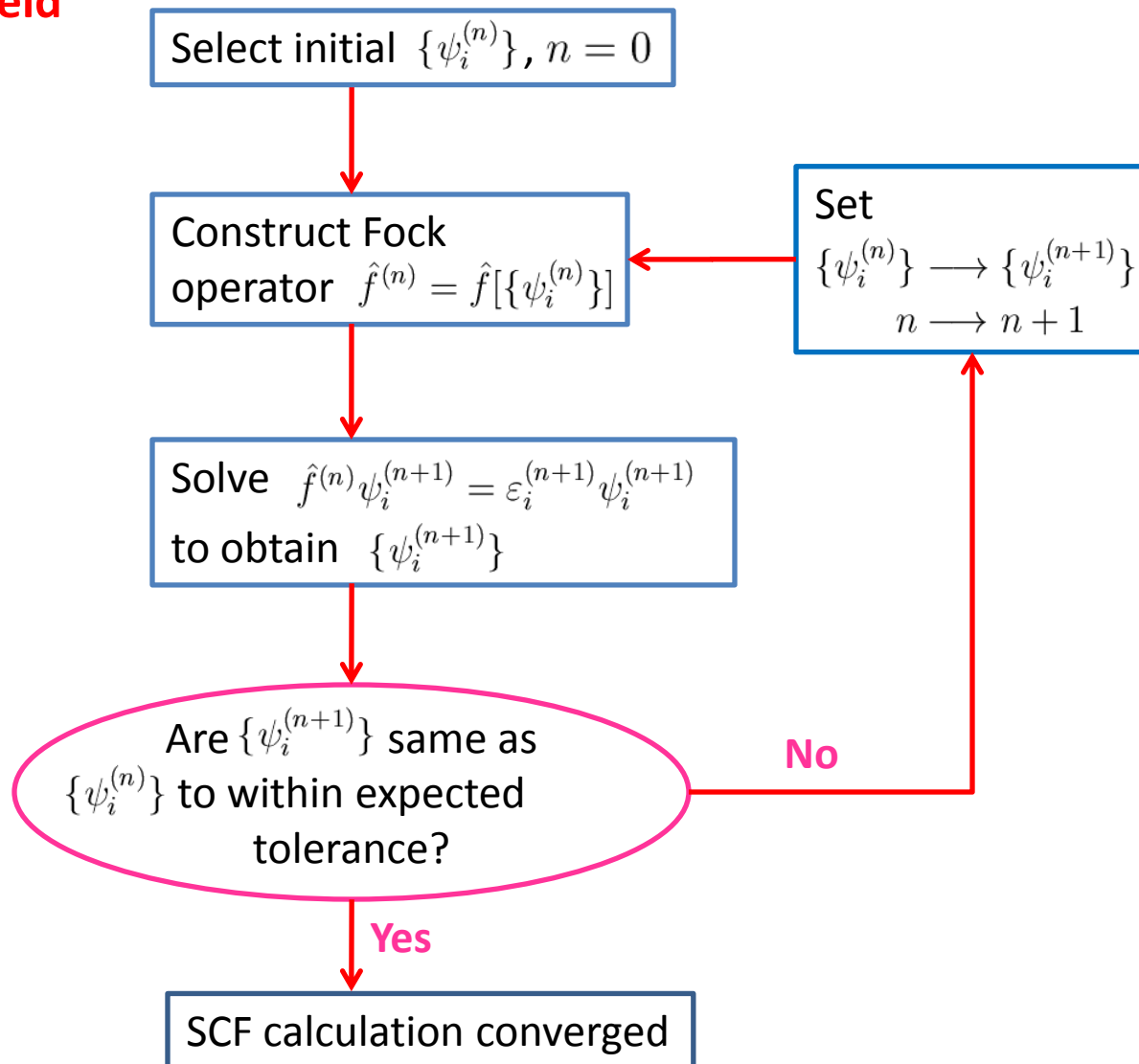# Example of the Hartree-Fock equations

- Let's write down the Hartree-Fock eigenvalue equation for a molecule with 6 electrons, e.g. BeH_2

- Observe the structure of this equation. Can you suggest a way of solving it?

The Fock operator (continued)

- Is Hermitian (try to show this!)

- Its eigenfunctions are the optimal molecular orbitals we seek

- Its eigenvalues are the orbital energies

- It consists of three parts:

  - Core Hamiltonian operator: kinetic energy of an electron and its electrostatic attraction to all the nuclei

  - Coulomb operator: Electrostatic repulsion of an electron from all other electrons

  - Exchange operator: A purely quantum effect (no classical analogue), consequence of the antisymmetry of the electronic wavefunction

The Self-Consistent Field (SCF) procedure

- The Fock operator depends on the molecular orbitals which we seek

- Therefore an iterative procedure needs to be used to find these orbitals

- This procedure is often called a Self-Consistent Field (SCF) calculation

Select initial $\{\psi_i^{(n)}\}$, $n = 0$

Construct Fock operator $\hat{f}^{(n)} = \hat{f}[\{\psi_i^{(n)}\}]$

Set $\{\psi_i^{(n)}\} \longrightarrow \{\psi_i^{(n+1)}\}$
$n \longrightarrow n+1$

Solve $\hat{f}^{(n)} \psi_i^{(n+1)} = \varepsilon_i^{(n+1)} \psi_i^{(n+1)}$ to obtain $\{\psi_i^{(n+1)}\}$

Are $\{\psi_i^{(n+1)}\}$ same as $\{\psi_i^{(n)}\}$ to within expected tolerance?

No

Yes

SCF calculation converged

Summary / Reading assignment

- Variational principle (Cramer, pages 108-110)

- Hartee-Fock method (Cramer, pages 126-129)

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Appendix: The eigenfunctions of a Hermitian operator are orthogonal

Assume A is a Hermitian operator. Let's pick two of its non-degenerate eigenfunctions:

$$\hat{A}|f_i\rangle = a_i|f_i\rangle \qquad \hat{A}|f_j\rangle = a_j|f_j\rangle \qquad a_i \neq a_j$$

$$\langle f_j|\hat{A}|f_i\rangle = a_i\langle f_j|f_i\rangle \qquad \langle f_i|\hat{A}|f_j\rangle = a_j\langle f_i|f_j\rangle$$

$$\langle f_i|\hat{A}|f_j\rangle^* = a_j^*\langle f_i|f_j\rangle^*$$

Because A is Hermitian

$$\langle f_j|\hat{A}|f_i\rangle = a_j\langle f_j|f_i\rangle$$

subtract

$$(a_i - a_j)\langle f_j|f_i\rangle = 0 \quad \longrightarrow \quad \langle f_j|f_i\rangle = 0$$

- Therefore non-degenerate eigenfunctions are orthogonal
- Degenerate eigenfunctions can always be chosen to be orthogonal

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