

# Lecture 29 — The Hartree-Fock Self-Consistent Field Method

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**Reading:** Engel 4th ed., Chapter 10 (Sections 10.4–10.5)

## Learning Objectives

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- Describe the Hartree-Fock (HF) method and the self-consistent field (SCF) procedure
  - Explain the role of Slater determinants in satisfying the Pauli principle
  - Define Coulomb and exchange integrals and interpret them physically
  - Outline Koopman's theorem and its connection to ionization energies
  - Recognize the limitations of Hartree-Fock theory (electron correlation)
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## 1. The Hartree Method

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### The Idea

Each electron moves in the average potential of all other electrons. Replace the exact electron-electron interactions with an effective one-electron potential.

### Self-Consistent Field (SCF) Procedure

1. **Guess** initial orbitals  $\{\phi_i^{(0)}\}$
2. **Calculate** the effective potential  $V_{\text{eff}}^{(0)}$  from these orbitals
3. **Solve** single-electron Schrödinger equations with  $V_{\text{eff}}^{(0)} \rightarrow$  new orbitals  $\{\phi_i^{(1)}\}$
4. **Recalculate**  $V_{\text{eff}}^{(1)}$  from the new orbitals
5. **Repeat** until the orbitals (and energies) converge — **self-consistency**

This iterative process typically converges in 10–50 cycles.

[!NOTE] **Concept Check 29.1** Explain why the Hartree-Fock method is called "self-consistent." Why can't we just solve the equations in a single step like we did for the

## 2. The Slater Determinant

### Problem with Simple Products

A simple product wavefunction  $\psi = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)$  does not satisfy the **antisymmetry requirement** (Pauli principle):

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$$

### Solution: The Slater Determinant

For two electrons:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_a(\mathbf{x}_1) & \chi_b(\mathbf{x}_1) \\ \chi_a(\mathbf{x}_2) & \chi_b(\mathbf{x}_2) \end{vmatrix}$$

where  $\chi_i(\mathbf{x}) = \phi_i(\mathbf{r})\sigma_i(s)$  are **spin-orbitals** (spatial part  $\times$  spin part) and  $\mathbf{x} = (\mathbf{r}, s)$ .

For  $N$  electrons:

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

### Properties of Slater Determinants

1. **Antisymmetric:** exchanging two rows (= exchanging two electrons) changes the sign
2. **Pauli exclusion:** if two columns are identical (= two electrons in same spin-orbital), the determinant is zero
3. **Indistinguishability:** electrons are not assigned to specific orbitals

## 3. The Hartree-Fock Equations

Applying the variational principle to a single Slater determinant gives the **Hartree-Fock equations**:

$$\hat{f}_i \chi_i = \epsilon_i \chi_i$$

where  $\hat{f}_i$  is the **Fock operator**:

$$\hat{f}_i = \hat{h}_i + \sum_{j \neq i} (\hat{J}_j - \hat{K}_j)$$

Term	Name	Physical meaning
$\hat{h}_i$	Core Hamiltonian	KE + nuclear attraction for electron $i$
$\hat{J}_j$	Coulomb operator	Classical repulsion from electron $j$ 's charge cloud
$\hat{K}_j$	Exchange operator	Quantum exchange interaction (no classical analog)

### Coulomb Integral

$$J_{ij} = \iint |\chi_i(\mathbf{x}_1)|^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} |\chi_j(\mathbf{x}_2)|^2 d\mathbf{x}_1 d\mathbf{x}_2$$

This is always **positive** (repulsive) — it is the classical electrostatic repulsion between two charge clouds.

### Exchange Integral

$$K_{ij} = \iint \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{e^2}{4\pi\epsilon_0 r_{12}} \chi_j^*(\mathbf{x}_2) \chi_i(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

This is also **positive** but has no classical counterpart. It arises from the antisymmetry of the wavefunction and is nonzero only for electrons of **parallel spin**.

### Exchange Stabilization

Parallel-spin electrons benefit from exchange: each pair contributes  $-K_{ij}$  to the energy. This is the quantum-mechanical basis for **Hund's first rule** (maximize spin in degenerate orbitals).

[!NOTE] **Concept Check 29.2** Contrast the Coulomb ( $J$ ) and Exchange ( $K$ ) integrals. Which one has a classical electrostatics analogy, and which one is strictly a quantum mechanical consequence of the Pauli principle?

## 4. Koopman's Theorem

$$IE_i \approx -\epsilon_i$$

The ionization energy for removing electron  $i$  is approximately equal to the negative of its orbital energy. This assumes that the remaining orbitals don't relax upon ionization (the "frozen orbital" approximation).

Works well for outer electrons; less accurate for core electrons where relaxation effects are larger.

## 5. Electron Correlation: What HF Misses

The Hartree-Fock method treats each electron as moving in the **average** field of all others. It misses:

- **Instantaneous** electron-electron repulsion (electrons avoid each other more than the average suggests)
- This missing physics is called **electron correlation**

$$E_{\text{correlation}} = E_{\text{exact}} - E_{\text{HF}}$$

$E_{\text{correlation}}$  is always negative (HF gives an energy that is too high).

Methods to recover correlation energy (Week 14):

- Configuration interaction (CI)
- Møller-Plesset perturbation theory (MP2, MP4)
- Coupled cluster (CCSD(T))
- Density functional theory (DFT) — approximate but efficient

## Key Equations Summary

Equation	Expression
Slater determinant	$\Psi = \frac{1}{\sqrt{N!}} \det[\chi_i(\mathbf{x}_j)]$
Fock operator	$\hat{f}_i = \hat{h}_i + \sum_j (\hat{J}_j - \hat{K}_j)$
HF equation	$\hat{f}\chi_i = \epsilon_i\chi_i$
Koopman's theorem	$IE \approx -\epsilon_i$

Equation	Expression
Correlation energy	$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$

## Recent Literature Spotlight

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**"GPU-Accelerated Resolution-of-the-Identity Hartree-Fock Exchange for Large Molecules"** *K. D. Vogiatzis, D. Ma, J. Olsen, L. Gagliardi, W. A. de Jong*, Journal of Chemical Theory and Computation, **2020**, 16, 6753–6764. [DOI](#)

This paper describes how GPU computing dramatically accelerates Hartree-Fock calculations for large molecular systems. By exploiting the resolution-of-the-identity approximation on graphics processing units, the authors achieve orders-of-magnitude speedups over conventional implementations — making the variational SCF method taught in this lecture practical for systems with thousands of basis functions.

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## Practice Problems

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- Slater determinant.** Write the Slater determinant for the ground state of Li ( $1s^2 2s^1$ ). How many terms does it have when expanded?
  - Exchange.** For the carbon atom ( $1s^2 2s^2 2p^2$ ), count the number of exchange pairs for parallel-spin electrons in the ground state ( $^3P$ ). Use this to explain why the  $^3P$  state is lower in energy than the  $^1D$  state.
  - Koopman's theorem.** The HF orbital energies for  $\text{N}_2$  are  $\epsilon_{2\sigma_g} = -1.47$  au,  $\epsilon_{1\pi_u} = -0.61$  au,  $\epsilon_{3\sigma_g} = -0.57$  au. Predict the first three ionization energies (in eV) and identify which orbital the electron is removed from.
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*Next lecture: Electron Spin, Pauli Exclusion & the Aufbau Principle*