

# Lecture 4 – Hartree-Fock theory

## HF theory

Wave Function  
in Terms of  
Orbitals

Hartree Fock  
Theory

Correlation

- 1 The electronic Hamiltonian
- 2 Coulomb and exchange operators.
- 3 One- and two electron integrals
- 4 The total energy of the closed shell.
- 5 Fock equations.
- 6 Koopman's theorem.
- 7 Roothaan equations.
- 8 The correlation problem.

# The electronic Hamiltonian

HF theory

Molecule with  $N_A$  atoms and  $N$  electrons. Born-Oppenheimer approximation in action – nuclei are a set of charges.

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=2}^N \sum_{j=1}^{i-1} \frac{Z_e^2}{|r_i - r_j|} + \sum_{A=2}^{N_A} \sum_{B=1}^{A-1} \frac{Z_A Z_B}{|\vec{r}_A - \vec{r}_B|} + \sum_{A=1}^{N_A} \sum_{i=1}^N \frac{Z_A Z_e}{|\vec{r} - r_A|}$$

- Two last terms establish an external potential. Atomic units:

Electron charge	$Z_e = -1$
Electron mass	$m_e = 1$
Planck constant	$\hbar = 1$
Length	$1\text{au} = 0.529177\text{\AA}$

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# Wave-Function ansatz

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The norm of the wave function determines electron probability distribution

$$P(\vec{r}_1, \dots, \vec{r}_N) = |\Psi(\vec{r}_1, \dots, \vec{r}_N)|^2 \quad (1)$$

Wave function  $\Psi_k(\vec{r}_1, \dots, \vec{r}_N)$  is unwieldy because of its complexity.

# Simplified case with no e-e interaction

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Consider case of  $N$  non-interacting electrons:

$$\hat{H} = \sum_{j=1}^N \hat{h}(j), \quad \hat{h}(j) = - \sum_{I=1}^{N_A} \frac{Z_I}{|r_I - r_j|} - \frac{1}{2} \nabla_j^2 + v_{\text{eff}}(\vec{r}_j) \quad (2)$$

Solve eigenproblem for one-electron Hamiltonians:

$$\hat{h}(j)\psi_k(\vec{r}_j) = \epsilon_k\psi_k(\vec{r}_j) \quad (3)$$

# Wave Function as a Hartree Product

HF theory

The solution to Schrödinger equation with noninteracting Hamiltonian as given by Eq. 2 will be a product of some electron wave functions

$$\Psi_k(\vec{r}_1, \dots, \vec{r}_N) = \psi_i(\vec{r}_1)\psi_j(\vec{r}_2) \dots \psi_k(\vec{r}_N) \quad (4)$$

and the total energy will be a sum of one electron energies

$$E = \epsilon_i + \epsilon_j + \dots + \epsilon_k \quad (5)$$

This product of one-electron wave functions – *Hartree product*. Hartree product does not fulfill the antisymmetry principle (the electronic wave function must change its sign on swapping two electrons) – use Slater determinants instead

$$\Psi_H(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\psi_i(\vec{r}_1)\psi_j(\vec{r}_2) - \psi_i(\vec{r}_2)\psi_j(\vec{r}_1)) \quad (6)$$

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# Wave Function as a Determinant

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The general function  $\Psi(\vec{r}_1, \dots, \vec{r}_N)$  can be represented as a single determinant of one electron functions (so called Slater determinant):

$$\Psi(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & \cdots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \cdots & \psi_N(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix}. \quad (7)$$

Using a Slater determinant to represent the total wave function is an assumption. It makes deriving further expressions simple but it limits the solution space. In particular, electrons appear to move in an uncorrelated fashion with this type of the wave function. Fortunately, it is not a fatal problem.

# The Total Energy of the Closed Shell

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Use Slater determinant as the ansatz for the wave function. Introduce basis set of  $K$  functions and compute the expectation value of the Hamiltonian:

$$E = \langle H \rangle = \sum_{p,q=1}^K h_{pq} d_{pq} + \sum_{p,q,r,s=1}^K d_{pq} g_{pqrs} d_{rs} - \frac{1}{2} \sum_{p,q,r,s=1}^K d_{pq} g_{prqs} d_{rs}$$

Total energy is expressed in terms of one- and two-electron integrals  $h_{pq}$  and  $g_{pqrs}$  that depend only on the basis set and unknown density matrix  $d_{pq}$ .

# One- and Two-Electron Integrals

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The definitions:

$$h_{pq} = \int b_p(\vec{r}) \left( -\frac{1}{2} \nabla^2 \right) b_q(\vec{r}) d\vec{r} + \int \sum_{A=1}^{N_A} \frac{b_p(\vec{r}) b_q(\vec{r})}{|\vec{r} - \vec{r}_A|} d\vec{r}$$

$$g_{pqrs} = \int \int b_p(\vec{r}_1) b_q(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} b_r(\vec{r}_2) b_s(\vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

# Closed-shell Energy Using Orbital Coeff's

HF theory

Express density matrix in terms of orbital coefficients:

$$E = \langle H \rangle = \text{Tr}(h_0 D) + \sum_{p,q,r,s=1}^K g_{pqrs} (d_{pq} d_{rs} - \frac{1}{2} d_{pr} d_{qs})$$

Introduce

$$h_i = \sum_{pq} c_{pi} h_{pq} c_{qi}$$

$$J_{ij} = \sum_{pqrs} c_{pi} c_{qi} g_{pqrs} c_{rj} c_{sj}$$

$$K_{ij} = \frac{1}{2} \sum_{pqrs} c_{pi} c_{qi} g_{prqs} c_{rj} c_{sj}$$

$$E = \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i,j=1}^K (J_{ij} - K_{ij})$$

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# Orbital Energy

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Sometimes, orbital energies  $\varepsilon_k = \langle k|F|k\rangle$  are of special interest:  $d_{pq}^k = c_{pk}c_{qk}$

$$\begin{aligned}\varepsilon_k &= \sum_{pq} h_{pq} c_{pk} c_{qk} + \sum_{pqrs} \sum_i c_{pk} c_{qk} g_{pqrs} c_{ri} c_{si} \\ &\quad - \frac{1}{2} \sum_{pqrs} \sum_i c_{pk} c_{qk} g_{pqrs} c_{ri} c_{si} \\ &= h_i + \sum_i (J_{ik} - K_{ik})\end{aligned}$$

# Hartree-Fock Theory

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The components:

- 1 Use single Slater determinant.
- 2 Optimize total energy as a function of orbital coefficients, keep the norm constant.

# Hartree-Fock approximation – The Essence

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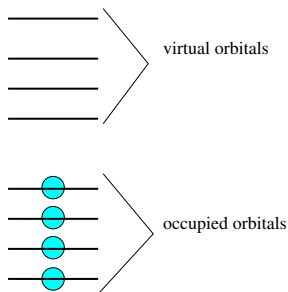


Figure: *auf-bau* principle – occupy lowest orbitals.

- 1 Form an one-electron Fock operator paying attention to the  $v_{\text{eff}}$  part.
- 2 solve Eq. 3 for eigenvalues  $\epsilon_k$  and eigenvectors  $\psi_k(\vec{r})$
- 3 form complete wave function from Eq. 7.

# Koopman's theorem.

Compute  $E_N - E_{N-1}$  where the second energy is for a Slater determinant with one electron removed from a  $k$ th orbital.

$$E_N = \sum_{i=1}^N h_i + \sum_{i,j=1}^K (J_{ij} - K_{ij})$$

$$E_{N-1} = \sum_{i=1}^{i \neq k} h_i + \sum_{i,j=1}^{i,j \neq k} (J_{ij} - K_{ij})$$

The result becomes:

$$\begin{aligned} E_N - E_{N-1} &= h_k + \frac{1}{2} \sum_{i=1}^N (J_{ik} - K_{ik}) + \frac{1}{2} \sum_{j=1}^N (J_{kj} - K_{kj}) \\ &= h_k + \sum_{i=1}^N (J_{kj} - K_{kj}) = \varepsilon_k \end{aligned}$$

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# Roothaan equations

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These are equations that are actually evaluated in programs.  
Density matrix on input, Fock matrix on output.

$$F_{pq} = h_{pq} + \sum_{rs} (2g_{pqrs} - g_{prqs}) d_{rs}$$

Generalized eigenvalue problem generates the orbitals

$$FC = \epsilon SC$$

New density is computed from orbitals

$$d_{pq} = \sum_{i=1}^N c_{pi} c_{qi} \Leftrightarrow D = C_{\text{occ}} C_{\text{occ}}^T$$

# The correlation problem

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$$E_{\text{CORR}} = E - E_{\text{HF}}$$

- Let the wave function consist of many determinants: Configuration Interaction.
- Optimize orbital coefficients and determinant weights simultaneously: MC-SCF with variants.
- Geminal basis sets.
- dynamic correlation: PT2 and CAS-PT2/NEVT-PT2.
- $R_{12}$  explicit correlation.