

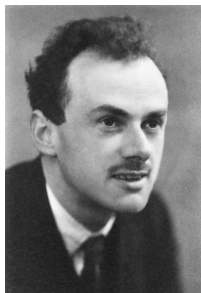


جامعة الملك فهد للبترول والمعادن
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Hartree–Fock Theory

Introduction to Quantum–Chemical Calculations

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*The underlying physical laws necessary for **the mathematical theory** of a large part of physics and **the whole of chemistry are thus completely known**, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be solvable.*

Paul Dirac, 1902-1984

Outline

1 Molecular Model

2 Born–Oppenheimer Approximation

3 Hartree–Fock Theory

Motivation

What can be achieved with quantum–chemical calculations?

- Obtain the geometry of stable molecules
Geometry Optimization, Conformations, Products, etc.
- The relative energies between
Activation and Free Energy, Thermodynamics, etc.
- Chemical and physical properties
Dipole Moment, Polarizability, Ionization Potentials, etc.
- Intermolecular interactions between molecules
Hydrogen bonding, Wan der Vaal, etc.
- Outcomes of experiments
IR Spectrum, UV-Vis, NMR, etc.
- Deepen understanding of data
- Study theoretical and short-lived intermediates

Molecular Model

Bulding a Model

Let us consider the of the molecular system to consist of electrons and atomic nuclei as fundamental units.

Fundamental Interactions

The Coulomb interaction is sufficient (in atomic units):

$$V(\mathbf{r}_{ij}) = \frac{q_i q_j}{r_{ij}}$$

Dynamical Equation

The relevant dynamical equation is Schrödinger equation:

$$H\Psi = i\partial_t\Psi$$

Time and space variables are readily separated as
 $V(\mathbf{r}) = V(\mathbf{r}, t)$:

$$H(\mathbf{r})\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (\text{TISE})$$

The Molecular Hamiltonian

$$H_{mol}(\mathbf{r}) = \underbrace{\sum_{A=1}^M -\frac{1}{2}\nabla_A^2}_{T_n} + \underbrace{\sum_{i=1}^N -\frac{1}{2}\nabla_i^2}_{T_e} + \underbrace{\sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{r_{AB}}}_{V_{nn}} +$$
$$\underbrace{\sum_{A=1}^M \sum_{i=1}^N \frac{-Z_A}{r_{Ai}}}_{V_{ne}} + \underbrace{\sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}}_{V_{ee}}$$

Born–Oppenheimer Approximation

Born–Oppenheimer Approximation

- Nuclei are much heavier than electrons. So electrons reconfigure themselves almost instantly to the relatively very slow changes in nuclear coordinates.
- This justifies an approximate model where the separation of nuclear and electronic coordinates is possible by assuming stationary nuclei while solving the dynamics of electrons. This is known as the **Born–Oppenheimer approximation**.
- This allows us to reduce the computational complexity of the problem by **solving the electronic schrodinger equation with parameteric dependence on nuclear coordinates**.
- This separates Schrödinger into two equations:
 - 1 **nuclear**, describing a potential energy surface
 - 2 **electronic**, providing E_e for given nuclear coordinates

With $\Psi_{mol}(\mathbf{r}, \mathbf{R}) = \Psi_n(\mathbf{R})\Psi_e(\mathbf{r}; \mathbf{R})$ and $H_{mol} = T_n + V_{nn} + H_e$:

The Electronic Schrödinger Equation (ESE)

$$H_e(\mathbf{r}; \mathbf{R})\Psi_e(\mathbf{r}; \mathbf{R}) = E_e(\mathbf{R})\Psi_e(\mathbf{r}; \mathbf{R})$$

H_e , the electronic hamiltonian: $H_e(\mathbf{r}; \mathbf{R}) = T_e + V_{en} + V_{ee}$

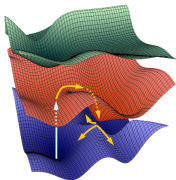
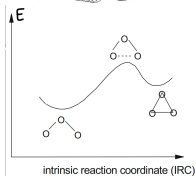
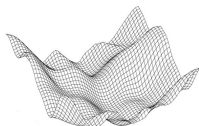
ESE may be solved to give E_e , Ψ_e for given a \mathbf{R} .

The Nuclear Schrödinger Equation

$$(T_n + V_{nn} + E_e(\mathbf{R}))\Psi_n(\mathbf{R}) = E_{mol}\Psi_n(\mathbf{R})$$

NSE maybe though of as mapping between the internuclear coordinates configuration space and E_{mol} , which represented as a parametric hypersurface called the **Potential Energy Surface**.

Potential Energy Surface (PES)



Chemistry in the PES

- minima on the PES represent stable molecules
- paths between minima represent reactions
- 1^o saddle points generally represent transition states

Molecular Properties

Many properties are known by the response of PES under an external field or a perturbation.

The Many-Electron Wavefunction

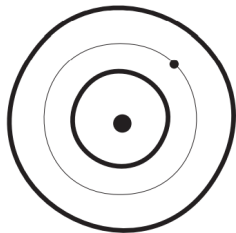
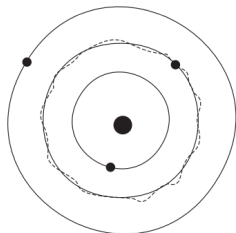
- We talked about the hamiltonian, but what about Ψ ?
- In order to satisfy the **Pauli principle**, fermion systems must be antisymmetric under particle interchange
$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_n) = -\Psi(\sigma_{\text{odd}}(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_n))$$
where \mathbf{x} represent spacial and spin coordinates.
- Therefore, **simple multiplication of individual wavefunction will not obey Pauli's principle.**
- The **Slater Determinant** is a form of the many-electron wavefunction that satisfies Pauli's principle:

$$\Psi_{SD}(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_i(\mathbf{x}_1) & \phi_j(\mathbf{x}_1) & \cdots & \phi_n(\mathbf{x}_1) \\ \phi_i(\mathbf{x}_2) & \phi_j(\mathbf{x}_2) & \cdots & \phi_n(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_i(\mathbf{x}_N) & \phi_j(\mathbf{x}_N) & \cdots & \phi_n(\mathbf{x}_N) \end{vmatrix}$$

where ϕ represent spin-orbitals. Notice how the Determinant reflect indistinguishability.

Hartree–Fock Theory

Mean-Field Theory



- Even with BO approximation, our system has $4n$ non-separable degrees of freedom due to electron-electron interactions.
- **Mean-field theory** studies an approximate model in which for each particle, all interactions with other particles are replaced by average interactions.
- Thus transforming a many-body problem into many one-body problems.
- Example of a mean-field approximation for the solar system (left).

Hartree–Fock Theory

- **Hartree–Fock approximation** assumes the interaction of each electron with the **average electron density** of all other electrons in place of electron-electron repulsion.
- The goal in HF theory is to find the **single slater determinant Ψ_{SD} solution** to the electronic Schrödinger equation corresponding to the ground state, E_{gs} .
- But how do we know what the average is here?

The Variational Principle

The variational principle states that the energy expectation value $\langle E \rangle$ of **any trial wavefunction ψ is always an overestimate of the ground state energy unless it is equal E_{gs}** :

$$E_{gs} \leq \langle E_{\text{trial}} \rangle = \langle \psi_{\text{trial}} | H_e | \psi_{\text{trial}} \rangle$$

- The variational method provides the needed approximation technique as it always provides an energy upper bound.
- **Thus, the trial wavefunction minimizing the expectation energy corresponds to the solution Ψ_{SD} and E_{gs} !**

Before proceeding further, let's introduce some notation:

One-electron and Two-electron operators

We can re-write H_e as a summation of the **one-** and **two-electron operators**, h and v , over the electrons:

$$H_e = \sum_i \hat{h}(i) + \hat{v}(i)$$
$$\hat{h}(i) \equiv \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{\text{Nuclei}} \frac{Z}{r_{Ai}} \quad \hat{v}(i) \equiv \sum_{j>i}^n r_{ij}^{-1}$$

To calculate the expectation energy:

$$\langle E \rangle = \langle \Psi | H_e | \Psi \rangle = \sum_i \overbrace{\langle \Psi | \hat{h}(i) | \Psi \rangle}^{\text{One-electron Integral}} + \overbrace{\langle \Psi | \hat{v}(i) | \Psi \rangle}^{\text{Two-electron Integral}}$$

One-electron and Two-electron Integrals

$$h_{ij} \equiv [i|h|j] = \int d\mathbf{x}_1 \phi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \phi_j(\mathbf{x}_1)$$

$$[ij|kl] \equiv \int d\mathbf{x}_1 d\mathbf{x}_2 \phi_i^*(\mathbf{x}_1) \phi_j(\mathbf{x}_1) r_{12}^{-1} \phi_k^*(\mathbf{x}_2) \phi_l(\mathbf{x}_2)$$

$$J_{ij} \equiv [ii|jj] \quad \text{Coulomb Integral}$$

$$K_{ij} \equiv [ij|ji] \quad \text{Exchange Integral}$$

$$\langle E \rangle = \sum_i^n h_i + \sum_{j>i} J_{ij} - K_{ij}$$

Hartree–Fock Equations

- We have to obtain a nice expression for the expectation energy, but **the objective is to find the set of molecular orbitals (MOs) that minimize the energy.**
- For that we can use the *Lagrange multipliers* with the orthonormal constraint of MOs.
- The solution MOs define an energy minima, so small variation in the MOs should not change the Lagrangian:

$$\delta L = \delta E - \sum_{ij} \lambda_{ij} (\langle \delta \phi_i | \phi_j \rangle - \langle \phi_i | \delta \phi_j \rangle) = 0$$

- Solving this and diagonalizing the matrix λ , we obtain:

HF equations: $\boxed{F_i \phi_i = \epsilon_i \phi_i}$ $F_i \equiv h_i + \sum_j^n J_{ij} - K_{ij}$

We note the following about the HF equation, $F_i\phi_i = \epsilon_i\phi_i$:

- 1 Because MOs depend on the Fock operator F which depends on MOs, it is a **pseudo-eigenvalue equation** that must be solved iteratively.
- 2 **Physical interpretation**: the expectation value of the Fock operator are MO energies ϵ_i .
- 3 Because it requires knowledge of the occupied MOs, the HF equations are **difficult to solve numerically**.

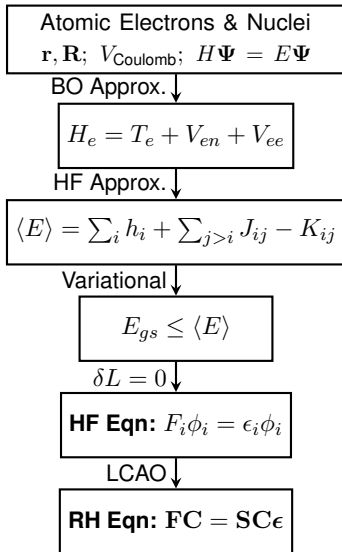
Considering MOs as a **Linear Combination of Atomic Orbitals (LCAO)**, that is as an expansion in the in the *atomic orbital* (AO) basis functions χ . Expanding in AOs in the HF equations yields:

Roothaan–Hall equation

$$\mathbf{FC} = \mathbf{SC}\epsilon$$

$$F_{ab} = \langle \chi_a | \mathbf{F} | \chi_b \rangle \quad ; \quad S_{ab} = \langle \chi_a | \chi_b \rangle$$

Summary



Thank you!

Questions?

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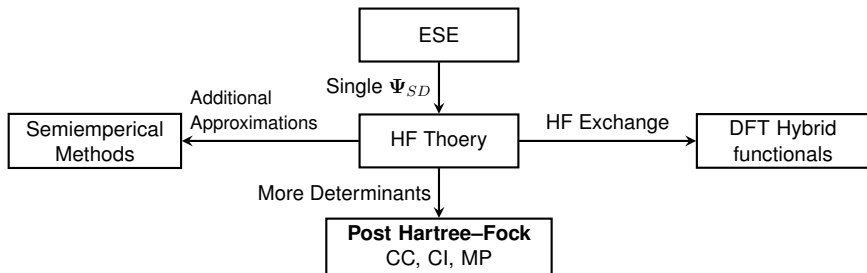
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Limitations

- Electron correlation $E_{\text{Exact}} = E_{\text{HF}} + E_{\text{Corr}}$ (model error)
- Incomplete Basis set error
- Neglect of magnetic and relativistic effects, nuclear spin, external fields.
- Nuclear–electron correlation (e.g. John–Teller)

Application of Hartree–Fock

- HF energy, PES, and chemical kinetics
- Equilibrium geometry -> vibrational frequencies
- Electrostatic potential, dipole moment, polarizability
- Molecular orbitals, Ionization potential, electron affinity



- Post Hartree–Fock models account for electron correlation by considering excited configurations and perturbations.
- The HF energy is **the zeroth or first order term** in **Post-HF Methods**: configuration interaction, coupled cluster, Moller-Plesset perturbation theory.
- In Kohn–Sham DFT, hybrid functionals incorporate exchange Hartree–Fock terms.
- HF is an approximate theory that can be solved exactly while DFT is an exact theory that is solved approximately.

SCF Procedure

- 1 Input geometry and choose basis set
- 2 Calculate all one- and two-electron integrals
- 3 Generate initial guess for the MO coefficients
- 4 Form the density matrix $D_{ab} = \sum_i^{occ.MO} c_{aj}c_{bj}$
- 5 Form the Fock matrix $\mathbf{F} = \mathbf{h} + 2\mathbf{J} - \mathbf{K}$
- 6 Diagonalize the Fock matrix. The eigenvectors contain the new MO coefficients.
- 7 Form the new density matrix.
- 8 Check converges, if not otherwise go to step 4.

