Hartree-Fock: Review

And answers to basic questions in QM and Computational Chemistry

Inbal Oz

Computational Chemistry Lab,
March 2018

TEL AVIV UNIVERSITY אוניברסיטת תל אביב

Outline

- Introduction

- The Slater determinant

- The SCF procedure

- Restricted and unrestricted HF

- Basis sets

- Reference energies

"The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved."

— Paul A. M. Dirac

'Quantum Mechanics of Many-Electron Systems', *Proceedings of the Royal Society* (1929),

Introduction

- Molecular quantum mechanics aims to solve the time-independent Schrödinger equation (SE).

→Determine the electronic structures of atoms and molecules.

- In this lab we introduce some of the computational techniques that are used to solve the SE for electrons in molecules.

→Equations

→Approximations

Introduction

- We concentrates on the calculation of the electronic wavefunction and the electronic energy.

- Single point calculations → potential energy surface.

- Once those quantities are known:

- Minimum of potential energy surface: equilibrium structure.

- Gradient: force constants and vibrational frequencies.

- Stationary points: transition states in a reactive system.

Introduction

HyperChem:

- Molecular Mechanics

→ Newtonian particles under (different) force field.

→ Cut-off interaction distance to reduce computational burden.

- Ab-initio

→ Arbitrary basis set for expanding the molecular orbitals.

- Semiempirical

→ Solve the SE, with certain approximations (only valence electrons, neglecting the integrals for certain interactions, using non-optimized electron orbital basis functions…)

Outline

- Introduction

- The Slater determinant

- The SCF procedure

- Restricted and unrestricted HF

- Basis sets

- Reference energies

Formulation

- The crucial complication: electron-electron interactions.

- As a first step, we assume that the solution is similar to the form without interactions.

$$H^\circ \psi^\circ = E^\circ \psi^\circ \qquad H^\circ = \sum_{i=1}^{n} h_i$$

$$\psi^\circ = \psi_a^\circ(1)\psi_b^\circ(2)\dots\psi_z^\circ(n)$$

Formulation

- Taking into account the spin:

$$\psi^\circ(\boldsymbol{x}; \boldsymbol{R}) = (n!)^{-1/2}\det|\phi_a(1)\phi_b(2)\dots\phi_z(n)|$$

→Slater determinant.

→Goes to zero if any two spin orbitals are the same (=Pauli exclusion principle).

Mean Field Approximation

- In the HF method, we search for a Slater determinant using an average electron-electron repulsion.

- Each electron moves in the field created by the nuclei and the other $n - 1$ electrons.

- The spinorbital that give the lowest energy are found using variational theory.

Outline

- Introduction

- The Slater determinant

- The SCF procedure

- Restricted and unrestricted HF

- Basis sets

- Reference energies

The Roothaan equations

- For a given spatial function,

$$f_1 \psi_a(1) = \varepsilon_a \psi_a(1)$$

- where the Fock operator is

$$f_1 = h_1 + \sum_u \{2J_u(1) - K_u(1)\}$$

$$J_r \psi_s(1) = \left\{ \int \psi_r^*(2) \left(\frac{e^2}{4\pi\varepsilon_0 r_{12}} \right) \psi_r(2) \mathrm{d}\tau_2 \right\} \psi_s(1)$$

$$K_r \psi_s(1) = \left\{ \int \psi_r^*(2) \left(\frac{e^2}{4\pi\varepsilon_0 r_{12}} \right) \psi_s(2) \mathrm{d}\tau_2 \right\} \psi_r(1)$$

The Roothaan equations

- We introduce a set of M basis functions θ_j,

$$\psi_i = \sum_{j=1}^{M} c_{ji}\theta_j$$

- Our goal: find the coefficients.
- We substitute the expansion into the equation for a given spatial function

$$f_1 \sum_{j=1}^{M} c_{ja}\theta_j(1) = \varepsilon_a \sum_{j=1}^{M} c_{ja}\theta_j(1)$$

- Multiplying both sides by the ket and integrating,

$$\sum_{j=1}^{M} c_{ja} \int \theta_i^*(1)f_1\theta_j(1)\,\mathrm{d}r_1 = \varepsilon_a \sum_{j=1}^{M} c_{ja} \int \theta_i^*(1)\theta_j(1)\,\mathrm{d}r_1$$

The Roothaan equations

- The structure becomes more simple if we introduce a compact notation.

$$S_{ij} = \int \theta_i^*(1)\theta_j(1)\, \mathrm{d}\mathbf{r}_1$$ Overlap matrix

$$F_{ij} = \int \theta_i^*(1)f_1\theta_j(1)\, \mathrm{d}\mathbf{r}_1$$ Fock matrix

- We get

$$\sum_{j=1}^{M} F_{ij}c_{ja} = \varepsilon_a \sum_{j=1}^{M} S_{ij}c_{ja} \quad \Longrightarrow \quad \mathbf{Fc} = \mathbf{Sc\varepsilon}$$

Roothaan equations

The Roothaan equations

- Roothan equations:

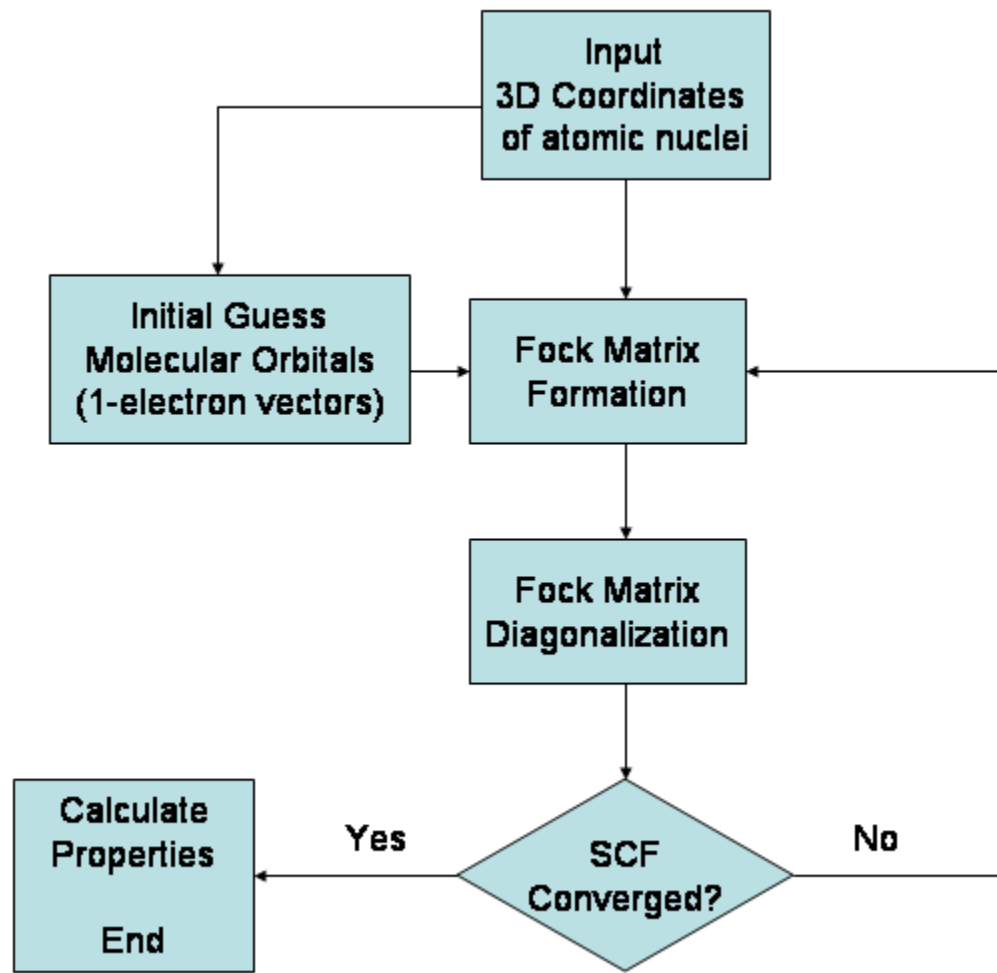$$Fc = Sc\varepsilon$$

- Solution for

$$\det|F - \varepsilon_a S| = 0$$

- The matrix elements F_{ij} involve integrals over the Coulomb and exchange operators which themselves depend on the spatial wavefunctions.

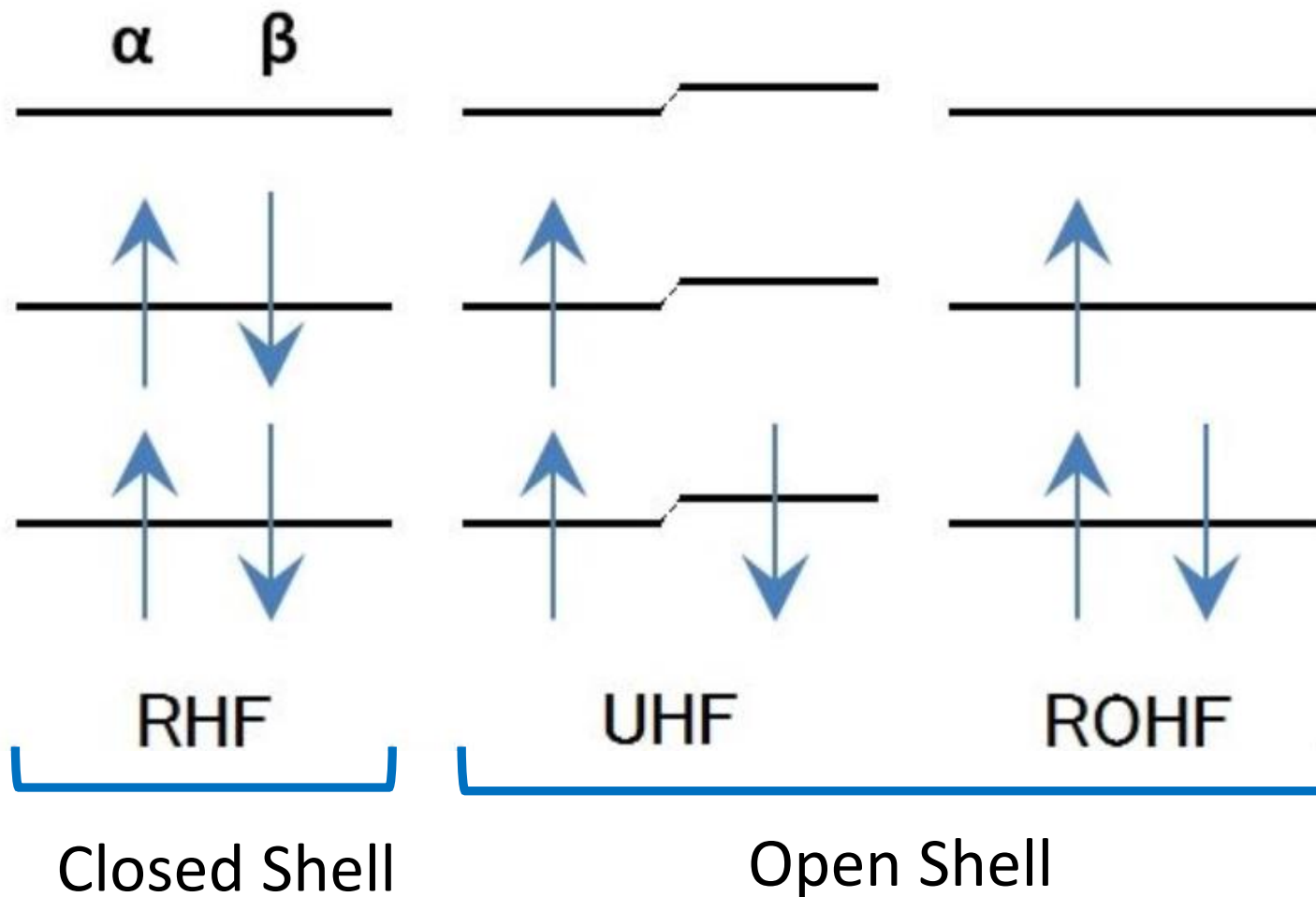→ Self-consistent field approach.

The SCF Procedure

Outline

- Introduction

- The Slater determinant

- The SCF procedure

- Restricted and unrestricted HF

- Basis sets

- Reference energies

Outline

- Introduction

- The Slater determinant

- The SCF procedure

- Restricted and unrestricted HF

- Basis sets

- Reference energies

Basis Sets

- In principle, a complete set of basis functions must be used to represent spinorbitals exactly.

→HF limit.

- Because an infinite basis set is not computationally feasible, a finite basis set is always

→basis-set truncation error.

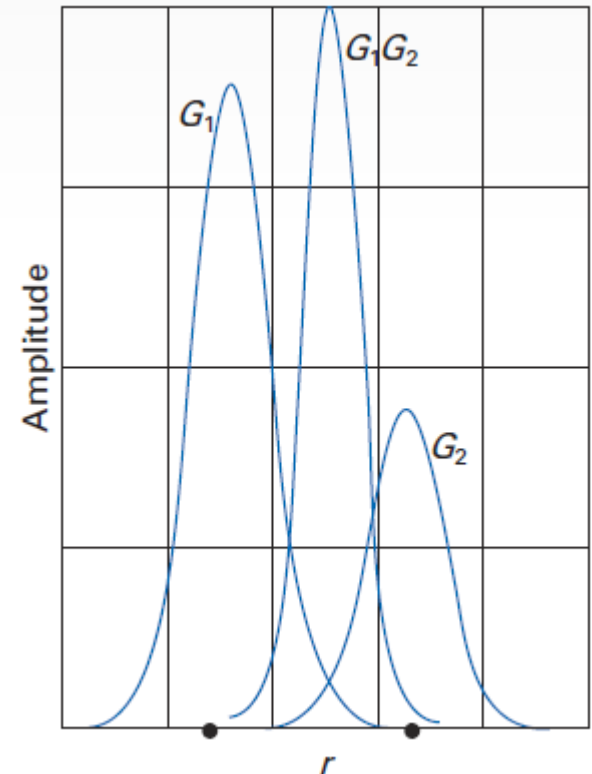- Slater-type orbitals:

$$R(r) = Nr^{n-1}e^{-\zeta r}$$

Gaussian-Type

- Cartesian Gaussians are functions of the form

$$\theta_{ijk}(\mathbf{r}_1 - \mathbf{r}_c) = (x_1 - x_c)^i (y_1 - y_c)^j (z_1 - z_c)^k e^{-\alpha|\mathbf{r}_1 - \mathbf{r}_c|^2}$$

where i, j, k are integers and α is a positive exponent.

- The central advantage: the product of two Gaussians at different centers is another Gaussian.
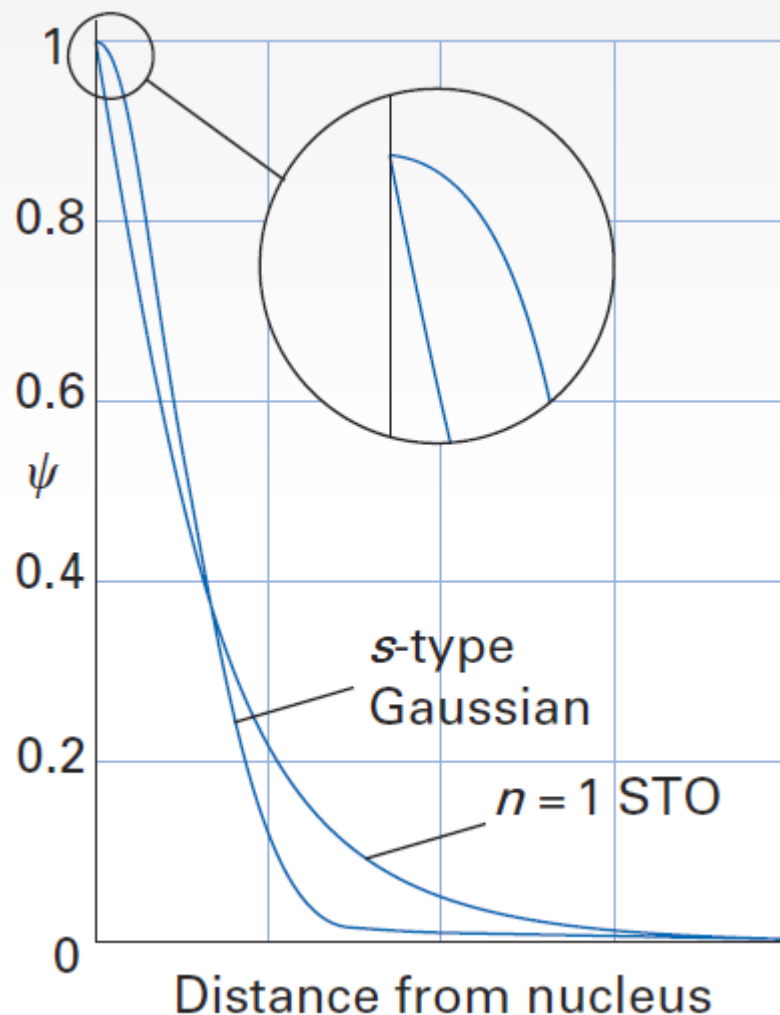
Gaussian-Type

- Disadvantage: a $1s$ hydrogenic atomic orbital has a cusp at the atomic nucleus.

→a larger basis must be used relative to STOs.

- To alleviate the problem: linear combinations of Gaussians.

$$\chi_j = \sum_i d_{ji} g_i$$

$$\psi_i = \sum_j c_{ji} \chi_j$$

Outline

- Introduction

- The Slater determinant

- The SCF procedure

- Restricted and unrestricted HF

- Basis sets

- Reference energies

Reference energies

- Molecular Mechanics: zero when all nuclei are at rest, all springs are at equilibrium and all nuclei are separated by infinite distances.

- Note: we still have a potential energy term.

- HF: Zero when all particles (nuclei and electrons) are at rest, and are separated by infinite distances.

- Note: we can deduce that the LUMO is the energy needed to bring an electron from infinity to our system, and the HOMO is the energy needed to take an electron from the system and place it at infinity.