

Computational Chemistry: Hartree-Fock (HF) Basics

Developed for Physical Chemistry II

Spring 2018

How do we solve Electronic S.E.?

- For systems involving more than 1 electron, still isn't possible to solve it exactly.

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e'^2}{r_{i\alpha}} + \sum_j \sum_{i>j} \frac{e'^2}{r_{ij}}$$

4 $\pi\epsilon_0$ missing b/c
"atomic units"
used – don't worry

- The electron-electron interaction is the culprit
- Orbital approximation not really justified with it because Hamiltonian not separable

If electron-electron repulsion is ignored, Hamiltonian is separable

$$H = \sum_{i=1}^N h_i \quad h_i = -\frac{1}{2} \nabla_i^2 - \sum_{k=1}^M \frac{Z_k}{r_{ik}}$$

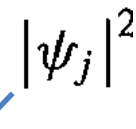
Sum over nuclei

- Set of one-electron equations: solved easily
- Total energy: sum of one-electron energies
- Total wavefunction: product of one-electron wavefunctions

$$h_i \psi_i = \varepsilon_i \psi_i \quad \Psi_{\text{HP}} = \psi_1 \psi_2 \cdots \psi_N \quad E = \sum_i \varepsilon_i$$

"Hartree Product" – for the time being, we are neglecting the Pauli Principle (anti-symmetry) – will add it back in later

Hartree equations: electron-electron repulsion included in an average way

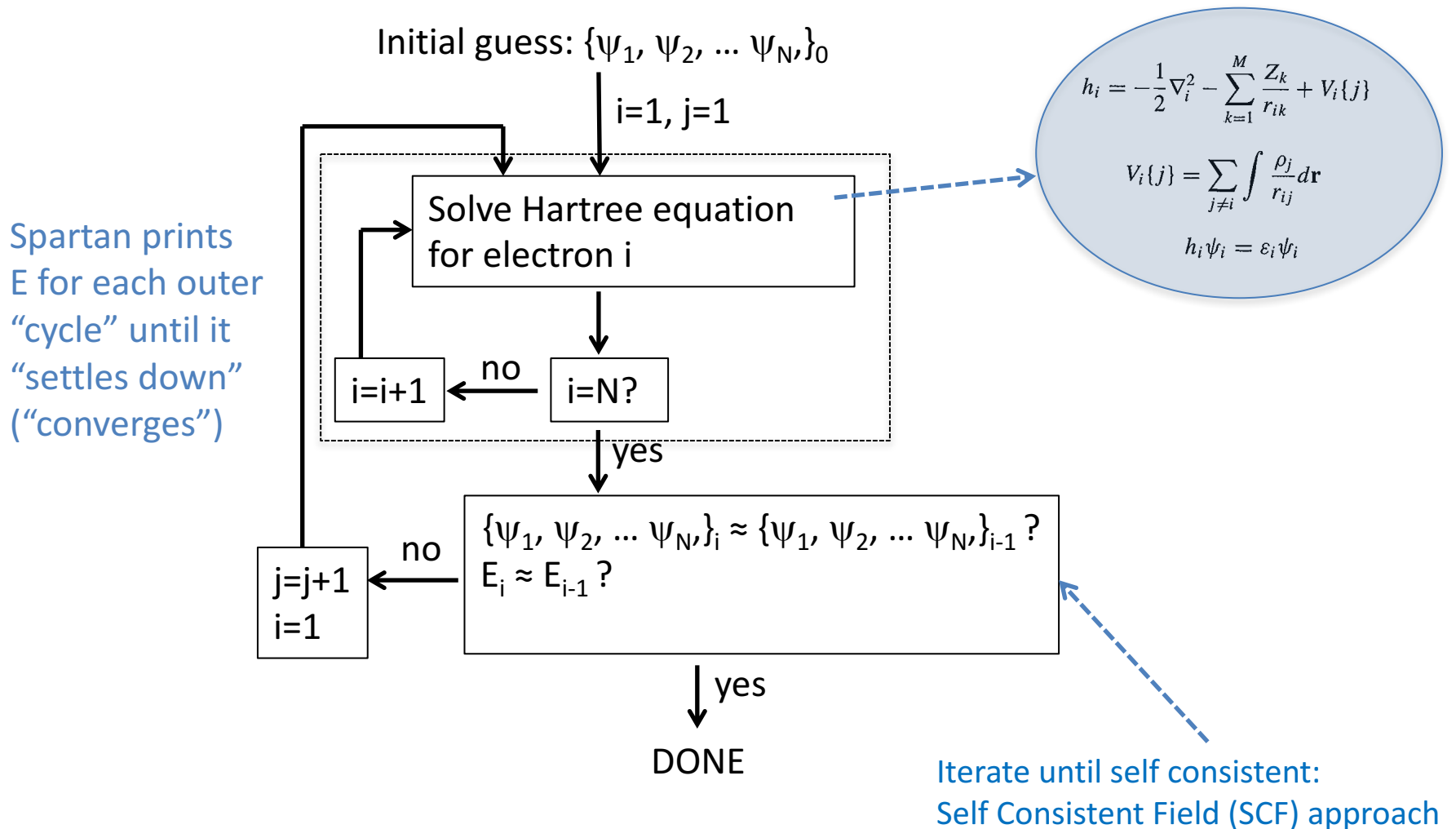
$$h_i = -\frac{1}{2}\nabla_i^2 - \sum_{k=1}^M \frac{Z_k}{r_{ik}} + V_i\{j\} \quad V_i\{j\} = \sum_{j \neq i} \int \frac{\rho_j}{r_{ij}} d\mathbf{r}$$


Can still be treated as separable – with a catch (next slide).

$$h_i \psi_i = \varepsilon_i \psi_i \quad \Psi_{\text{HP}} = \psi_1 \psi_2 \cdots \psi_N$$

Written in atomic units: $m_e = 1, \hbar = 1, 4\pi\epsilon_0 = 1$

Flowchart for solving Hartree equations



Anti-symmetrize: Hartree-Fock method

Fock extended Hartree method so Pauli principle was satisfied.

→ Reformulated using Slater determinants

→ “Roothaan equations”

Solving HF (Roothaan) equations

- Solve with SCF approach (HF-SCF method)
- Big matrix equation to solve → expensive
- Lots of integrals to evaluate → expensive

Semi-empirical methods reduce computer time by replacing some integrals with constants derived from experiment:

- Examples of semi-empirical methods: AM1, PM3, ...
- Fast calculations
- Lower accuracy than full HF-SCF (usually)
- Accuracy limited to class of compounds for which parameters were derived

Accuracy of Hartree-Fock Calculations

- Hartree-Fock wavefunctions typically recover $\sim 99\%$ of the total electronic energy.
 - total energy of O-atom $\approx -75.00 E_h$ (1 Hartree = $1 E_h = 2625.5$ kJ/mol).
 - 1 % of total energy is $0.7500 E_h$ or ~ 1969 kJ/mol
 - With more electrons this gets worse. Total energy of S atom $\approx -472.88 E_h$ (1% of energy is 12415 kJ/mol)
- Fortunately for the Hartree-Fock method (and all Quantum Chemists) chemistry is primarily interested in energy differences, not total energies. Hartree-Fock calculations usually provide at least qualitative accuracy in this respect.
 - Bond lengths, bond angles, vibrational force constants, thermochemistry, ... can generally be predicted qualitatively with HF theory.

Spectroscopic Constants of CO (Total $E_e \approx -300,000$ kJ/mol)

	R_e (Å)	ω_e (cm ⁻¹)	D_e (KJ/mol)
HF/cc-pV6Z	1.10	2427	185
Experiment	1.13	2170	260
% Error	2.7%	11.8%	28.8%