ADF
Technical overview

Mirko Franchini

TCCM Workshop
April 19 | Amsterdam

The Kohn–Sham equations

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{nuc}}(\mathbf{r}) + V_{\mathrm{C}}[\rho,\mathbf{r}] + V_{\mathrm{XC}}[\rho,\mathbf{r}]\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \qquad \rho = \sum_i |\phi_i(\mathbf{r})|^2$$

The Kohn–Sham equations

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{nuc}}(\mathbf{r}) + V_{\mathrm{C}}[\rho,\mathbf{r}] + V_{\mathrm{XC}}[\rho,\mathbf{r}]\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \qquad \rho = \sum_i |\phi_i(\mathbf{r})|^2$$

Kinetic energy

The Kohn–Sham equations

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{nuc}}(\mathbf{r}) + V_{\text{C}}[\rho, \mathbf{r}] + V_{\text{XC}}[\rho, \mathbf{r}]\right)\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$\rho = \sum_i |\phi_i(\mathbf{r})|^2$$

Kinetic energy

Electrostatic potential due to nuclei

$$V_{\text{nuc}}(\mathbf{r}) = \sum_{I \in \text{nuclei}} \frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$

The Kohn–Sham equations

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{nuc}}(\mathbf{r}) + V_{\text{C}}[\rho, \mathbf{r}] + V_{\text{XC}}[\rho, \mathbf{r}]\right)\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$\rho = \sum_i |\phi_i(\mathbf{r})|^2$$

Kinetic energy

Electrostatic potential due to nuclei

Electrostatic potential due to electrons

$$V_{\text{nuc}}(\mathbf{r}) = \sum_{I \in \text{nuclei}} \frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$

$$V_{\text{C}}[\rho, \mathbf{r}] = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}'$$

SCM

The Kohn–Sham equations

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{nuc}}(\mathbf{r}) + V_{\text{C}}[\rho,\mathbf{r}] + V_{\text{XC}}[\rho,\mathbf{r}]\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \qquad \rho = \sum_i |\phi_i(\mathbf{r})|^2$$

Kinetic energy

Electrostatic potential due to nuclei

$$V_{\text{nuc}}(\mathbf{r}) = \sum_{I\in\text{nuclei}} \frac{-Z_I}{|\mathbf{r}-\mathbf{R}_I|}$$

Electrostatic potential due to electrons

$$V_{\text{C}}[\rho,\mathbf{r}] = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}'$$

Exchange-correlation Potential (*e.g.* Xα)

$$V_{\text{XC}}[\rho,\mathbf{r}] \propto \rho(\mathbf{r})^{\frac{1}{3}}$$

SCM

Self-Consistent Field: SCF

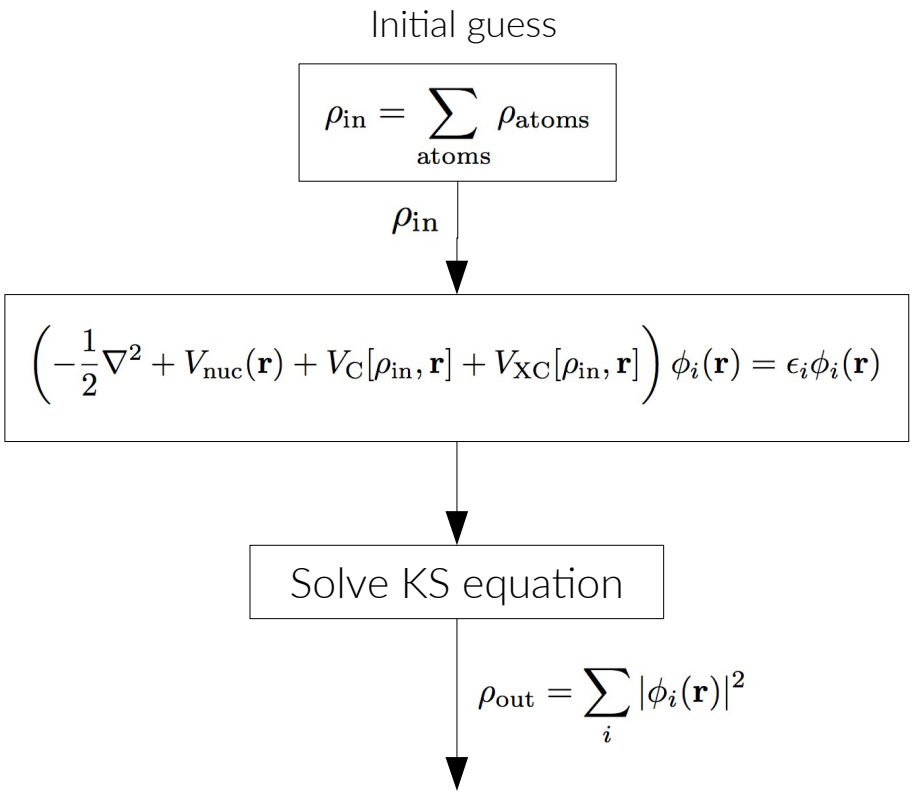
Initial guess

$$\rho_{\text{in}} = \sum_{\text{atoms}} \rho_{\text{atoms}}$$

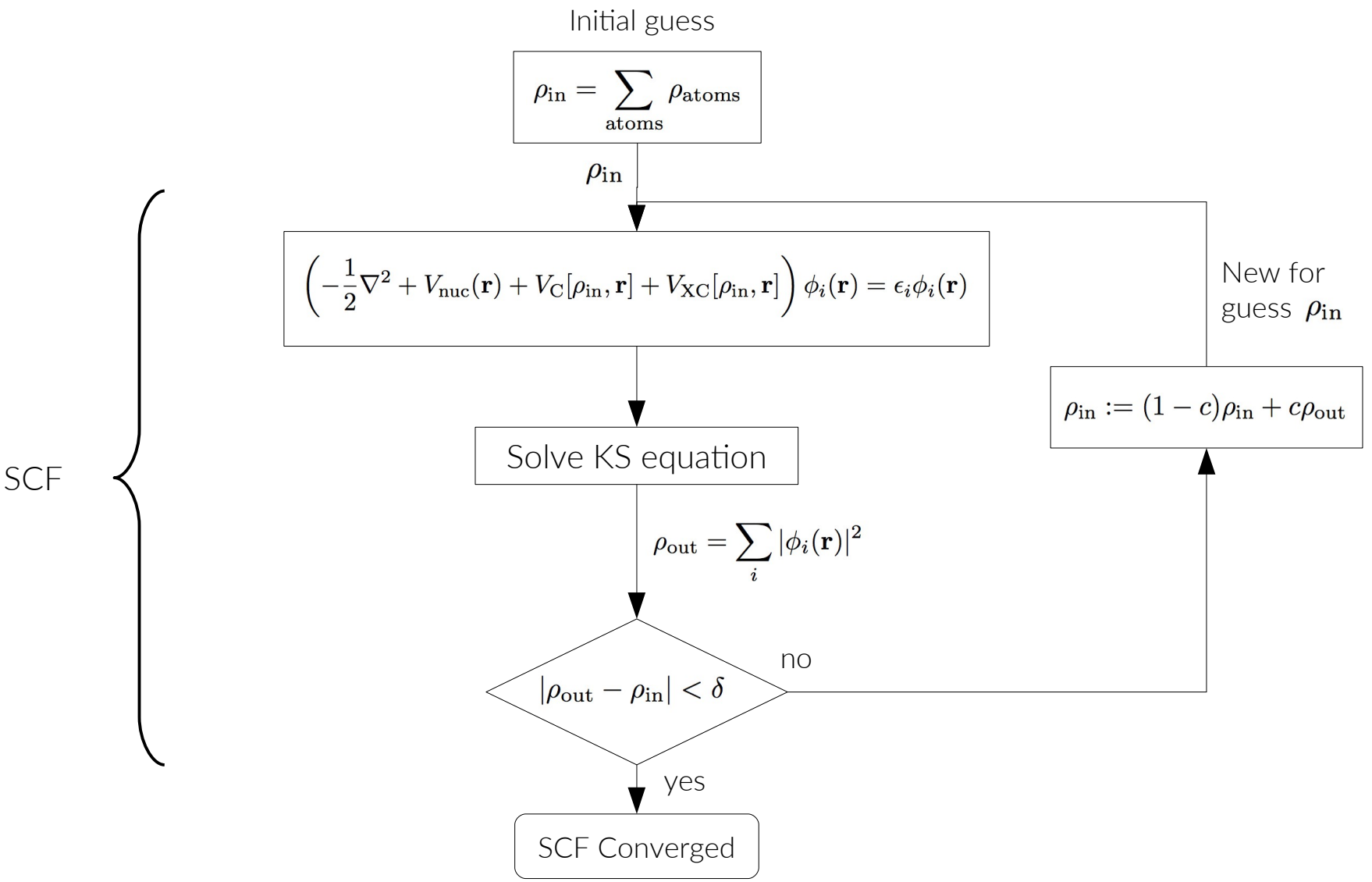
ρ_{in}

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{nuc}}(\mathbf{r}) + V_{\text{C}}[\rho_{\text{in}}, \mathbf{r}] + V_{\text{XC}}[\rho_{\text{in}}, \mathbf{r}]\right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

Self-Consistent Field: SCF



Self-Consistent Field: SCF



Basis set expansion and Fock-Matrix

Kohn-Sham Equation
(difficult to solve)

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{nuc}}(\mathbf{r}) + V_{\mathrm{C}}[\rho,\mathbf{r}] + V_{\mathrm{XC}}[\rho,\mathbf{r}]\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

SCM

Basis set expansion and Fock-Matrix

Kohn-Sham Equation
(difficult to solve)

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{nuc}}(\mathbf{r}) + V_{\mathrm{C}}[\rho,\mathbf{r}] + V_{\mathrm{XC}}[\rho,\mathbf{r}]\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

⇩

basis set expansion

$$\phi_i(\mathbf{r}) = \sum_j c_{ij}\chi_j(\mathbf{r})$$

orbital — expansion coefficients — basis functions

SCM

Basis set expansion and Fock-Matrix

Kohn-Sham Equation
(difficult to solve)

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{nuc}}(\mathbf{r}) + V_{\mathrm{C}}[\rho,\mathbf{r}] + V_{\mathrm{XC}}[\rho,\mathbf{r}]\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

⇩

basis set expansion

$$\phi_i(\mathbf{r}) = \sum_j c_{ij}\chi_j(\mathbf{r})$$

orbital — expansion coefficients — basis functions

⇩

Kohn-Sham Equation
In matrix form
(easy to solve)

$$\sum_j F_{ij}C_{jk} = \epsilon_i \sum_j C_{ij}S_{jk}$$

Fock Matrix — Overlap matrix

$$F_{ij} = \int \chi_i(\mathbf{r})\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{nuc}}(\mathbf{r}) + V_{\mathrm{C}}[\rho,\mathbf{r}] + V_{\mathrm{XC}}[\rho,\mathbf{r}]\right)\chi_j(\mathbf{r})d\mathbf{r}$$

$$S_{ij} = \int \chi_i(\mathbf{r})\chi_j(\mathbf{r})d\mathbf{r}$$

SCM

Basis set expansion and Fock-Matrix

- What basis function do we use in ADF?

$$\phi_i(\mathbf{r}) = \sum_j c_{ij}\chi_j(\mathbf{r})$$

orbital — expansion coefficients — basis functions

- How do we calculate the integrals?

Fock matrix $$F_{ij} = \int \chi_i(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + V_{\text{nuc}}(\mathbf{r}) + V_{\text{C}}[\rho,\mathbf{r}] + V_{\text{XC}}[\rho,\mathbf{r}] \right) \chi_j(\mathbf{r}) d\mathbf{r}$$

Overlap matrix $$S_{ij} = \int \chi_i(\mathbf{r})\chi_j(\mathbf{r}) d\mathbf{r}$$

SCM

Basis functions: LCAO (linear combination of atomic orbitals)

Basis set expansion: $\phi_i(\mathbf{r}) = \sum_j c_{ij}\chi_j(\mathbf{r})$

orbital — expansion coefficients — basis functions

ADF	STO (slater type orbital)	$r^n e^{-\zeta r} Z_{\ell m}(\theta, \phi)$	Solutions of H atom
Band	NAO (numerical atomic orbital)	$N(r) Z_{\ell m}(\theta, \phi)$	Numerical solutions for isolated atoms
	GTO (gaussian type orbital)	$r^n e^{-ar^2} Z_{\ell m}(\theta, \phi)$	Mathematically convenient (looks a bit like a STO)

Fock-Matrix: how do we calculate these integrals?

Khon-Sham Equation
In matrix form

$$\sum_j F_{ij} C_{jk} = \epsilon_i \sum_j C_{ij} S_{jk}$$

Fock Matrix

Overlap matrix

$$F_{ij} = \int \chi_i(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + V_{\text{nuc}}(\mathbf{r}) + V_{\text{C}}[\rho_{\text{in}}, \mathbf{r}] + V_{\text{XC}}[\rho_{\text{in}}, \mathbf{r}] \right) \chi_j(\mathbf{r}) d\mathbf{r}$$

$$S_{ij} = \int \chi_i(\mathbf{r}) \chi_j(\mathbf{r}) d\mathbf{r}$$

$$\int -\frac{1}{2}\chi_i(\mathbf{r}) \nabla^2 \chi_j(\mathbf{r}) d\mathbf{r}$$

$$\int \chi_i(\mathbf{r}) V_{\text{nuc}}(\mathbf{r}) \chi_j(\mathbf{r}) d\mathbf{r}$$

$$\int \chi_i(\mathbf{r}) V_{\text{C}}[\rho, \mathbf{r}] \chi_j(\mathbf{r}) d\mathbf{r}$$

$$\int \chi_i(\mathbf{r}) V_{\text{XC}}[\rho, \mathbf{r}] \chi_j(\mathbf{r}) d\mathbf{r}$$

SCM

Fock-Matrix: how do we calculate these integrals?

Khon-Sham Equation
In matrix form

$$\sum_j F_{ij} C_{jk} = \epsilon_i \sum_j C_{ij} S_{jk}$$

Fock Matrix

Overlap matrix

$$F_{ij} = \int \chi_i(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + V_{\text{nuc}}(\mathbf{r}) + V_{\text{C}}[\rho_{\text{in}}, \mathbf{r}] + V_{\text{XC}}[\rho_{\text{in}}, \mathbf{r}] \right) \chi_j(\mathbf{r}) d\mathbf{r}$$

$$S_{ij} = \int \chi_i(\mathbf{r}) \chi_j(\mathbf{r}) d\mathbf{r}$$

$$\int -\frac{1}{2}\chi_i(\mathbf{r}) \nabla^2 \chi_j(\mathbf{r}) d\mathbf{r}$$

$$\int \chi_i(\mathbf{r}) V_{\text{nuc}}(\mathbf{r}) \chi_j(\mathbf{r}) d\mathbf{r}$$

$$\int \chi_i(\mathbf{r}) V_{\text{C}}[\rho, \mathbf{r}] \chi_j(\mathbf{r}) d\mathbf{r}$$

$$\int \chi_i(\mathbf{r}) V_{\text{XC}}[\rho, \mathbf{r}] \chi_j(\mathbf{r}) d\mathbf{r}$$

Analytical integration?

SCM

Fock-Matrix: how do we calculate these integrals?

Khon-Sham Equation
In matrix form

$$\sum_j F_{ij} C_{jk} = \epsilon_i \sum_j C_{ij} S_{jk}$$

Fock Matrix

Overlap matrix

$$F_{ij} = \int \chi_i(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + V_{\text{nuc}}(\mathbf{r}) + V_{\text{C}}[\rho_{\text{in}}, \mathbf{r}] + V_{\text{XC}}[\rho_{\text{in}}, \mathbf{r}] \right) \chi_j(\mathbf{r}) d\mathbf{r}$$

$$S_{ij} = \int \chi_i(\mathbf{r}) \chi_j(\mathbf{r}) d\mathbf{r}$$

$$\int -\frac{1}{2}\chi_i(\mathbf{r}) \nabla^2 \chi_j(\mathbf{r}) d\mathbf{r}$$

$$\int \chi_i(\mathbf{r}) V_{\text{nuc}}(\mathbf{r}) \chi_j(\mathbf{r}) d\mathbf{r}$$

$$\int \chi_i(\mathbf{r}) V_{\text{C}}[\rho, \mathbf{r}] \chi_j(\mathbf{r}) d\mathbf{r}$$

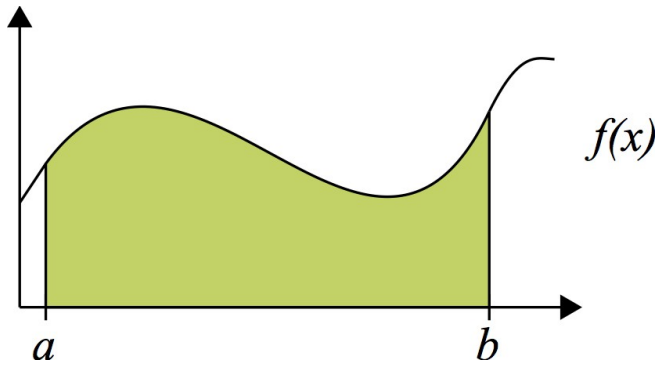
$$\int \chi_i(\mathbf{r}) V_{\text{XC}}[\rho, \mathbf{r}] \chi_j(\mathbf{r}) d\mathbf{r}$$

~~Analytical integration?~~

Numerical integration

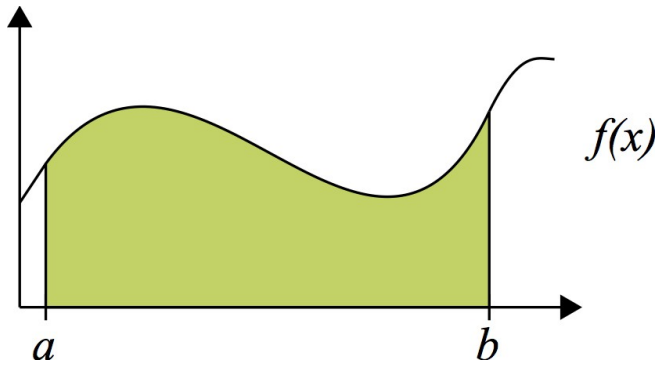
SCM

Numerical Integration

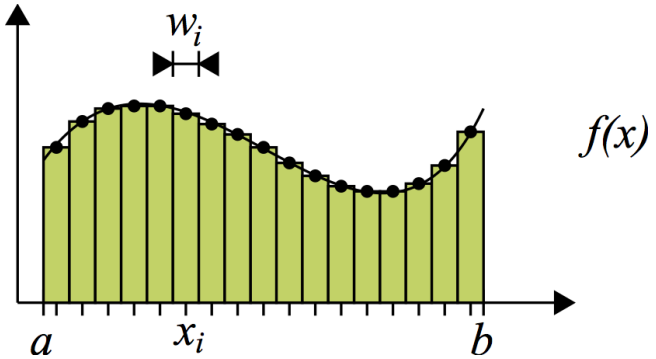


$$\int_a^b f(x)dx$$

Numerical Integration

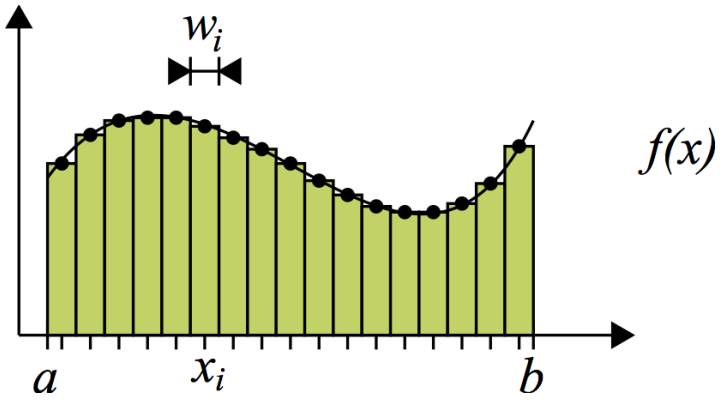


$$\int_a^b f(x)dx$$

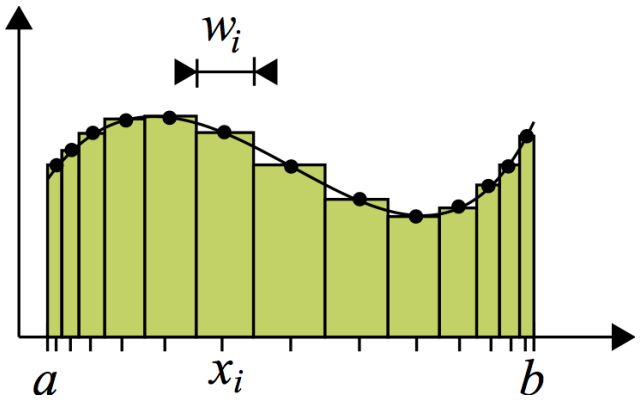


$$\int_a^b f(x)dx = \sum_i w_i f(x_i)$$

Numerical Integration



Regular grid



Gauss-Legendre grid

Choosing the right integration grid is important!

Numerical Integration

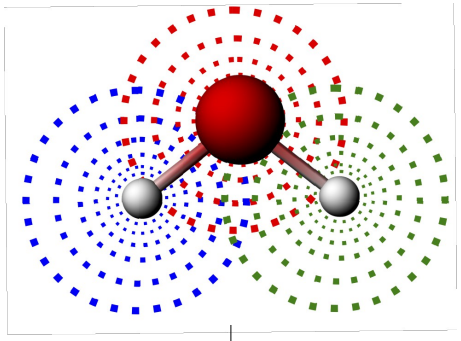
Khon-Sham Equation
In matrix form

$$\sum_j F_{ij} C_{jk} = \epsilon_i \sum_j C_{ij} S_{jk}$$

$$\begin{cases} F_{ij} = \int \chi_i(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + V_{\text{nuc}}(\mathbf{r}) + V_{\text{C}}[\rho_{\text{in}}, \mathbf{r}] + V_{\text{XC}}[\rho_{\text{in}}, \mathbf{r}] \right) \chi_j(\mathbf{r}) d\mathbf{r} \\ S_{ij} = \int \chi_i(\mathbf{r}) \chi_j(\mathbf{r}) d\mathbf{r} \end{cases}$$

$$\begin{cases} \int -\frac{1}{2}\chi_i(\mathbf{r})\nabla^2\chi_j(\mathbf{r})d\mathbf{r} \\ \int \chi_i(\mathbf{r})V_{\text{nuc}}(\mathbf{r})\chi_j(\mathbf{r})d\mathbf{r} \\ \int \chi_i(\mathbf{r})V_{\text{C}}[\rho,\mathbf{r}]\chi_j(\mathbf{r})d\mathbf{r} \\ \int \chi_i(\mathbf{r})V_{\text{XC}}[\rho,\mathbf{r}]\chi_j(\mathbf{r})d\mathbf{r} \end{cases}$$

$$\int \chi_i(\mathbf{r}) V_{\text{XC}}[\rho,\mathbf{r}] \chi_j(\mathbf{r}) d\mathbf{r}$$



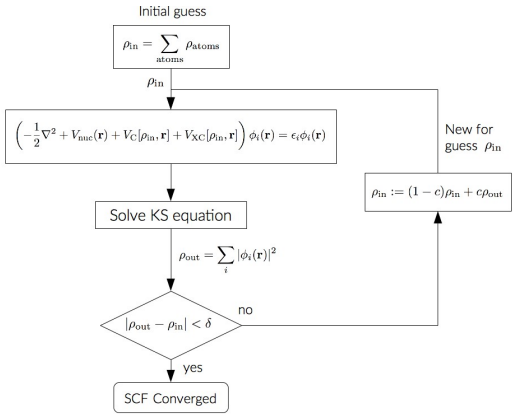
Becke fuzzy cells
integration scheme

$$\sum_k w_k \times \chi_i(\mathbf{r}_k) V_{\text{XC}}[\rho,\mathbf{r}_k] \chi_j(\mathbf{r}_k)$$

SCM

Wrapping up

- Kohn-Sham Equation: high non-linearity → SCF



- Basis set: integro-differential eq. → eq. in matrix form

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{nuc}}(\mathbf{r}) + V_{\text{C}}[\rho, \mathbf{r}] + V_{\text{XC}}[\rho, \mathbf{r}]\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

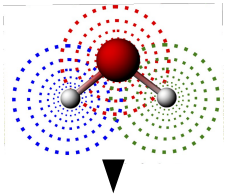
$$\downarrow$$

$$\sum_j F_{ij}C_{jk} = \epsilon_i \sum_j C_{ij}S_{jk}$$

- Matrix elements? Numerical integration

$$\int \chi_i(\mathbf{r}) V_{\text{XC}}[\rho, \mathbf{r}] \chi_j(\mathbf{r}) d\mathbf{r}$$

$$\downarrow$$



$$\downarrow$$

$$\sum_k w_k \times \chi_i(\mathbf{r}_k) V_{\text{XC}}[\rho, \mathbf{r}_k] \chi_j(\mathbf{r}_k)$$

ADF: selected features

Technical:
- Relativistic effects (ZORA, spin-orbit coupling)
- XC: GGAs, meta-GGAs, Hybrids, RS-hybrids
- Efficiently parallelized, linear scaling techniques

Miscellaneous Features:
- Geometry optimization, transition state, IR frequencies
- Solvents and environments: COSMO, QM/MM
- Analysis: energy decomposition, bond analysis
- Electronic transport: NEGF, transfer integrals

Spectroscopy:
- IR, Raman, VCD, Franck-Condon factors
- UV/Vis spectra (TD-DFT)
- Frequency-dependent (hyper-)polarizability
- NMR chemical shift and spin-spin coupling
- ESR (EPR) g-tensor, hyperfine A-tensor, ZFS
- Mössbauer spectroscopy, NRVS

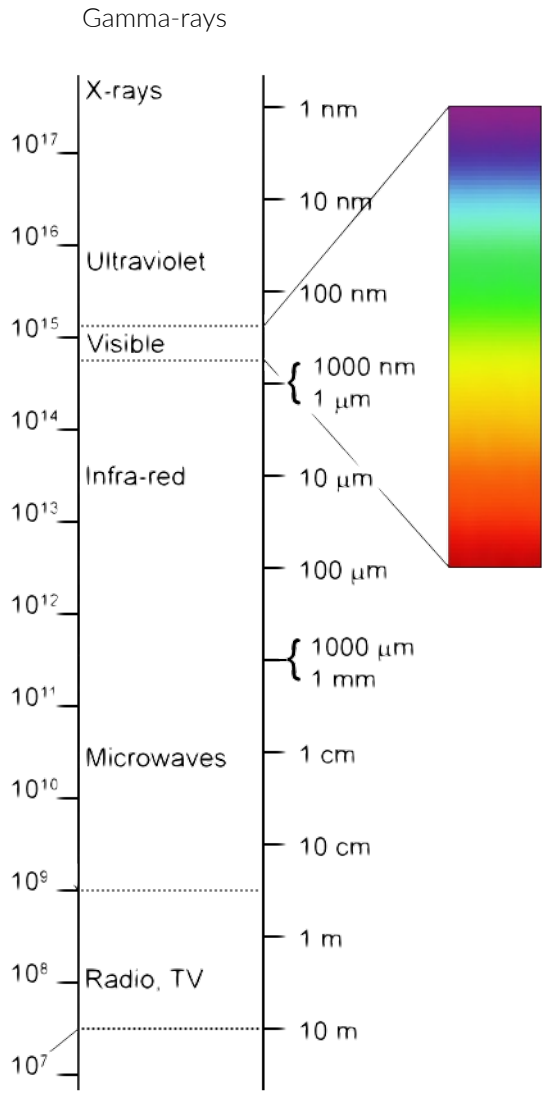
Hands-on session

ADF tutorials: https://www.scm.com/documentation/Tutorials/

- ADF-GUI Tutorial 1: Excitation energies and UV/Vis spectrum of ethene
- ADF-GUI Tutorial 2: Vibrational frequencies and IR spectrum of ethane
- Exercises / AMA (ask me anything)

Spectroscopy

Interaction between matter and electromagnetic radiation



- Mössbauer spectroscopy, NRVS

- Core excitations

- UV/Vis spectra
  oscillator strength, (hyper-)polarizability
  circular dichroism, optical rotation, ...

Electronic Spectroscopy

- IR frequencies
  VCD, Raman, Frank-Condon, VROA

Vibrational Spectroscopy

- EPR
  g-tensor and hyperfine interaction (A-tensor)

- NMR
  chemical shift, spin-spin coupling

SCM

Electronic excitations: Time-dependent DFT (TD-DFT)

Kohn-Sham equations
(ground state)

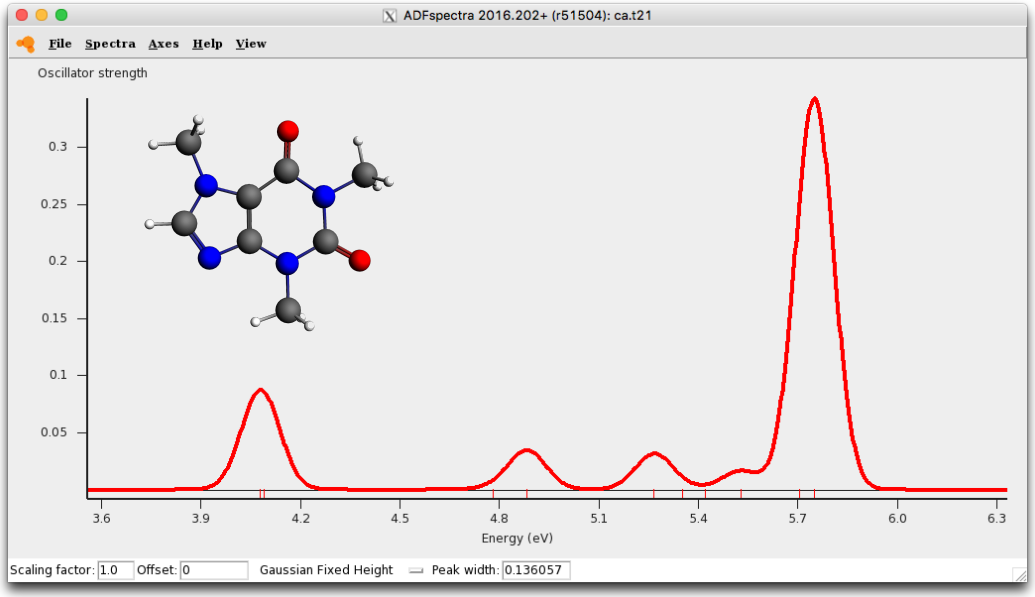
$$(T + V_{\text{nuc\&el}}[\rho] + V_{\text{XC}}[\rho])\phi_i = \epsilon_i \phi_i$$

Time dependent Kohn-Sham equations
(excited states)

$$i\frac{\partial \phi_i}{\partial t} = (T + V_{\text{el-el\&nuc}} + V_{\text{ext}}(t))\phi_i$$

Linear response:
- excitations energies
- oscillator strength

(Line width: gaussian convolution)



Vibrational spectroscopy

Infra red (IR) spectroscopy: absorption of light to excite molecular vibrations

Molecular vibration ⟶ Newtonian mechanics

Harmonic approximation (at the optimized geometry):
- parabolic potential wrt nuclear displacements

Normal modes 'Q': from Hessian $$H_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}$$

Absorption intensity: $$I_{IR} \propto \left(\frac{d\mu}{dQ} \right)^2$$

SCM