Methodology advice

How to be efficient?

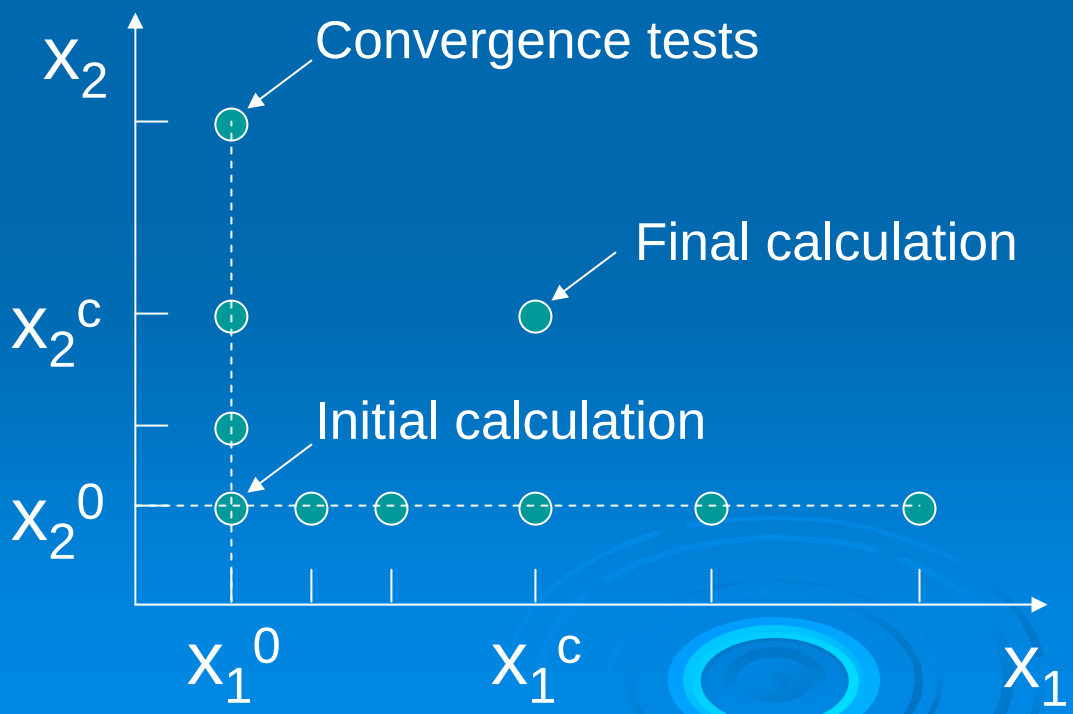
Basic Strategy

- *Explore the possibilities of your problem.*
  - What do you aim for?
  - Is it realistic?
  - Can you do it better?
  - Can you do it easier?
- *Do tests of convergence*
  - Real-space grid
  - Reciprocal-space grid
  - Basis set
  - Functional
- *Do your calculations with converged parameters*

A fully converged calculation is impossible without convergence tests!!

Convergence tests

- Choose relevant magnitude(s) A of the problem (e.g. an energy barrier or a magnetic moment)
- Choose set of qualitative and quantitative parameters x_i (e.g. xc functional, number of k-points, etc)



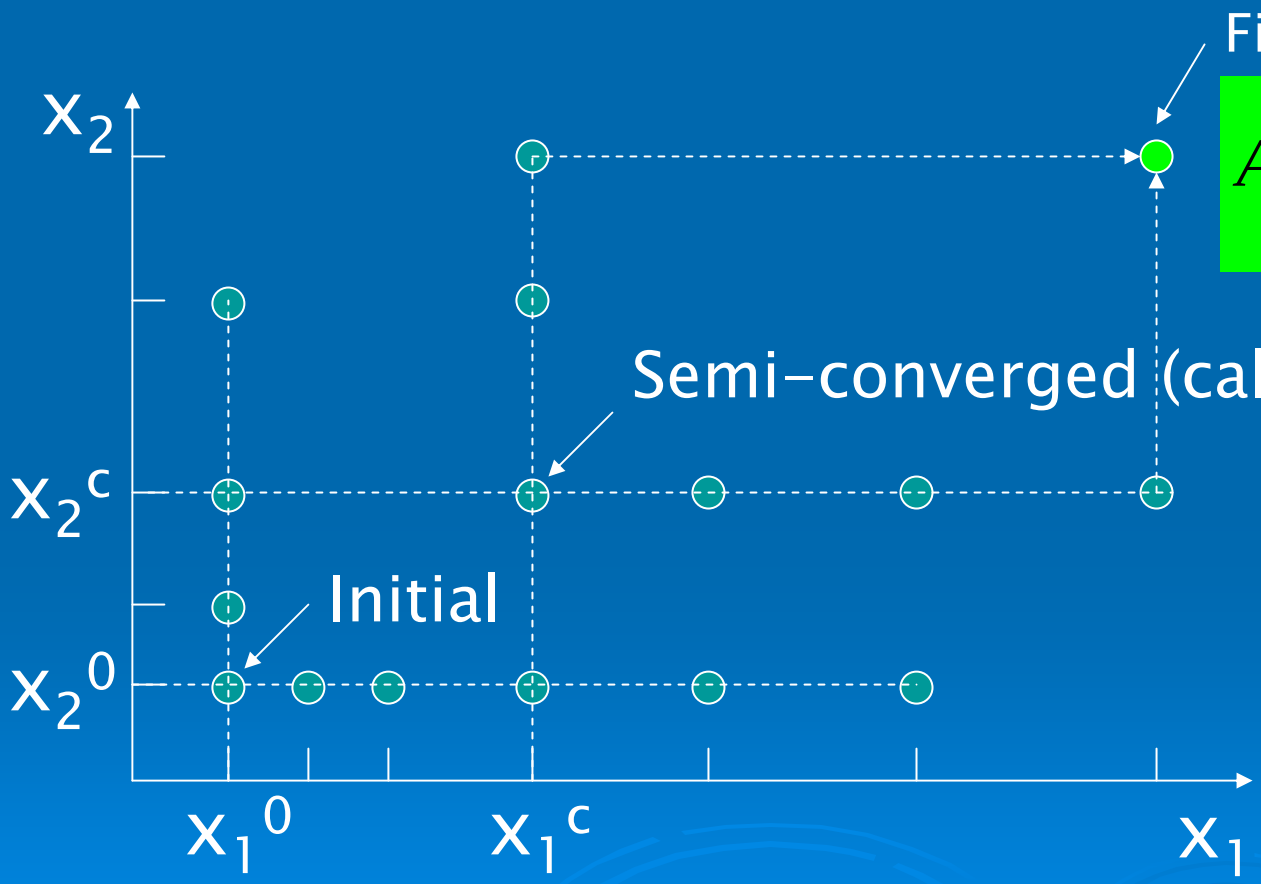
Parameter independence

$$A \approx A_0 + \sum_i \frac{\partial A}{\partial x_i} \delta x_i$$

Monitor:

- Convergence
- CPU time & memory

Multi-stage convergence

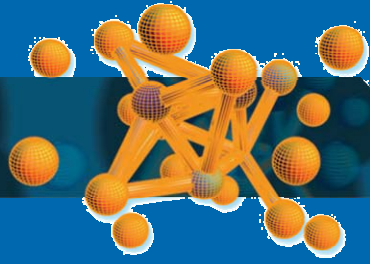


Practical hints

- Ask your objective: find the truth or publish a paper?
- Do not try a converged calculation from the start
- Start with minimum values of all x_i
- Do not assume convergence for any x_i
- Choose a simpler reference system for some tests
- Take advantage of error cancellations
- Refrain from stopping tests when results are “good”

Parameter list

- Pseudopotential
  - Method of generation
  - Number of valence states
  - Number of angular momenta
  - Core radii
  - Nonlinear core corrections
- Number of k-points
- Electronic temperature
- XC functional: LDA, GGAs
- Harris functional vs SCF
- Spin polarization
- SCF convergence tolerance
- Supercell size (solid & vacuum)
- Basis set
  - Number of functions
    - Highest angular momentum
    - Number of zetas
  - Range
  - Shape
    - Sankey
    - Optimized
- Real space mesh cutoff
  - Grid-cell sampling
- Neglect nonoverlap interactions
- O(N) minimization tolerance
- Geometry relaxation tolerance
  - Check of final stability



Harris functional

$$\rho(r) = \Sigma_i |\psi_i(r)|^2$$

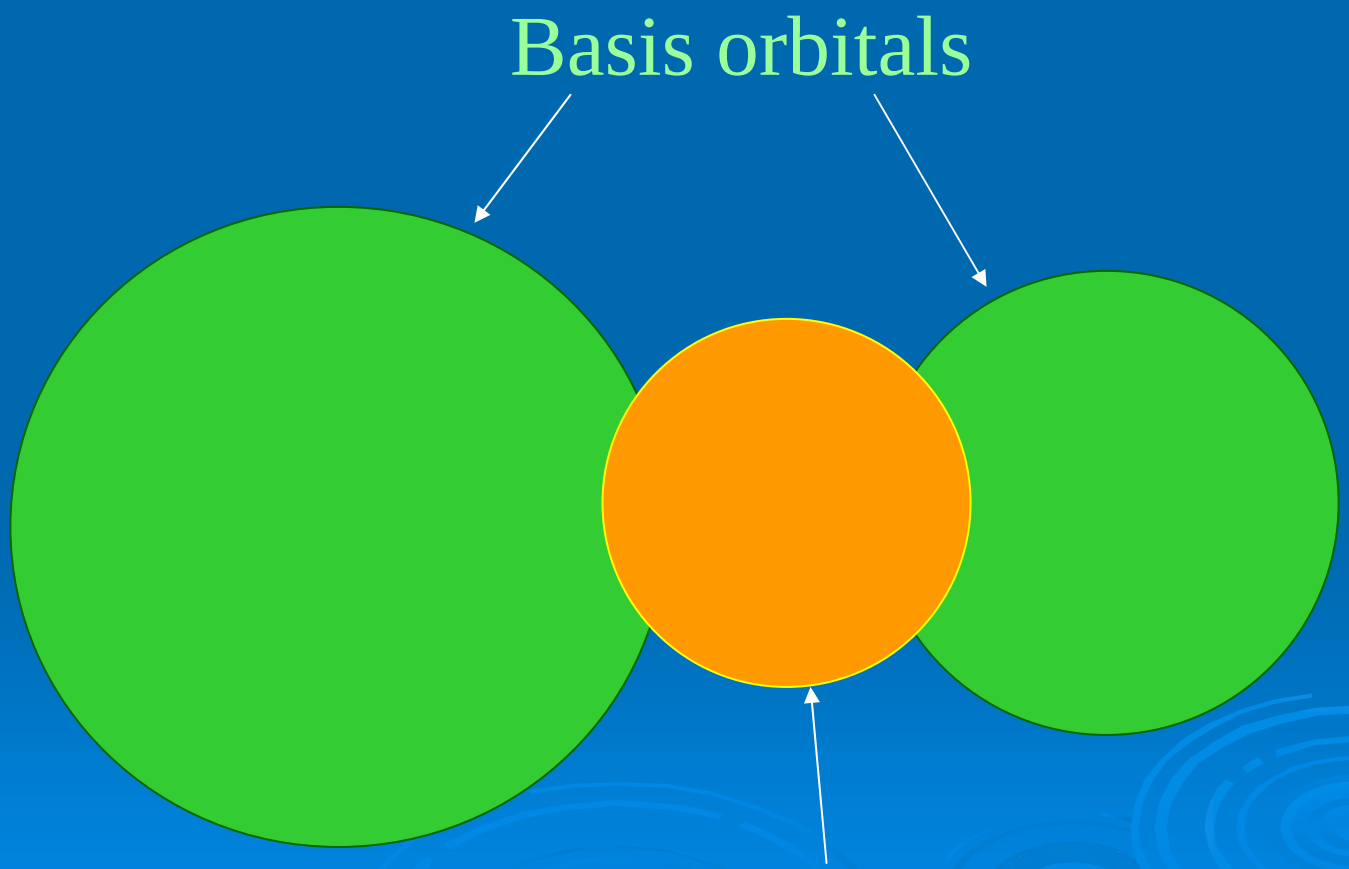
$$E_{KS}[\rho] = -(1/2)\,\Sigma_i |\nabla\psi_i(r)|^2 + \int V_{ext}(r)\,\rho(r)\,dr$$

$$+(1/2)\int V_H(r)\,\rho(r)\,dr + \int \varepsilon_{xc}(r)\,\rho(r)\,dr$$

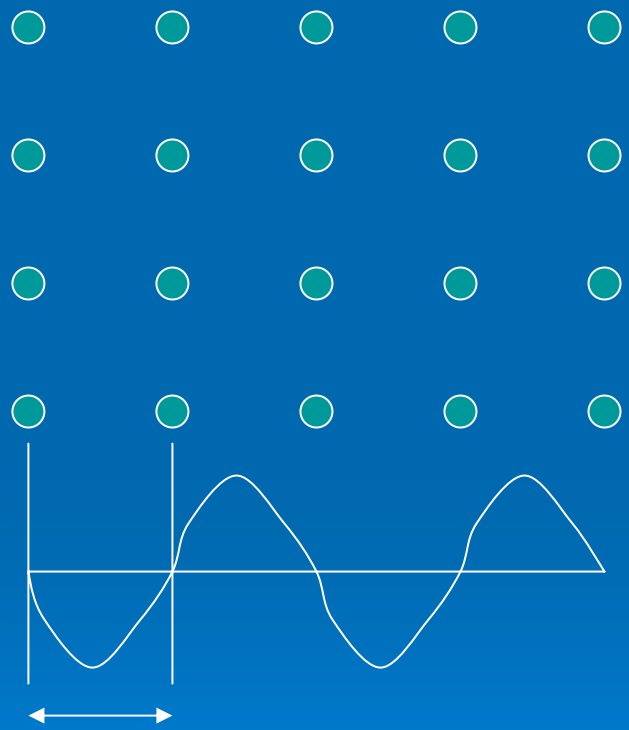
$$E_{Harris}[\rho_{in}] = E_{KS}[\rho_{in}] + Tr[(\rho_{out}-\rho_{in})H_{in}]$$

- Much faster SCF convergence
- Usually $\rho_{in} = \Sigma\, \rho_{atoms}$ and no SCF

Neglect of non-overlap interactions



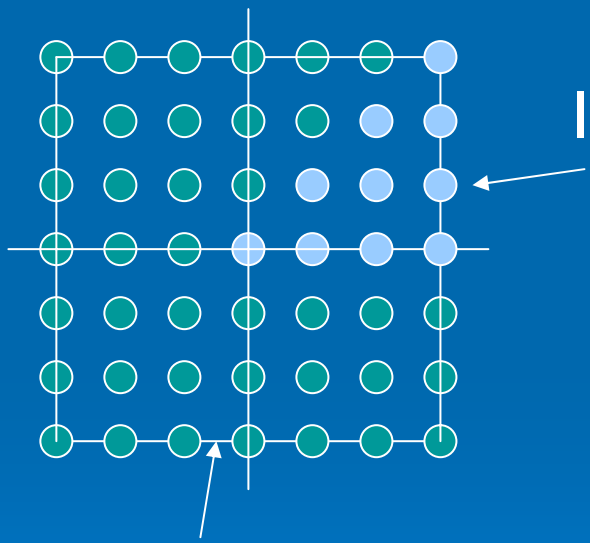
Mesh cutoff



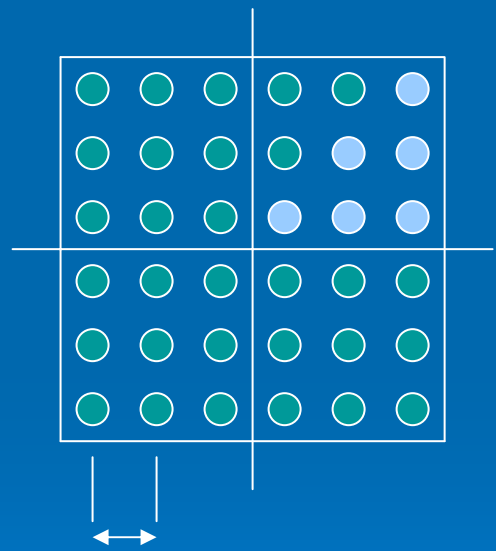
$$\Delta x \Rightarrow k_c = \pi/\Delta x \Rightarrow E_c = \hbar^2 k_c^2 / 2m_e$$

K-point sampling

Regular k-grid



Monkhorst-Pack



$\Delta k \Rightarrow l_c = \pi / \Delta k$

Mimimal initial parameters

- Smaller system (e.g. Si(111)3x3 vs Si(111)7x7)
- Small supercell (e.g. 2-layer slab)
- Fixed geometry (no relaxation)
- Harris functional (no selfconsistency)
- Minimum pseudo-valence states (e.g. Ti 3s3p3d)
- No nonlinear core correction
- Minimal basis set (single zeta)
- Small basis range (e.g. E_{shift}=0.5eV)
- Gamma point
- Large electronic temperature (e.g. 3000 K)
- LDA
- Neglect non-overlap interactions

Parameter interactions

$$\partial^2 A / \partial x_i \partial x_j \neq 0$$

Number of k-points:

- Supercell size
- Geometry
- Electronic temperature
- Spin polarization
- Harris vs SCF

Mesh cutoff:

- Pseudopotential
- Nonlinear core corrections
- Basis set
- GGA

Surface (slab) calculations