Systematics for realistic proyects: from quick & dirty to converged calculations

José M. Soler and Alberto García

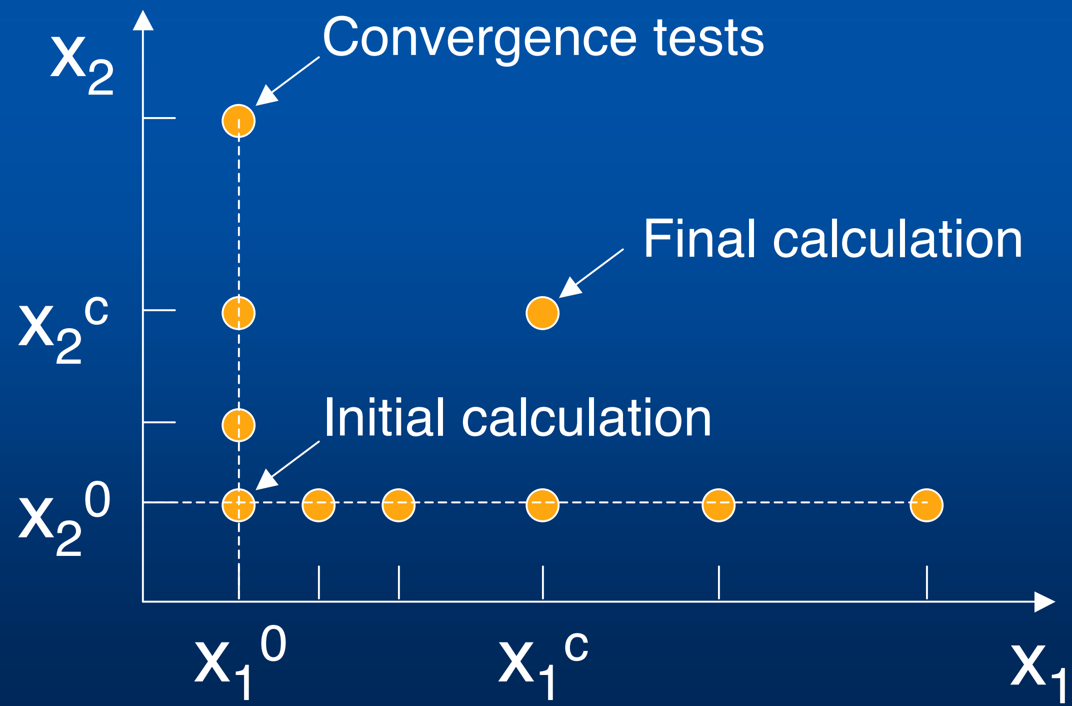
Basic strategy

- Exploratory-feasibility tests
- Convergence tests
- Converged calculations

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

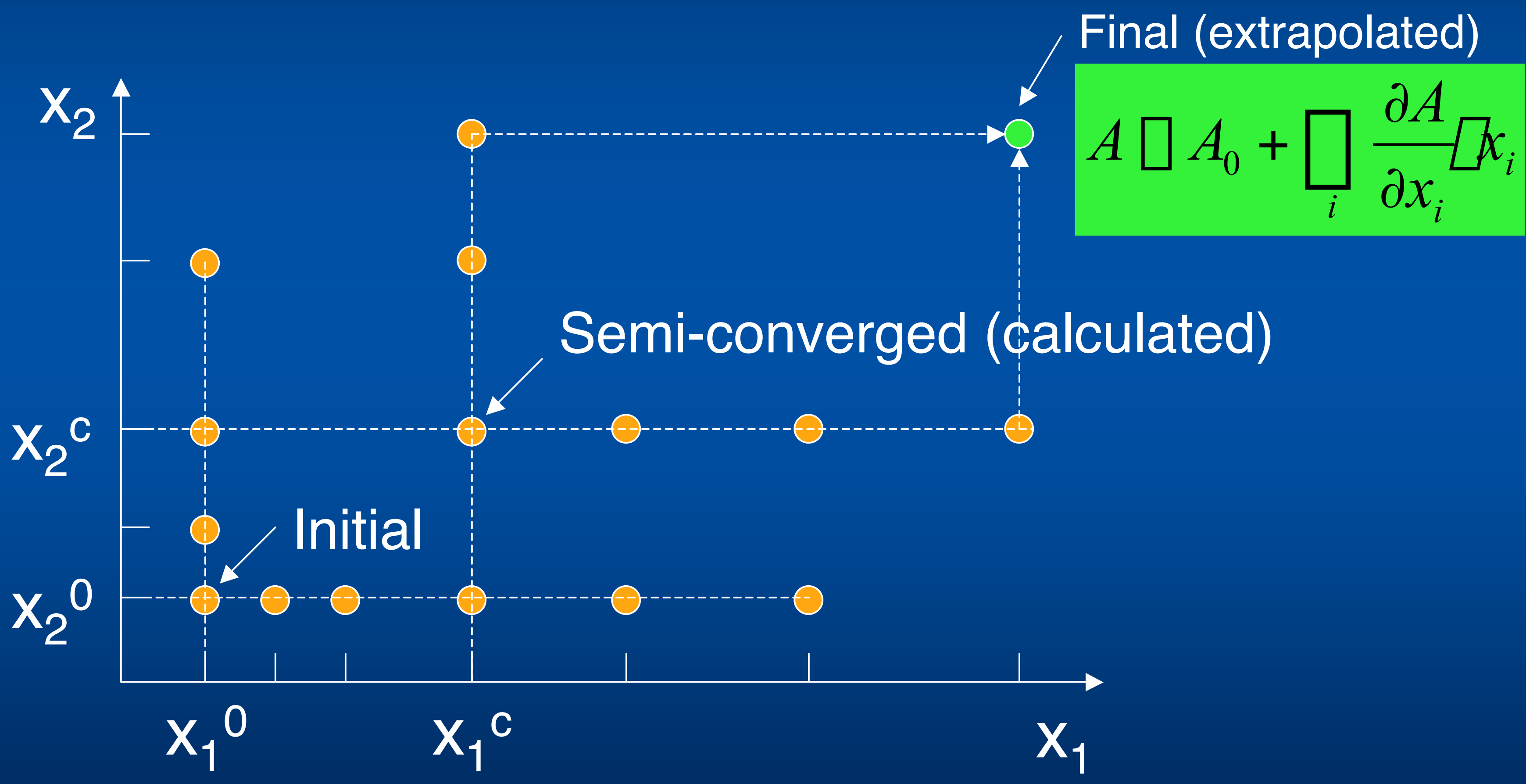
$$A \approx A_0 + \sum_i \frac{\partial A}{\partial x_i} \Delta x_i$$

Monitor:

•Convergence

•CPU time & memory

Multi-stage convergence



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

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)
- Geometry relaxation tolerance
  - Check of final stability
- 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

Harris functional

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

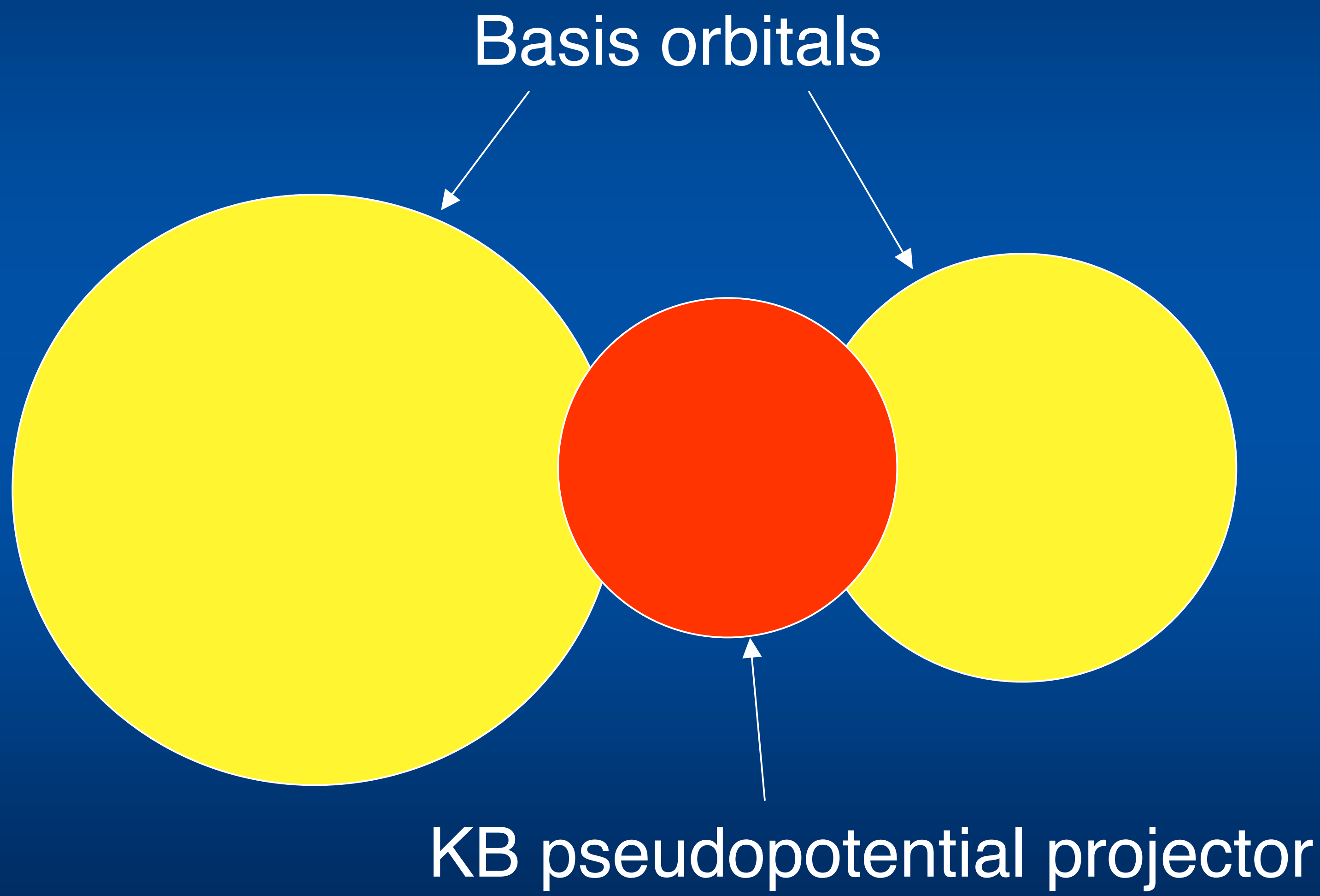
$$E_{KS}[\rho] = -(1/2) \sum_i |\nabla \psi_i(r)|^2 + \int V_{ext}(r)\, \rho(r)\, dr$$

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

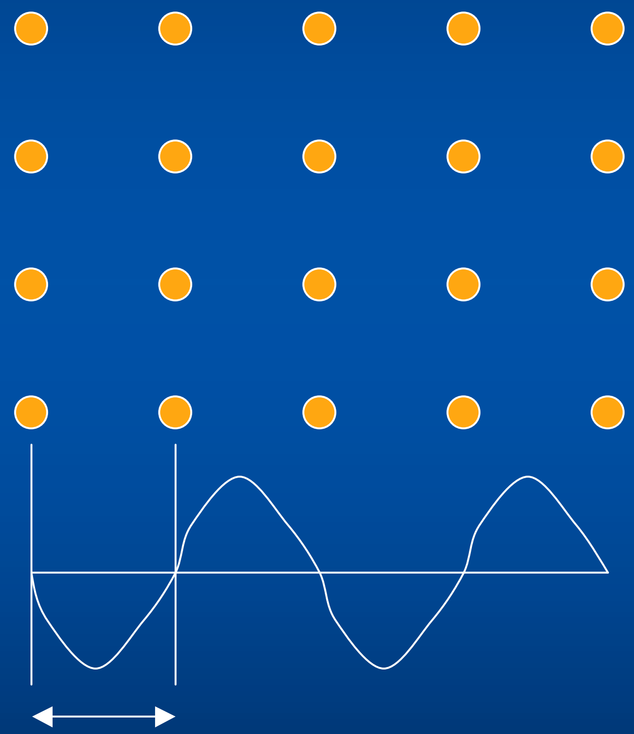
$$E_{Harris}[\rho_{in}] = E_{KS}[\rho_{in}] + Tr[(\rho_{out}-\rho_{in})H_{in}]$$

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

Neglect of non-overlap interactions



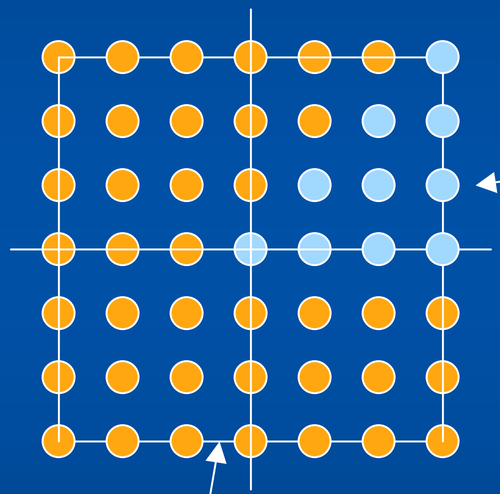
Mesh cutoff



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

K-point sampling

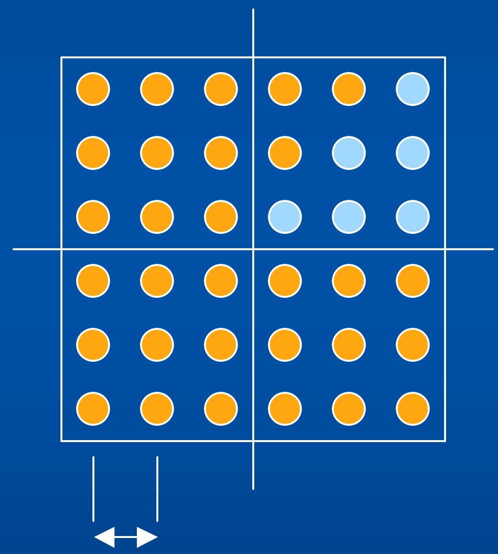
Regular k-grid



Inequivalent points

First Brillouin Zone

Monkhorst-Pack



□k □ l_c=□/□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