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

\[ A \approx A_0 + \sum_i \frac{\partial A}{\partial x_i} \delta x_i \]
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)

- 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

\[ \rho(r) = \sum_i |\psi_i(r)|^2 \]

\[ E_{KS}[\rho] = -\frac{1}{2} \sum_i |\nabla \psi_i(r)|^2 + \int V_{\text{ext}}(r) \rho(r) \, dr \]
\[ + \frac{1}{2} \int V_{\text{H}}(r) \rho(r) \, dr + \int \varepsilon_{\text{xc}}(r) \rho(r) \, dr \]

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

- Much faster SCF convergence
- Usually \( \rho_{\text{in}} = \sum \rho_{\text{atoms}} \) and no SCF
Neglect of non-overlap interactions

Basis orbitals

KB pseudopotential projector
Mesh cutoff

$$\Delta x \Rightarrow k_c = \frac{\pi}{\Delta x} \Rightarrow E_c = \frac{\hbar^2 k_c^2}{2m_e}$$
**K-point sampling**

**Regular k-grid**

**First Brillouin Zone**

**Monkhorst-Pack**

\[ \Delta k \Rightarrow l_c = \pi / \Delta k \]
Minimal 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. $E_{\text{shift}}=0.5\text{eV}$)
- Gamma point
- Large electronic temperature (e.g. 3000 K)
- LDA
- Neglect non-overlap interactions
Parameter interactions

\[ \frac{\partial^2 A}{\partial x_i \partial x_j} \neq 0 \]

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

Bulk

Surface (3x3)

Same $d_{xy}$

Same $k_{xy}$ points

$z$