Density Functional Theory: Performing Practical Calculations

the plane-wave pseudopotential approach

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May 31st, 2012

Science & Technology Facilities Council
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  - compare with available experimental data or previous calculations

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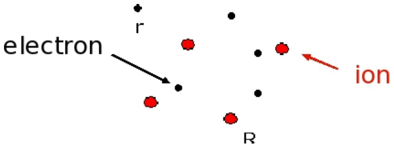
Outline

- A dusting of density functional theory
- Choosing the functional to fit my system
- How do I solve the equations?
- How do I represent the electrons?
    - Plane Waves (choosing the kinetic energy cutoff)
    - Pseudopotentials
- What geometry? (in periodic boundary conditions)
- Reciprocal space sampling (special case: metals)
- Rules of good practice for computations

The *Ab Initio* Approach

- Free of adjustable parameters
- Electrons treated explicitly
- Cost of the calculations limits system size



Born-Oppenheimer approximation decouples nuclei and electrons:

- Nuclei treated as classical particles
- Electrons treated with density functional theory

Density Functional Theory

Hohenberg & Kohn, PRB **136**, 864 (1964):

$$\delta \left[E[n] - \mu \left(\int n(\mathbf{r}) d\mathbf{r} - N \right) \right] = 0$$

There is a functional $E[n]$ which could be inserted in the above equation and minimised to obtain the exact ground state electron charge density and system's total energy

Kohn-Sham Implementation

Write the electron density in terms of a set of N non-interacting orbitals:

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$$

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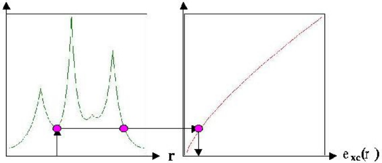
... BUT the exchange-correlation energy E_{xc} is unknown!

Kohn & Sham, PRA **140**, 1133 (1965)

Approximating E_{xc}

- Local density approximation (LDA):

$$E_{xc}^{LDA} = \int \epsilon_{xc}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$$



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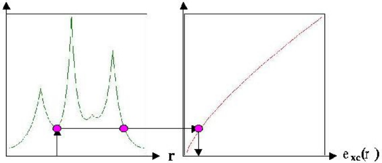

Kohn & Sham, PRA (1965)

- Generalized gradient approximation (GGA):

$$E_{xc}^{GGA} = \int f\left(n(\mathbf{r}), \nabla n(\mathbf{r})\right) n(\mathbf{r})d\mathbf{r}$$

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  - better results when comparing with experiments

PBE: Perdew, Burke, Ernzerhof, PRL (1996)

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4. Compare $|\psi_i\rangle$ and $|\psi_i'\rangle$. Go back to 3. until the difference between solutions is smaller than set tolerance

Basis Set Functions: Plane Waves

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$$N_{PW} \approx \frac{V_{cell}}{2\pi^2} E_{cut}^{3/2}$$

Cost of the calculation increases with system size and accuracy required.

How to choose the kinetic energy cut-off?

- It depends on the element
- It depends on the type of pseudopotential. E.g., for ultra-soft pseudopotentials:

Element	C	O	Si	Al	Cu
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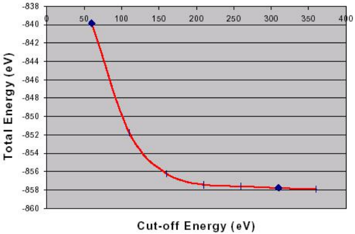
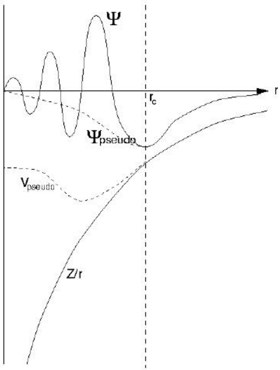


- Required E_{cut} is the largest of any element in the system
- E_{tot} decreases monotonically as E_{cut} increases
- It is independent of cell size and geometry
- Strategy: test E_{cut} on small bulk system

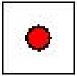
Pseudopotentials

- Core electrons too expensive in plane waves
- Frozen core approximation: do not solve the equations for the core electrons and keep their representation fixed during the calculation
- Interaction between core (i.e., ion+core electrons) and valence electrons is represented by a pseudopotential
- Always test the pseudopotential on the pure element to reproduce:
    - Experimental geometric structure
    - Cohesive energy
- Careful at high pressure!



Periodic Boundary Conditions

This is what you see:



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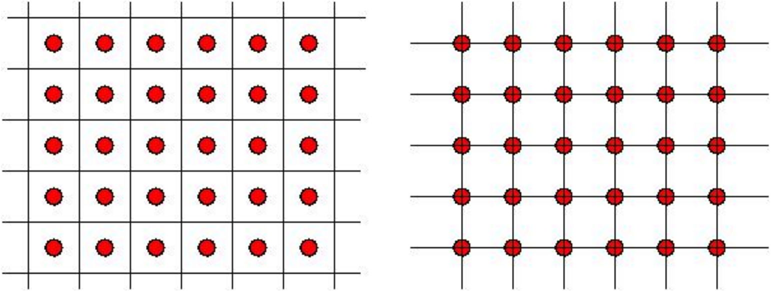
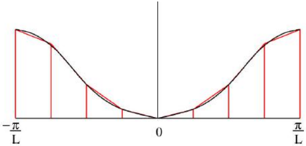


- Allow for vacuum gap when studying isolated atoms/molecules/clusters or surfaces
- For surfaces converge wrt slab thickness

Reciprocal Space Sampling

Integrals in reciprocal space discretised to sums on a grid of k points

$$I(\epsilon) = \frac{1}{V_{BZ}} \sum_k f_{k_i}(\epsilon) w_{k_i}$$



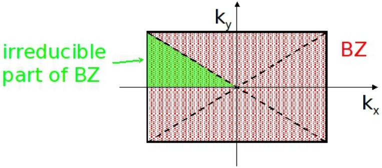
- Size and shape of BZ are set by size and shape of simulation cell
- Number of k-points is a function of the simulation cell

$$V_{BZ} = \frac{(2\pi)^3}{V_{cell}}$$

- The bigger the cell the fewer the k points required

Reciprocal Space Sampling: Exploiting Symmetry

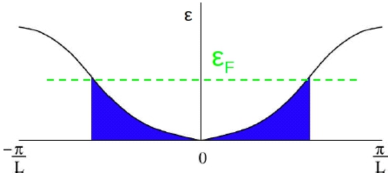
- Inversion symmetry always present in reciprocal space
- If system symmetry is used one only needs to sample irreducibla wedge of BZ

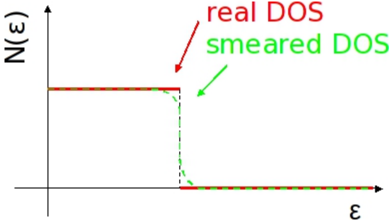


E.g., Monkhorst-Pack grid for FCC cell:

k point mesh	# k points (full)	# k points (symm)
1x1x1	1	1
2x2x2	4	2
4x4x4	32	10

Reciprocal Space Sampling: Metals





- In metals k space functions are discontinuous at the Fermi level
- Problem: integrals converge very slowly with k pont sampling
- Solution: smear electronic DOS out to render functions continuous
- Careful tuning of the smearing width and number of k points allows accurate calculations at an affordable computational cost

Reciprocal Space Sampling: Rules

- Check convergence of total energy wrt k point mesh
- The k point mesh depends on the simulation cell
- The larger the system, the fewer the k points needed
- Insulators typically need few k points
- When simulating systems with "aperiodic" directions, use grids with one k point only along that direction:
  - atoms/molecules/clusters: 1x1x1 grid
  - surfaces: NxMx1, if *z* axis is perpendicular to the surface
- In metals:
  - smearing of the electronic DOS is required
  - for simple metals a smallish k point grid will do
  - cases in which the Fermi surface is difficult to represent may require over 500 kpoints (e.g., hcp Zn)

Rules of Good Practice

- Test at the start:
  - Many different convergence parameters and tolerances
  - Always a trade-off between degree of convergence and accuracy
- Check the input:
  - Double check before running
  - Use graphics to see what you are calculating and consider periodic boundary conditions
- Scrutinize the output
  - The program tells you what it is doing and what is going wrong
  - Are the default values what you want?
  - Has the iterative procedure for solving the electronic problem reached a solution? Did it converge or run out of iterations?
  - Is the cohesive energy sensible? Compare with experiment
  - Total energy should be extensive quantity
  - Are forces and stresses reasonable (or close to zero if expected to be)?

Summary

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- Rules of good practice for computations