Densities and magnetization for metals and insulators.
PBC and the simulation of systems with reduced periodicity

Pietro Delugas
SISSA

Outline

- Densities
- Magnetic vs non magnetic
- Metal vs Insulators
- Potentials definition and meaning
- Non periodic systems with PBC formalism

Densities

- Non magnetic system: total density $n(\mathbf{r})$

- Magnetic system with collinear spin:

$$n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}) \qquad m(\mathbf{r}) = n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r})$$

- Magnetic noncollinear spin:

$$n(\mathbf{r}) \qquad \{m_x(\mathbf{r}), m_y(\mathbf{r}), m_z(\mathbf{r})\}$$

SISSA QUANTUMESPRESSO M4X DRIVING THE EXASCALE TRANSITION

PW cutoff for densities

- The cutoff lengt for densities is by construction 2 the one for wavefunctions. It means cutoff energy is 4 times.

$$n_v(\mathbf{r}) = \sum_{n,\mathbf{k}} \phi_{n,\mathbf{k}}^* \phi_{n,\mathbf{k}}$$

- In case of USPP or PAW we have also augmentation charges and `ecutrho` is tipically about 6 - 10 times larger than `ecut`.

$$n_v(\mathbf{r}) = \sum_{n,\mathbf{k}} \phi_{n,\mathbf{k}}^* \phi_{n,\mathbf{k}} \quad + \sum_{ij} \rho_{ij} Q_{ij}(\mathbf{r}) \qquad \rho_{ij} = \sum_{n,\mathbf{k}} \langle \phi_{n,\mathbf{k}} | \beta_i \rangle \langle \beta_j | \phi_{n,\mathbf{k}} \rangle$$

Non magnetic (nspin=1)

- The SCF loop starts from a non magnetic configuration
- Each Kohn-Sham state has an occupation from 0 to 2

$$n(r) = 2 * \sum_{n,\mathbf{k}} f_{n,\mathbf{k}} \phi^*_{n,\mathbf{k}} \phi_{n,\mathbf{k}}$$

- Non magnetic systems may be also studied with the noncollinear formalism (spinors). In this case each KS spinor state is doubly degenerate.

Collinear magnetic (nspin = 2)

- distinct KS states are used 2 different polarizations(spin up, spin down)
- The magnetization is a scalar

$$n(r)^{\uparrow} = \sum_{n,\mathbf{k}} f_{n,\mathbf{k},\uparrow} \phi^*_{n,\mathbf{k},\uparrow} \phi_{n,\mathbf{k},\uparrow} \qquad n(r)^{\downarrow} = \sum_{n,\mathbf{k}} f_{n,\mathbf{k},\downarrow} \phi^*_{n,\mathbf{k},\downarrow} \phi_{n,\mathbf{k},\downarrow}$$

- One needs to specify a starting magnetization or fix a total magnetization for the system.
  - Starting magnetization: the scf is free to converge to any magnetization
  - Total magnetization, occupations for majority and minority spin are computed separately in order to keep to specified total magnetization during the scf loop

SISSA

QUANTUMESPRESSO

M4X DRIVING THE EXASCALE TRANSITION

Non collinear magnetism

- Magnetization is a vector.

$$\vec{\mathbf{m}}(r) = \sum_{n,\mathbf{k}} f_{n,\mathbf{k}} \phi^*_{n,\mathbf{k}} \vec{\sigma} \phi_{n,\mathbf{k}}$$

- It is also possible to introduce the spin-orbit coupling. One has to use fully relativistic pseudo-potentials.

Metals vs insulators

- Insulators: there is a finite gap between occupied and emply levels it is possile to determine a number for occupied levels fixed for all k-points.
- Metals: there is no gap between occupied and empty levels, to make feasible the k-point summation is necessary use the smearing technique;
- The smearing at the Fermi level increases the total energy, this increase should be kept small.

from: M.Methfessel, A.T. Paxton PRB **40,** 3616 (1989)
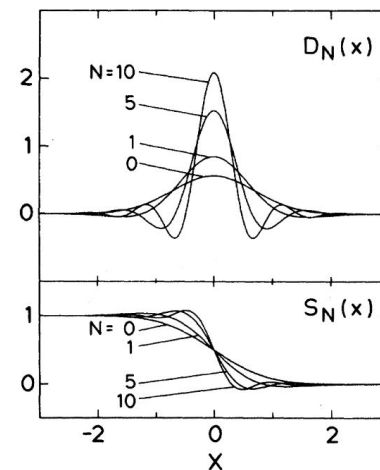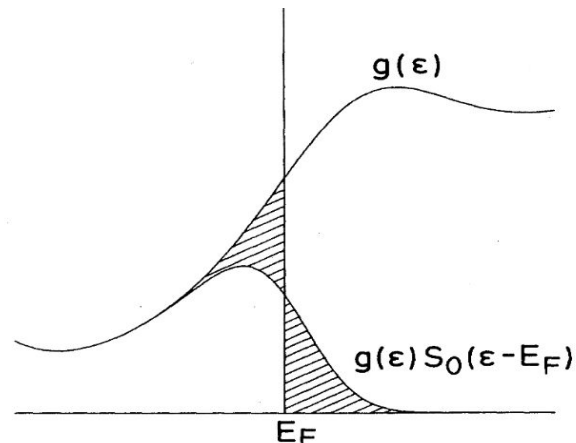
Occupations for magnetic systems

- One has to smearing when the scf loop is free to search for the ground state magnetization
- It is possible to use fixed occupations if total_magnetization is specified with an integer value.
- for atoms it is possible to specify occupations in input directly

Potentials

- $V_{Hartree}$:   The electrostatic potential generated by the electronic density. Long range
- V_{XC} : The exchange correlation potential, short range.
- V_{loc}: The long range part of the ion-electron interaction.
- E_{Ewald}: the electrostatic energy of the ion-ion interaction.

Electrostatics in PBC

- The net charge per unit cell must be 0 otherwise the energy would diverge.

- All potentials must be periodic, the net value of the electric field must be vanishing

- There is no direct reference the the vacuum level.

- The electrostatic moments per unit cell are generally ill defined.
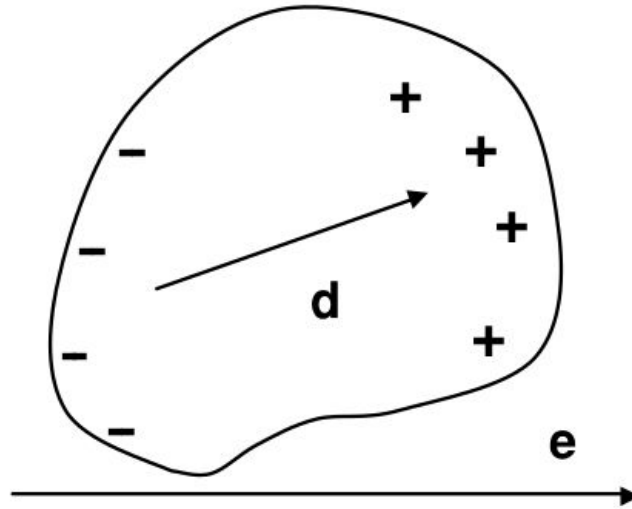
Picture from: Electronic Structure: Basic Theory and Practical Methods
R.M. Martin
Cambridge University Press (2008)
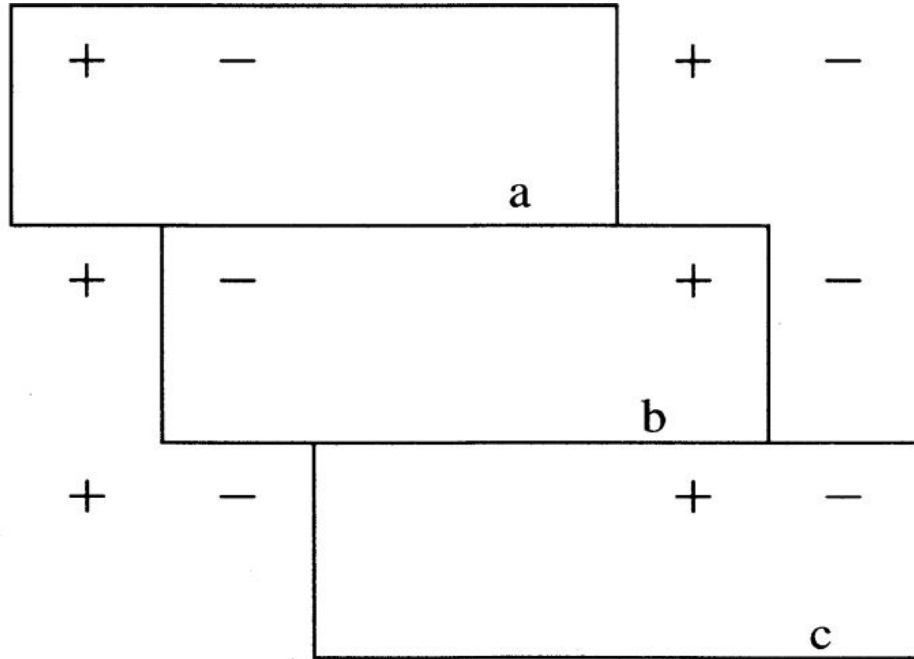
Picture from: G. Makov, M.C. Payne PRB **51,** 4014 (1995)

Electrostatics in PBC: Hartree potential

- The Hartree potential is computed as:

$$v_H(\mathbf{r}) = 4\pi e^2 \sum_{\mathbf{G} \neq 0} \frac{n(\mathbf{G})}{|\mathbf{G}|^2} e^{i\mathbf{G} \cdot \mathbf{r}}$$

- It is like we add a constant background n_+ such that

$$n'(G \equiv 0) = \int_{cell} (n(\mathbf{r}) + n_+) d^3 r = 0$$

Ionic electrostatic energy: (Ewald sum)

- The ionic electrostatic energy is computed as the energy of point positive changes immersed in a uniform negative compensating background (Ewald sum)
- If the system is neutral the two compensating backgrounds cancel each other
- If the system is charged it will be like we had added a non vanishing compensating background.
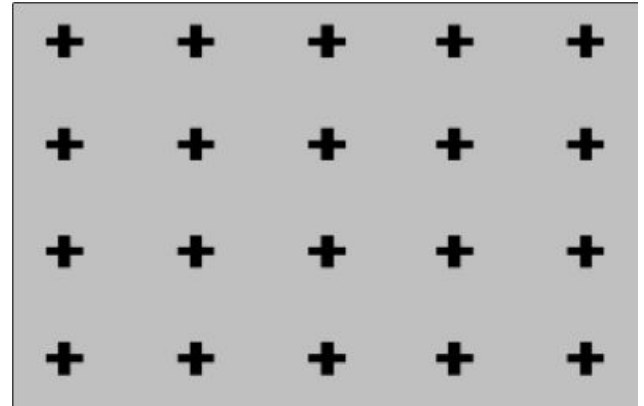
Picture from: Electronic Structure: Basic Theory and Practical Methods
R.M. Martin
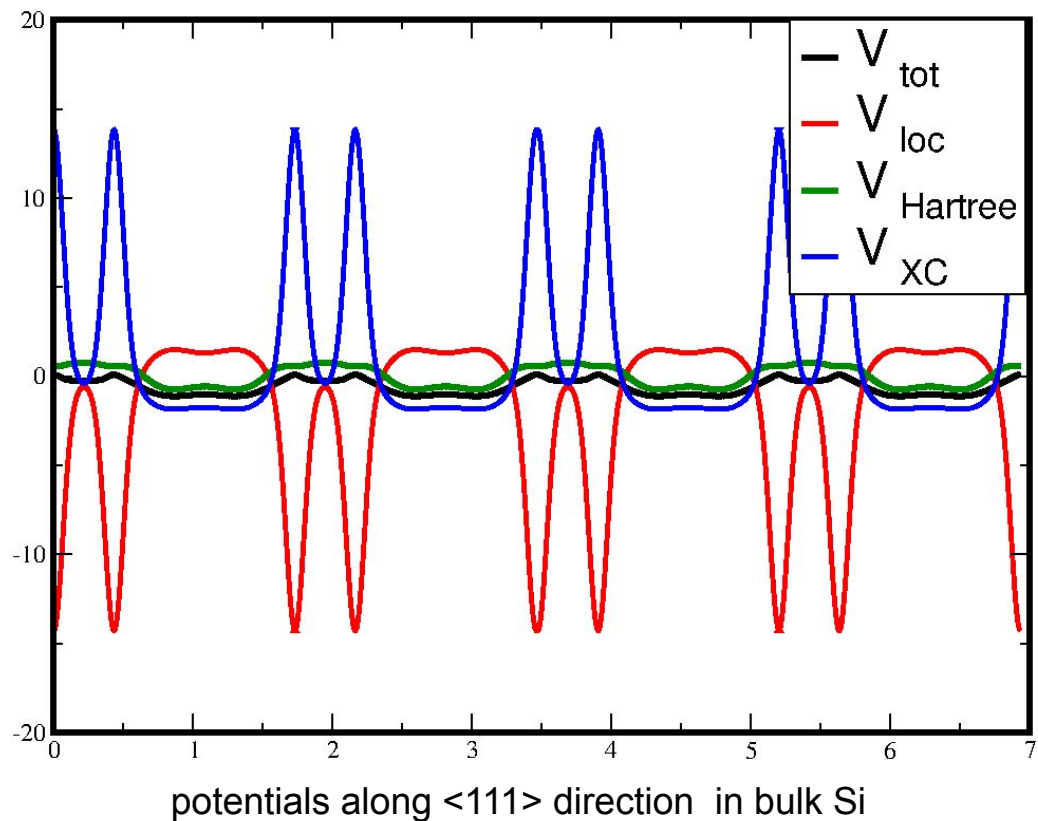Cambridge University Press (2008)

Ion-electron interaction

- The ion electron interaction is given by the pseudopotential

$$\hat{V}_{pseudo} = V_{loc}(r) + \sum |\beta_i\rangle D_{ij} \langle\beta_i|$$

- The non local part vanishes beyond the cutoff radii of the pseudopotential.
- The local part contains the long range coulombian part of the Ion electron interaction

SISSA

QUANTUMESPRESSO

M4X DRIVING THE EXASCALE TRANSITION

Potentials Si:

potentials along <111> direction in bulk Si

Simulating systems with reduced periodicity.

- Molecules and clusters. Finite systems with vanishing systems with the periodic images
- 1D systems: Periodicity along 1 direction: nanotube, nanorods etc/
- 2D systems: Periodicity along 2 dimensions with a vacuum layer between slabs.
- Mixed systems: structures embedded in a periodic system, point defects, interfaces, molecules on surfaces.

SISSA

QUANTUMESPRESSO

M4X DRIVING THE EXASCALE TRANSITION

Makov Payne corrections

- Neutral system
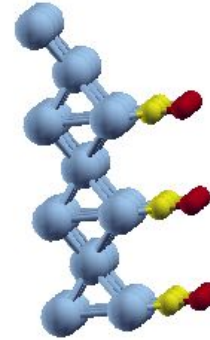 - No dipole the energy c or cubic lattice onvergese as $\mathcal{O}(L^{-5})$
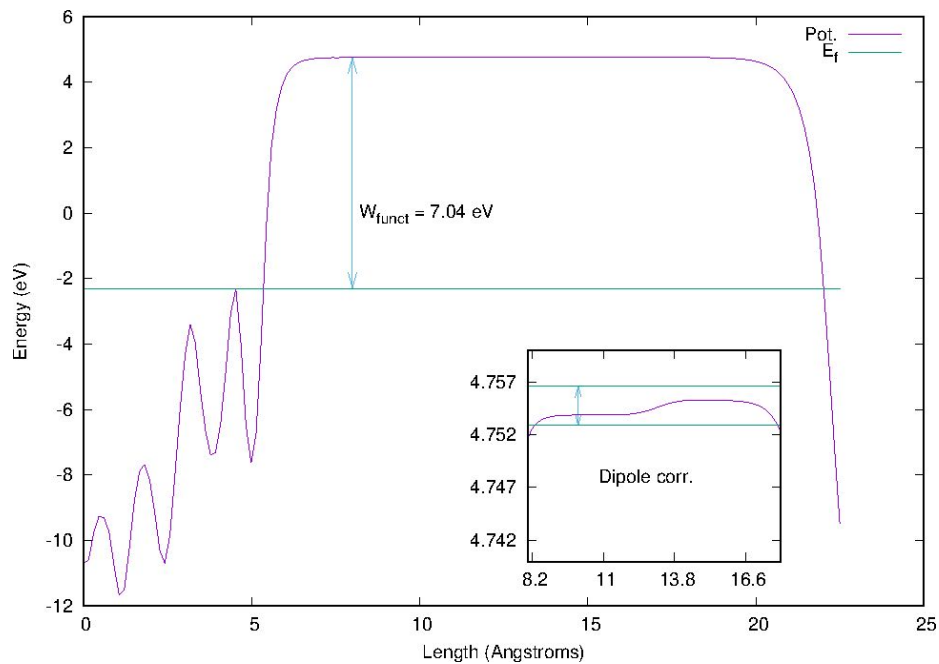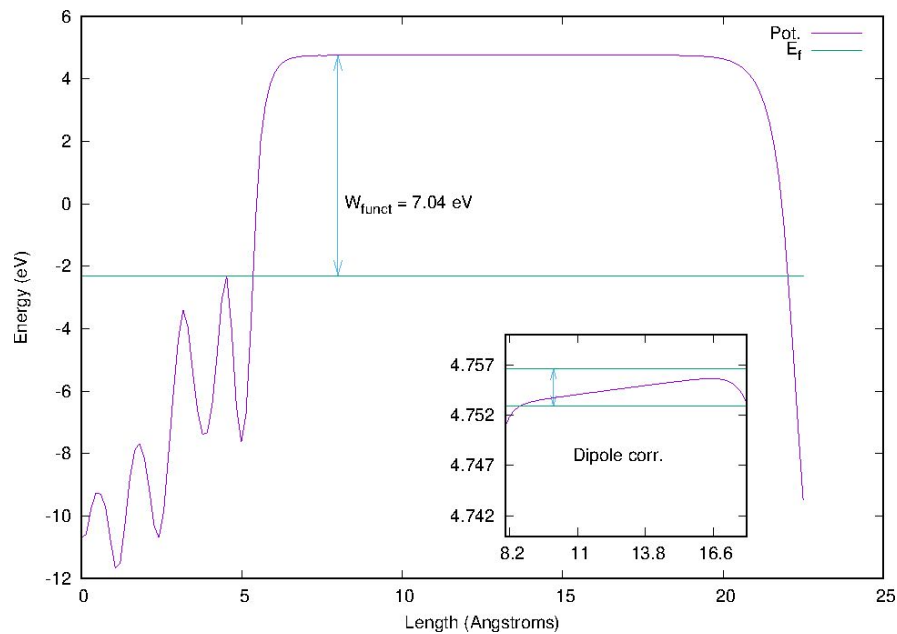 - dipole in non cubic system $\mathcal{O}(L^{-3})$
- Charged system
  -
$$E = E_0 - \frac{q^2 \alpha}{2L} - \frac{2\pi qQ}{3L^3} + \mathcal{O}(L^{-5})$$

SISSA

QUANTUMESPRESSO

MAX DRIVING THE EXASCALE TRANSITION
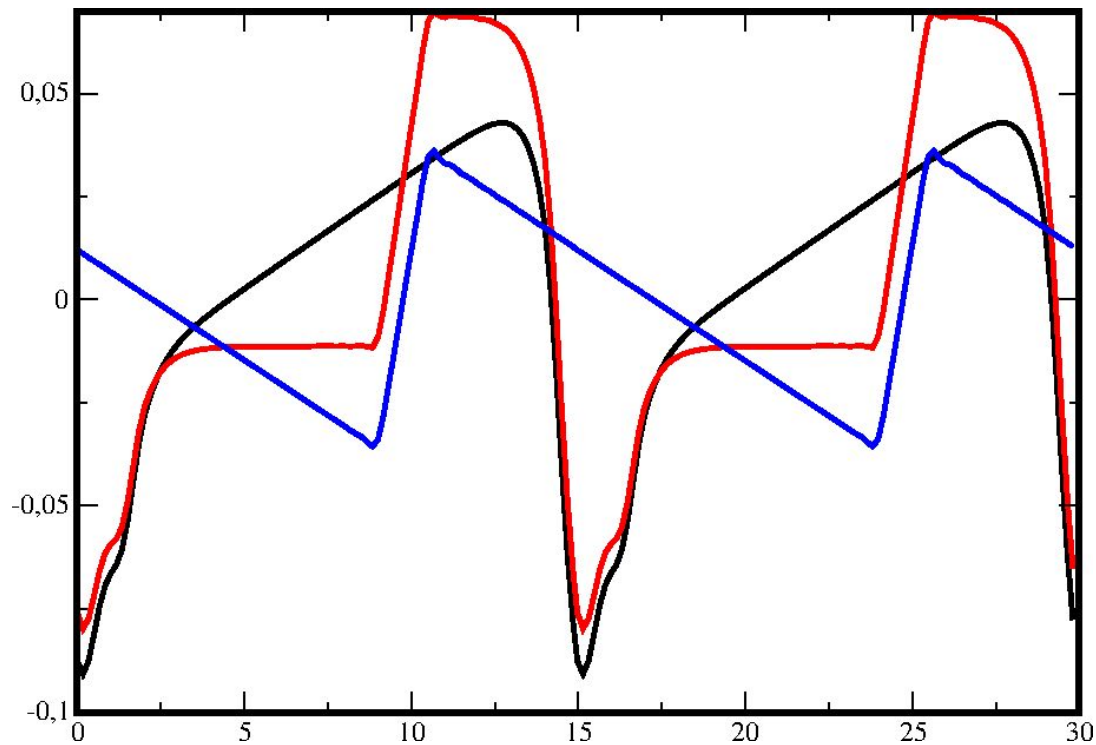
Polar surfaces

- In Polar 2D systems we can eliminate the artificial electric field with a sawtooth potential.

Dipole correction

Water molecule

That's all !!!
Thanks for you attention