Nano-Bio Spectroscopy Group
Universidad del País Vasco

ETSF

Real Space DFT: The gory details

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Objective

- Give an insight of how a real space grid base code works.
- What are the advantages and disadvantages of this method.

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- Partial Differential Equation: infinite degrees of freedom.
- Solve it numerically.
- Reduce it to a finite number.
- Retain information.

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Real space grid

- Functions are represented by its value over a set of points.
- Point distribution:
  - Uniform space grid.
  - Distance between points is constant: *Spacing*.
  - Non-uniform grids.
- Finite region of the space: *Box*

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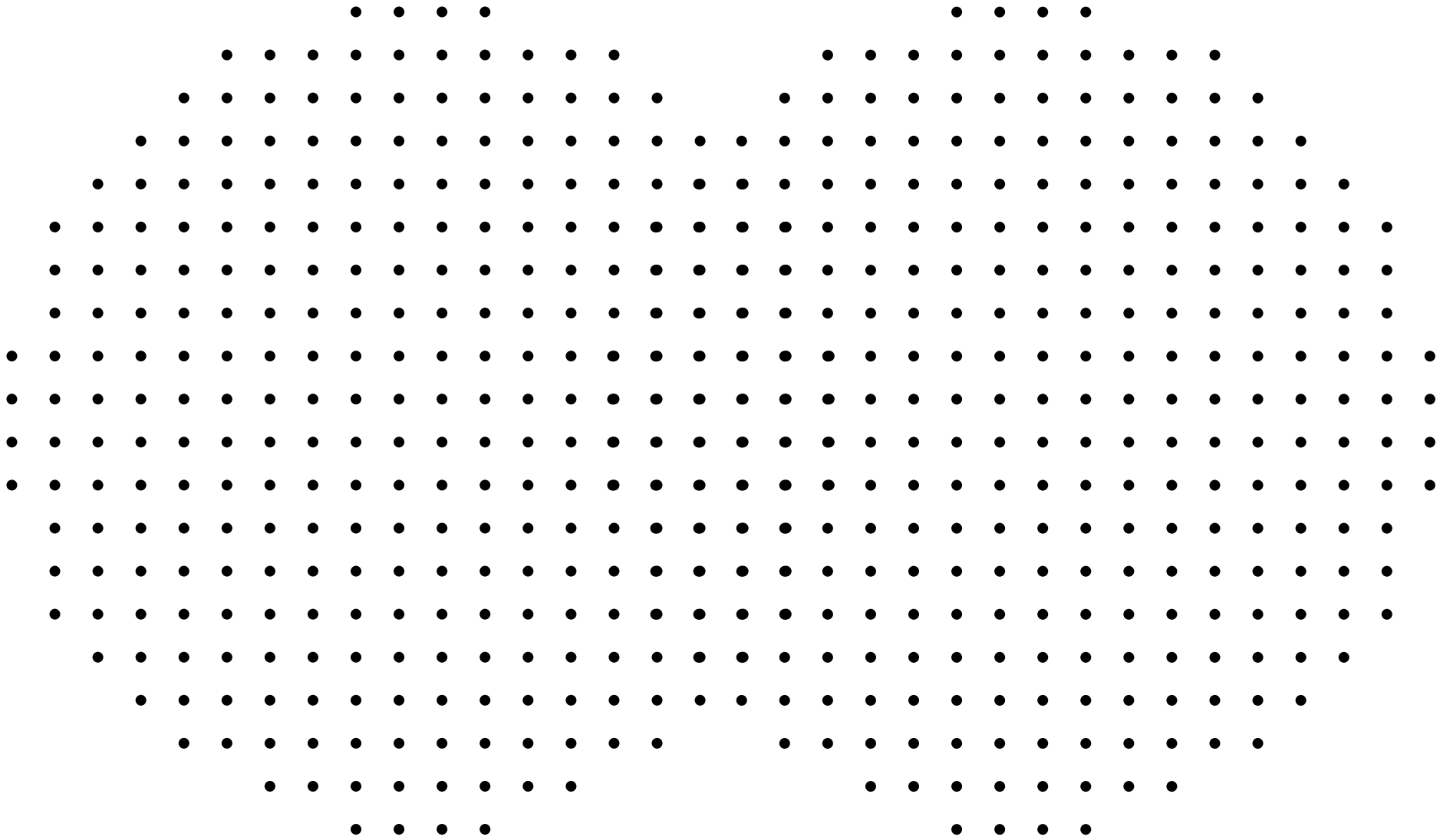
Real space grid: 2D Example



Boundary conditions

- For finite systems functions go to zero.
- Impose functions to be zero over the border of the box.
- The box has to be large enough to contain the functions.
- Optimize the shape of the box to minimize the number of points.
- Other BCs are possible: periodic, zero derivative, open.

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Real space grid characteristics

- Natural boundary conditions for different problems.
- Systematically improve discretization quality:
  - Decrease the spacing.
  - Increase the box size.
- Orthogonal “basis set”.
- Independent of atomic positions (no Pulay forces).
- Problems:
  - Break translational invariance: egg-box effect.
  - Break rotational invariance.

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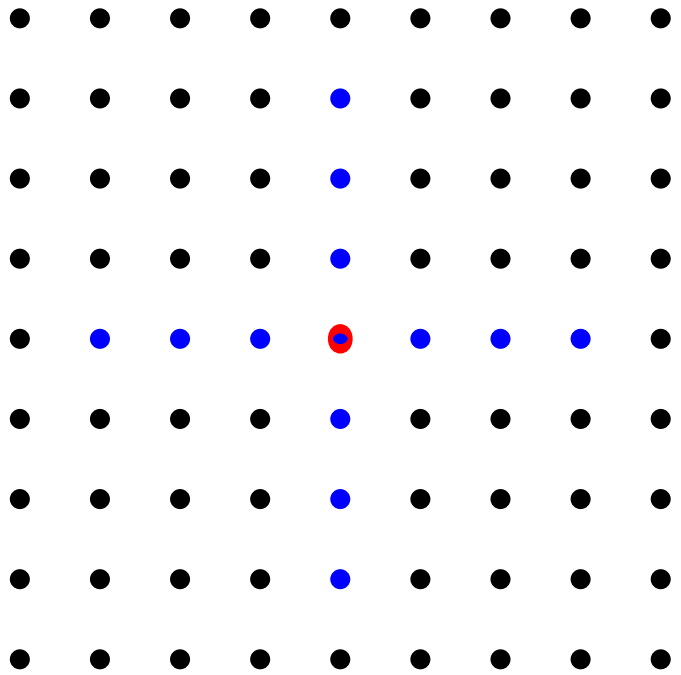
Differential operations

Finite difference approach

$$\nabla^2 f(n_x h,\, n_y h) = \sum_i^n \sum_j^n \frac{c_{ij}}{h}\, f(n_x h + ih,\, n_y h + jh)$$

- Derivative in a point: sum over neighbour points.
- c_{ij} depend on the points used: *the stencil*.
- More points $\rightarrow$ more precision.



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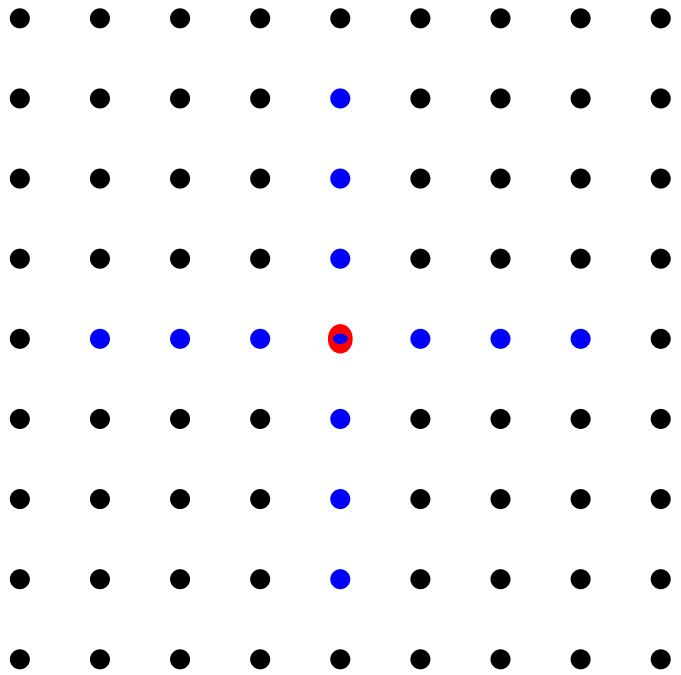

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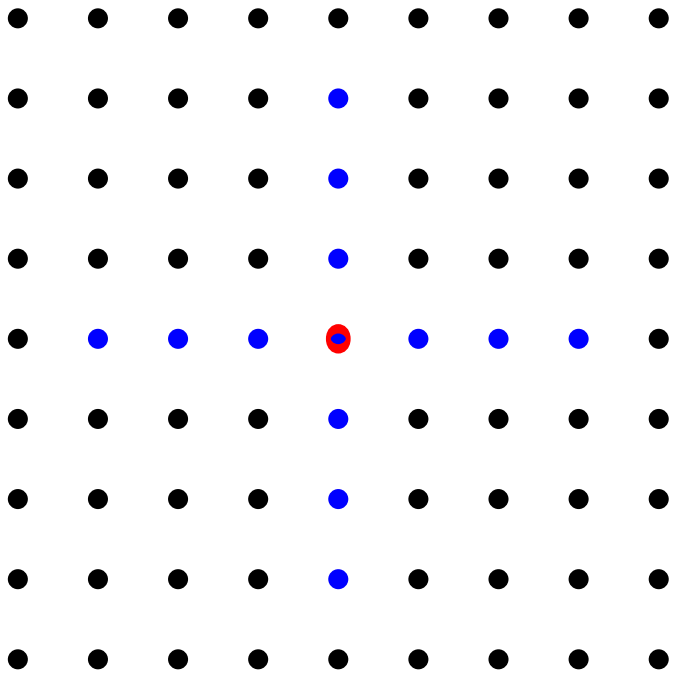

Integration

Trapezoidal rule

$$\int f(x,y)\,dx\,dy = h^2 \sum_{ij} f(ih, jh)$$

Ground state calculations

- What we want to solve:

Kohn-Sham equations

$$-\nabla^2\phi_k + V_{eff}\left[\rho\right](\boldsymbol{r})\phi = \epsilon_k\phi_k$$

- We use a self-consistency scheme to treat non-linearity.

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Discretization of the Hamiltonian

- For the laplacian we use finite differences
  - High order schemes are needed.
- The local part of the potential is direct.
- The non-local potential is applied in small spherical grid around the atoms.
- The Hamiltonian becomes a finite size matrix.

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- We need to find the eigenvectors and eigenvalues of a matrix.
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- We minimize (using conjugated gradient or other method):

Rayleigh-Ritz quotient

$$\epsilon(\psi) = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

- Works for the first state.
- For higher energy states it is necessary to orthogonalize against the lower ones.

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- Focused on finite systems (periodic systems not mature yet).
- Features:
  - Ground state DFT
  - TDDFT
    - Time propagation: linear response and strong fields.
    - Casida LR-TDDFT
    - Sternheimer linear and non-linear response
    - Car-Parrinello molecular dynamics
    - Ehrenfest molecular dynamics
    - (adiabatic and non-adiabatic)
    - Optimal control theory
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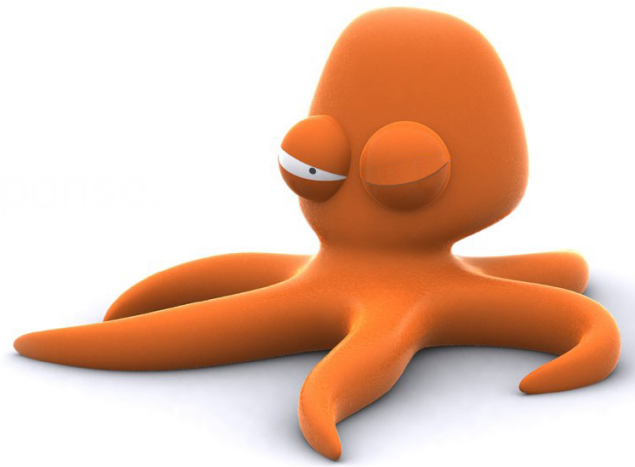

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