k points and plane waves

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Kohn-Sham equations

Self-consistent solution

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{KS}}[n](\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

$$V_{\mathrm{KS}}[n](\mathbf{r}) = V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{H}}[n](\mathbf{r}) + V_{\mathrm{xc}}[n](\mathbf{r})$$

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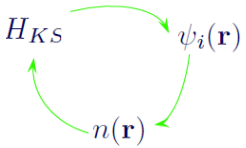

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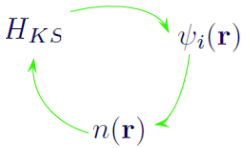

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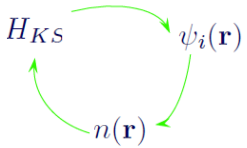

- We assume fixed ions. We will omit possible spin polarization (or spinors).
- Need boundary conditions.
- Actually most often energy minimization (with orthonormality constraint on ψ_i):

$$E = \sum_i f_i\langle\psi_i|T + V_{\mathrm{ext}}|\psi_i\rangle + E_{\mathrm{Hxc}}[n]$$

Periodic crystals

Bloch theorem

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$$\psi_i(\mathbf{r}) \longrightarrow \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N\Omega_0}} e^{i\mathbf{kr}} u_{n\mathbf{k}}(\mathbf{r})$$

Properties:

- Periodic part: $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}_j) = u_{n\mathbf{k}}(\mathbf{r})$
- $\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}_j) = e^{i\mathbf{kR}_j} \psi_{n\mathbf{k}}(\mathbf{r})$

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- $\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}_j) = e^{i\mathbf{k}\mathbf{R}_j} \psi_{n\mathbf{k}}(\mathbf{r})$
- Born-von Karman cyclic boundary conditions : supercell $N_j\mathbf{R}_j$ with $N = N_1 N_2 N_3$
  $\psi_{n\mathbf{k}}(\mathbf{r} + N_j\mathbf{R}_j) = \psi_{n\mathbf{k}}(\mathbf{r})$ (+ gradient)
  (in the thermodynamic limit: $N \to \infty$)
- normalisation in the primitive unit cell: $\frac{1}{\Omega_0} \int_{\Omega_0} d\mathbf{r}\, u^*_{n\mathbf{k}}(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) = 1$

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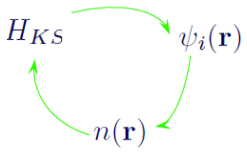

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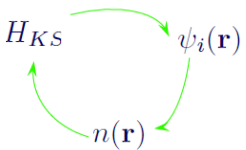

How to calculate integrals in a computer?

Brillouin zone sampling

Uniform grid of **k** points

$$n(\mathbf{r}) = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}}^{N_{\mathbf{k}}} \sum_{n} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2$$

- Equally spaced in reciprocal space.

$$\mathbf{k}_{n_1 n_2 n_3} = \sum_{i=1}^{3} \frac{2n_i - N_i - 1}{2N_i} \mathbf{b}_i \quad \text{with} \quad n_i = 1, 2, \ldots, N_i$$

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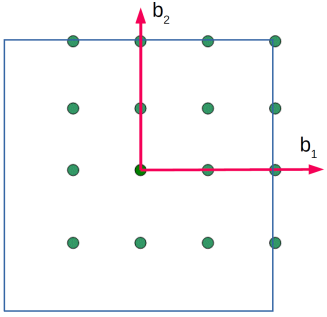
- Choice of divisions: space the grid in a way that is approximately commensurate with lengths of reciprocal lattice basis vectors $\mathbf{b}_i$ (note: inverse of lengths in real space).
- Other possibilities: tetrahedron method; (historical) special points (Chadi & Cohen; Baldereschi)

H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13, 5188 (1976).

Brillouin zone sampling



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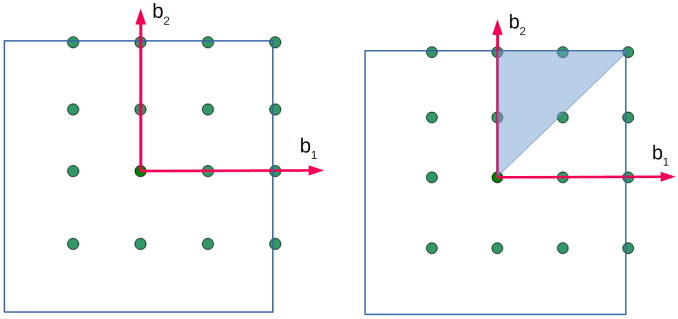
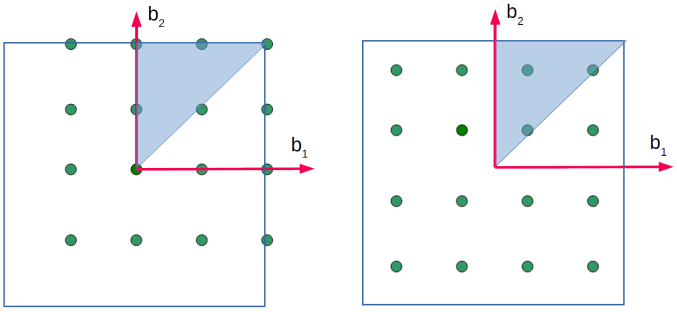


Irreducible Brillouin zone

- Only **k** points in the Irreducible Brillouin zone are actually needed. The other **k** points are reconstructed using crystal symmetries.

Brillouin zone sampling



Monkhorst-Pack shifted grids

- **k** point grids are generally offset from the Γ point ("shifted" grid) to reduce the number of points in the Irreducible Brillouin zone.
- Choice of the shift is done according to the crystal symmetry.

Brillouin zone sampling

How many **k** points are needed?

Brillouin zone sampling

How many **k** points are needed? Convergence!

Brillouin zone sampling

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Caution: metals

- Need improved sampling (smearing) with quickly varying functions.
  Example:

$$n(\mathbf{r}) = \frac{1}{N_{\mathbf{k}}} \sum_{n\mathbf{k}}^{N_{\mathbf{k}}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2$$

  In a metal the occupations $f_{n\mathbf{k}}$ have a sharp discontinuity across the Fermi surface.

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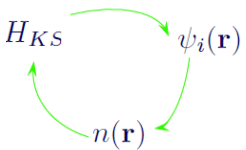

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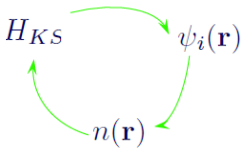

- Direct solution on a grid of points in real space.
- Choice of a **finite** basis set.

Kohn-Sham equations in a basis

Orthonormal basis set

If $\{\phi^\alpha\}$ is an orthonormal basis set:

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with matrixelements $H_{\mathrm{KS}}^{\alpha\beta} = \langle\phi^\alpha|H_{\mathrm{KS}}|\phi^\beta\rangle$.

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Solution: diagonalisation to obtain eigenvalues and eigenvectors (...needs a discrete+finite basis).

Plane waves

Plane wave expansion

- The **periodic** part of the Bloch wavefunction can be expanded in a **discrete** basis of plane waves:

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} u_{n\mathbf{k}}(\mathbf{G})$$

  where $\mathbf{G}$ are reciprocal lattice vectors.
- The plane waves $e^{i\mathbf{G}\mathbf{r}}$ have the periodicity of the real lattice: $e^{i\mathbf{G}\mathbf{R}_j} = 1$ and form a complete basis.
- The coefficients $u_{n\mathbf{k}}(\mathbf{G})$ are the Fourier transform of $u_{n\mathbf{k}}(\mathbf{r})$:

$$u_{n\mathbf{k}}(\mathbf{G}) = \frac{1}{\Omega_0} \int_{\Omega_0} d\mathbf{r}\, e^{i\mathbf{G}\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$$

- The Bloch wavefunctions are then:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N\Omega_0}} \sum_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} u_{n\mathbf{k}}(\mathbf{G})$$

Plane waves

Basis truncation

- The sum

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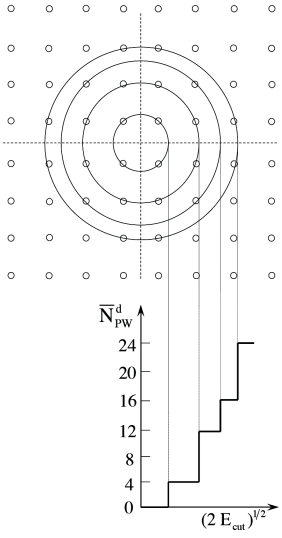
  is still infinite.

- In practice, the high $\mathbf{G}$ components, i.e., for large $|\mathbf{k}+\mathbf{G}|$, are small.
- The expansion can be then truncated according to:

$$\frac{|\mathbf{k}+\mathbf{G}|^2}{2} < E_{\text{cut}}$$

  with E_{cut} (kinetic) energy cutoff. It defines a plane-wave sphere.

- Note that the number of plane waves N_{PW} is discontinuous with E_{cut} (and depends on the unit cell volume).



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Caution: Pseudopotential needed!

- Details in real space are described if their length scale is larger than (approximately) the inverse of largest $|\mathbf{G}|$ (Nyquist sampling theorem).
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- Solution: pseudopotentials and smooth pseudowavefunctions.
- The cutoff E_{cut} generally depends on the pseudopotential.

Non-periodic materials

Supercells

- One cannot use a finite basis set for finite (or non-periodic) systems. Periodic boundary conditions are needed for plane waves.

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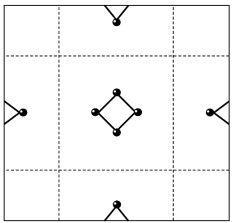
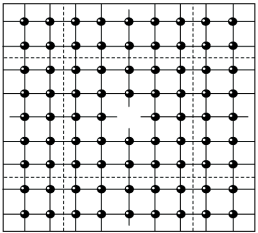
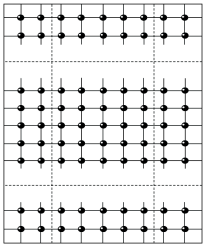
- One cannot use a finite basis set for finite (or non-periodic) systems. Periodic boundary conditions are needed for plane waves.
- Solution: One can use supercells, introducing an artificial periodicity.
- Set the finite system in a box big enough to avoid interaction between replicas. Similarly for point defects in bulk. Care with charged systems!
- Semi-infinite material (e.g. surface): slab geometry. Need to converge also slab thickness.







Life with plane waves

The charge density

- Calculation of the density requires products of the kind: $u^*_{n\mathbf{k}}(\mathbf{r})u_{n\mathbf{k}}(\mathbf{r})$.
- In Fourier space:

$$u^*_{n\mathbf{k}}(\mathbf{r})u_{n\mathbf{k}}(\mathbf{r}) = \left(\sum_{\mathbf{G}} e^{-i\mathbf{G}\mathbf{r}} u^*_{n\mathbf{k}}(\mathbf{G})\right)\left(\sum_{\mathbf{G}'} e^{i\mathbf{G}'\mathbf{r}} u_{n\mathbf{k}}(\mathbf{G}')\right)$$
$$= \sum_{\mathbf{G}\mathbf{G}'} e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}} \left[u^*_{n\mathbf{k}}(\mathbf{G})u_{n\mathbf{k}}(\mathbf{G}')\right]$$

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- Coefficients are non-zero for $|\mathbf{k}+\mathbf{G}|$ inside the sphere, and $|\mathbf{k}+\mathbf{G}'|$ also inside the sphere.
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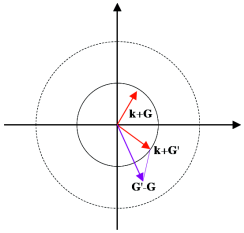
- The sphere for $n(\mathbf{G})$ has a doubled radius.



Life with plane waves

The potential

- Calculation of the action of the Kohn-Sham potential:

$$V_{\mathrm{KS}}\psi_{n\mathbf{k}} \longrightarrow \sum_{\mathbf{G}'} V_{\mathrm{KS}}(\mathbf{G}-\mathbf{G}')u_{n\mathbf{k}}(\mathbf{G}')$$

- Note: convolution theorem of Fourier transform (product $\leftrightarrow$ convolution)
- Again $\max(|\mathbf{G}-\mathbf{G}'|) = 2\max(|\mathbf{G}|)$.
- The kinetic energy cutoff for charge density and potentials is four times the cutoff for wavefunctions (i.e., with $8N_{\mathrm{PW}}$):

$$\frac{|\mathbf{G}|^2}{2} < 4E_{\mathrm{cut}}$$

Fast Fourier Transform (FFT)

Between real and reciprocal spaces

$$n(\mathbf{r}) = \sum_{\mathbf{G} \in \text{sphere2}} e^{i\mathbf{G}\mathbf{r}} n(\mathbf{G})$$

- Discrete Fourier transform: N^2 scaling.

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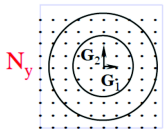
- Discrete Fourier transform: N^2 scaling.
- Fast Fourier Transform (FFT) algorithm: much more efficient $N\log N$ scaling.
- FFT grid in real space ($N_r > N_{\text{PW}}$).

$$n(\mathbf{G}) = \frac{1}{N_r} \sum_{\mathbf{r}_i}^{N_r} e^{i\mathbf{G}\mathbf{r}_i} n(\mathbf{r}_i)$$



Reciprocal lattice

Real lattice: original cell

Life with plane waves

The Hartree potential

$$V_H(\mathbf{r}) = \int d\mathbf{r}' \, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \longrightarrow \nabla^2 V_H(\mathbf{r}) = -4\pi n(\mathbf{r}) \longrightarrow V_H(\mathbf{G}) = \frac{4\pi}{G^2} n(\mathbf{G})$$

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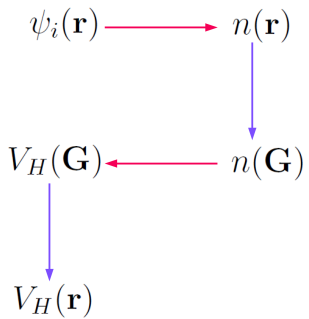
- The divergent $\mathbf{G} = 0$ component is set to 0 (compensation with ionic potential V_{ext}).
- Its value $V_H(\mathbf{G})$ is easy to compute in reciprocal space.
- Its action $V_H(\mathbf{r})\psi_i(\mathbf{r})$ is easy to compute in real space.

Life with plane waves



FFT allows one to switch between real and reciprocal spaces.

Life with plane waves

Operators in plane waves

- Kinetic operator:

$$\langle \mathbf{k}+\mathbf{G}| -\frac{\nabla^2}{2}|\mathbf{k}+\mathbf{G}'\rangle = \frac{|\mathbf{k}+\mathbf{G}|^2}{2}\delta_{\mathbf{G},\mathbf{G}'}$$

- Local potential:

$$\langle \mathbf{k}+\mathbf{G}|\, V_{\mathrm{KS}}(\mathbf{r})|\mathbf{k}+\mathbf{G}'\rangle = \int d\mathbf{r}\, e^{i\mathbf{G}\mathbf{r}} \sum_{\mathbf{G}''} e^{i\mathbf{G}''\mathbf{r}} V_{\mathrm{KS}}(\mathbf{G}'') e^{i\mathbf{G}'\mathbf{r}} = V_{\mathrm{KS}}(\mathbf{G}-\mathbf{G}')$$

Life with plane waves

The Kohn-Sham equations

$$\sum_{\mathbf{G}'} \left[\frac{|\mathbf{k}+\mathbf{G}|^2}{2} \delta_{\mathbf{G},\mathbf{G}'} + V_{\mathrm{KS}}(\mathbf{G}-\mathbf{G}') \right] u_{n\mathbf{k}}(\mathbf{G}') = \epsilon_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{G})$$

Life with plane waves

The Kohn-Sham equations

$$\sum_{\mathbf{G}'} \left[\frac{|\mathbf{k}+\mathbf{G}|^2}{2} \delta_{\mathbf{G},\mathbf{G}'} + V_{\mathrm{KS}}(\mathbf{G}-\mathbf{G}') \right] u_{n\mathbf{k}}(\mathbf{G}') = \epsilon_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{G})$$

- Diagonal in $\mathbf{k}$. Easy parallelisation over $\mathbf{k}$.
- Note that, in general, pseudopotentials are non-local operators in real space: $V_{\mathrm{ext}}(\mathbf{r}) \to V_{\mathrm{ext}}(\mathbf{r}, \mathbf{r}')$. Therefore, $V_{\mathrm{ext}}(\mathbf{G}-\mathbf{G}') \to V_{\mathrm{ext}}(\mathbf{k}, \mathbf{G}, \mathbf{G}')$

Plane waves: advantages/disadvantages

Plane-wave basis

- **Simple.** Plane-wave expansion is equivalent to interpolate functions in terms of sinus/cosinus that have lattice periodicity. Many analytic expressions. Best choice for theory and code developments.
- **Systematic.** Plane waves are eigenvectors of the kinetic energy operator (i.e., an orthonormal set). Easy to use: only one convergence parameter.
- **Efficient.** FFT algorithm allows one to switch seamlessly between real and reciprocal spaces.
- **Agnostic (blind).** Same for all states and delocalised everywhere. The precision is the same everywhere, independently of the atomic positions. Easy for calculation of forces and molecular dynamics (ionic displacements). However, no adaptation to different physical situations: many basis functions are needed for localised states.
- **Needs periodic boundary conditions.** Supercells are required for non-periodic systems.
- **Needs pseudopotentials.** They always come with approximations ("pseudization").

Summary

How to solve Kohn-Sham equations in a computer?

- Representation of all quantities in finite and discrete bases and grids.
- Converge carefully each quantity of interest.
- Here we have discussed two fundamental convergence parameters: grid of **k** points and energy cutoff E_{cut} (i.e., number of plane waves **G**).
- Basis set is not a religious faith....

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Image credits: X. Gonze, P. Giannozzi, ...

Many thanks

Many thanks ...and have fun!