Introduction
to
Plane Waves and $\vec{k}-$points

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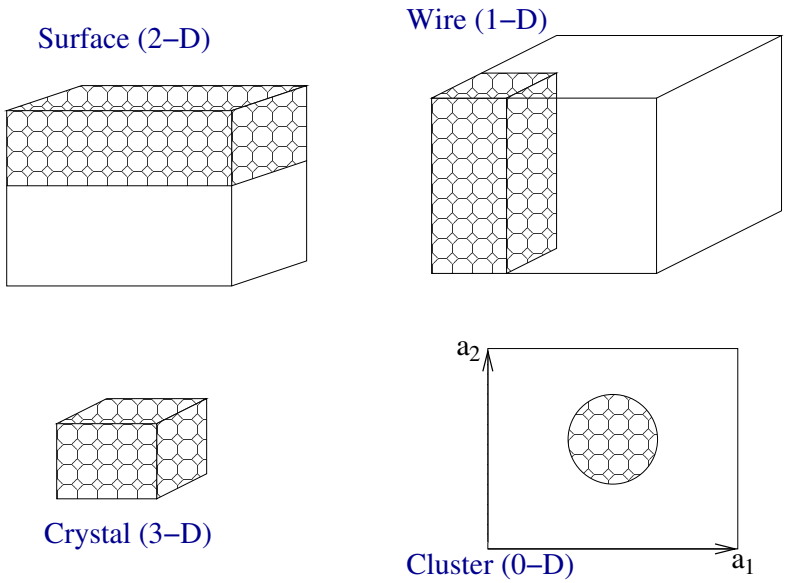
OUTLINE

- Periodic Systems
- Kohn-Sham wavefunctions of periodic systems
- Representations of wavefunctions: Plane Waves
- Consequences of symmetries
- Brillouin Zone Integrations
- Metallic Systems

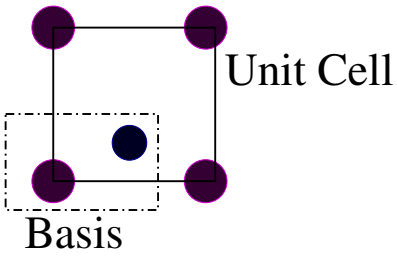
Periodic Systems

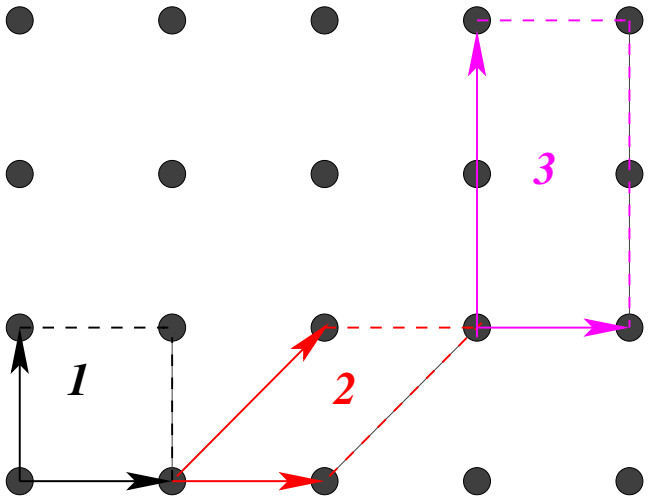
- Structure of periodic systems
  - Bravais Lattice: Periodicity
    periodic unit: *unit cell* vectors
    $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$
    Cell volume: Ω_{cell}
    Lattice points: $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$
  - Basis: Structure within a unit
    – positions and types of atoms: $\vec{\tau}_i$, Z_i

- Examples:



Unit Cell and Choices





N_a: Number of atoms per unit cell (basis)

For unit cells 1 and 2, $N_a = 2$.

For unit cell 3, $N_a = 4$.

Primitive unit cell: N_a is the *smallest*

All choices should give *equivalent* description

Reciprocal Space

- Fourier Transfrom: $f(\vec{r}) \rightarrow f(\vec{q})$

- Periodic Boundary Conditions:
  $f(\vec{r}) = f(\vec{r} + N_i \vec{a}_i)$
  Born – von Karman conditions:
  $\exp(i \vec{q} \cdot N_i \vec{a}_i) = 1$
  $\vec{q} \cdot \vec{a}_i = 2\pi \underset{i}{integer}\, N$
  $f(\vec{q}) = \frac{1}{\Omega_{crys}} \int_{\Omega_{crys}} d\vec{r} f(\vec{r}) exp(i\vec{q} \cdot \vec{r})$,
  $\Omega_{crys} = \Omega_{cell} \Pi_i N_i$

- For a function with lattice periodicity:
  $f(\vec{r}) = f(\vec{r} + \vec{R})$,
  $\vec{q} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3$ and $\vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$
  $\Rightarrow \vec{q} = \vec{G}$
  $\vec{b}_i$: primitive vectors of *reciprocal space lattice*
  eg. $\vec{b}_1 = 2\pi \vec{a}_2 \times \vec{a}_3 / \Omega_{cell}$
  $\vec{G}$: reciprocal space lattice (RSL) vector

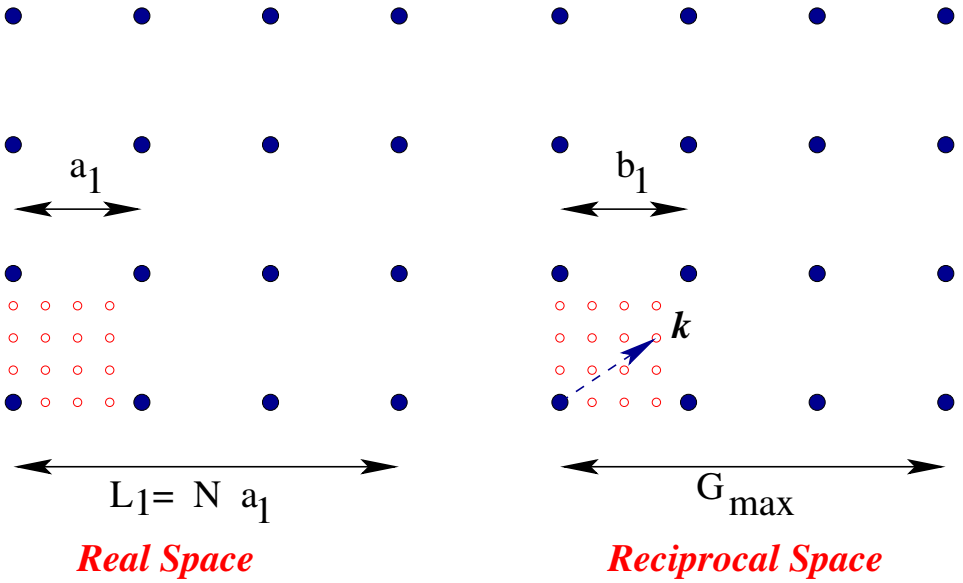
- Brillouin Zone (BZ):
  Wigner Seitz cell in RS,
  volume, $\Omega_{BZ} = (2\pi)^3/\Omega_{cell}$

- For a general function:

$$\vec{q} = \vec{k} + \vec{G},$$

$\vec{k} = \frac{n_1}{N_1}\vec{b}_1 + \frac{n_2}{N_2}\vec{b}_2 + \frac{n_3}{N_3}\vec{b}_3$

$\vec{k} \in$ primitive cell of the RSL or BZ.



- FFT meshes:
  Long length-scales: $L_i = N_i|\vec{a}_i|, \propto 1/\Delta k$
  Short length-scales: $\Delta r \propto 1/G_{max}$

Periodic systems: Electron wavefunctions

- Translational symmetry: $\hat{T}_{\vec{R}} H = H \hat{T}_{\vec{R}}$

- Bloch theorem:

$$\hat{R}\psi(\vec{r}) = \psi(\vec{r} + \vec{R}) = \exp(i\vec{k} \cdot \vec{R})\psi(\vec{r})$$

  $\vec{k}$ is a quantum number to label ψ:
  $\psi_k(\vec{r}) = exp(i\vec{k} \cdot \vec{r}) u_{\vec{k}}(\vec{r})$
  $u_{\vec{k}}(\vec{r} + \vec{R}) = u_{\vec{k}}(\vec{r})$ is lattice periodic.

- For each $\vec{k}$, discrete energy eigenvalues:
  $\epsilon_{i\vec{k}}$ form energy bands
  $\epsilon_{i\vec{k}}$: non-analytic only at BZ-boundary

- Integrals in $k-$space (in DFT):

$$\rho(\vec{r}) = \sum_i \int_{BZ} d\vec{k} |\psi_{i\vec{k}}(\vec{r})|^2$$

Representation of $\psi_{i\vec{k}}$: Plane Waves

$$\psi_{i\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega_{cell}}} \exp(i\vec{k}\cdot\vec{r}) \sum_{\vec{G}} C_{i\vec{k}}^{\vec{G}} \exp(i\vec{G}\cdot\vec{r})$$

Plane Waves: $< \vec{r}|G >= \frac{1}{\sqrt{\Omega_{cell}}} \exp(i\vec{G}\cdot\vec{r})$

- $C_{i\vec{k}}^{\vec{G}} = \int_{\Omega_{cell}} < G|\vec{r} > u_{i\vec{k}}(\vec{r}) d\vec{r}$

- Orthonormality: $< \vec{G}|\vec{G}' >= \delta_{\vec{G},\vec{G}'}$

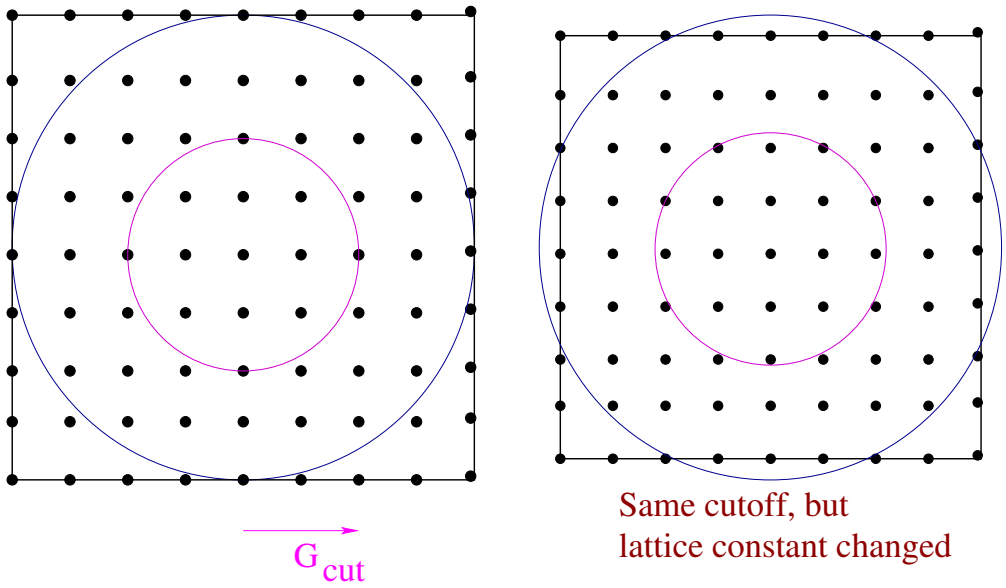
- No dependence on the *basis* of a crystal
  $\rightarrow$ Computation of forces easy!

- A single parameter: E_{cut}
  $\vec{G} \in$ basis set, if $\frac{1}{2}|\vec{G}|^2 < E_{cut}$

- Uniform resolution in direct space:
  $\Delta r \propto \frac{2\pi}{G_{cut}}$

Plane Waves (contd)

- Plane wave cutoff for density:
  $2G_{cut} \rightarrow 4E_{cut}$



- Basis set depends on the lattice constant: Pulay corrections

- FFT essential for efficiency $(\hat{T} + V_{KS})\psi$: eg. $V(\vec{r})\psi(\vec{r})$: convolution in G-space!

Symmetry

- Time reversal symmetry:
  non-magnetic systems $\psi_{i-\vec{k}} = \psi^{\star}_{i\vec{k}}$

- Inversion symmetry:
  $\vec{r} \rightarrow -\vec{r}$ leads to *real* $C^{\vec{G}}_{i\vec{k}}$.

- Point symmetries $\widehat{S}$: $\widehat{S}H = H\widehat{S}$
  rotations, reflections, inversions and combinations.

  $$\psi_{i,\widehat{S}^{-1}\vec{k}}(\vec{r}) = \psi_{i,\vec{k}}(\widehat{S}\vec{r})$$

  also an eigenfunction with energy $\epsilon_{i\vec{k}}$.

- Space Groups (230):
  combination of point and translational symmetries
  Irreducible representations (Irrep):
  $\star$ point group of $\vec{k}$: $S \in G_k$ if $S\vec{k} = \vec{k}$
  $\star$ *Star of* $\vec{k}$: $\vec{k}_i = S.\vec{k}$; N_s *vectors.*
  D(Irrep of the space group): $D = D_{irrepofG_k} \times N_s$

Symmetries (contd)

- Irreducible BZ (IBZ):
  The smallest region in the BZ such that there are no two $\vec{k}$'s that belong to the same *star*.

- Knowledge of wavefunctions in IBZ $\Rightarrow$ wavefunctions elsewhere in the BZ.

- Band structure plots often are shown along the high symmetry lines.

- Irrep labels at various $\vec{k}$'s determine the symmetry of localized Wannier functions.

BZ Integration: Special k-points

- Accurate integration:

$$\int_{BZ} d\vec{k} f(\vec{k}) = \frac{\Omega_{BZ}}{N_k} \sum_{i}^{N_k} f(\vec{k}_i)$$

- Symmetries: $\int_{BZ}$ replaced by $\int_{IBZ}$

  - A scalar property: eg. $\epsilon_{i\vec{k}}$
    $\sum_{\vec{k}_i \in BZ} f(\vec{k}_i) = \sum_{\vec{k}_i \in IBZ} w_k f(\vec{k}_i)$
    w_k: weight of a k-point.

  - Scalar field: eg. density
    $\rho_I(\vec{r}) = \sum_{\vec{k}_i \in IBZ} w_k \rho(\vec{k}_i, \vec{r})$
    $\rho(\vec{r}) = \frac{1}{N_S} \sum_S \rho_I(\hat{S}\vec{r})$

Special k-points

- $f(\vec{k}) = \sum_{\vec{R}} f(\vec{R}) \exp(i\vec{k} \cdot \vec{R})$
  $f(\vec{R})$ decays off exponentially (insulators).

- Baldereschi point:
  • there is a mean value point (MVP) where the integrand equals the integral
  • symmetries $\Rightarrow$ approx. location of MVP
  eg. SC: $\vec{k} = (\pi/2a)(1,1,1)$
  BCC: $\vec{k} = (2\pi/a)(1,1,3)/6$.

- Chadi and Cohen schemes:
  Generalization of the MVP idea to get larger sets

- Monkhorst-Pack k-points:

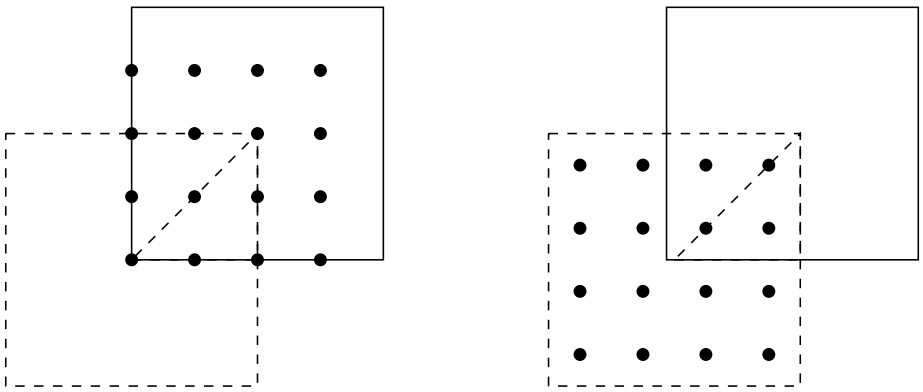
$$\vec{k}(n_1, n_2, n_3) = \sum_i^3 \frac{2n_i - N_i - 1}{2N_i} \vec{b}_i$$

- Uniform mesh; exact integration for Fourier components $\vec{R}$ up to $N_i a_i$.

- Scaled reciprocal lattice with an offset.

- $N_i = 2$ for SC gives the Baldereschi point

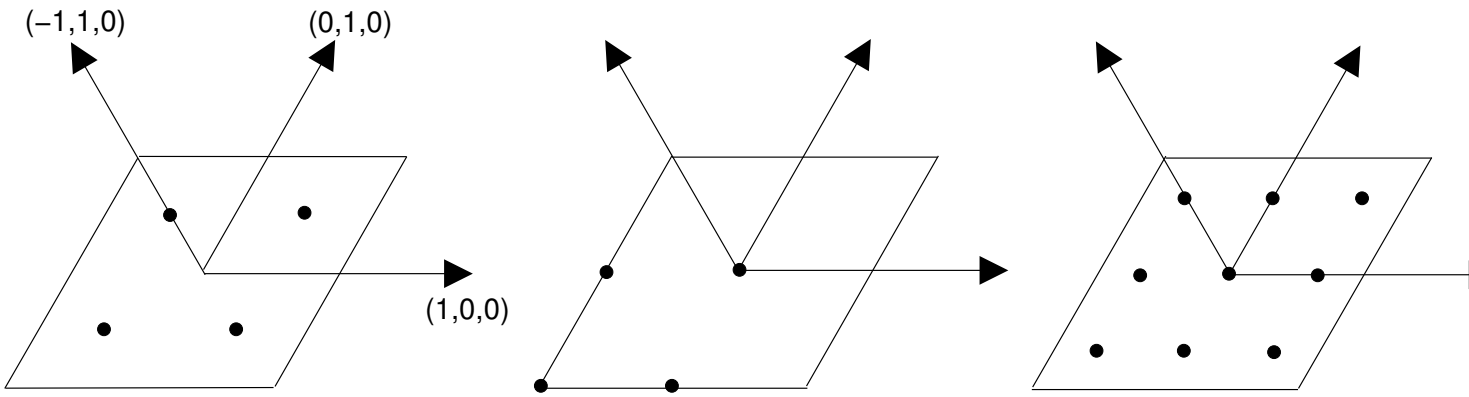
- For cubic case, even N_i recommended: avoids high symmetry $\vec{k}$'s (eg. (000) and BZ boundaries)



- See Moreno and Soler PRB 45, 13841 (92).

- **Note:** even N_i meshes do not satisfy BvK conditions.

Symmetry of MP k-point mesh



- Symmetry of the hexagonal lattice is broken by an even N_i Monkhorst-Pack mesh.

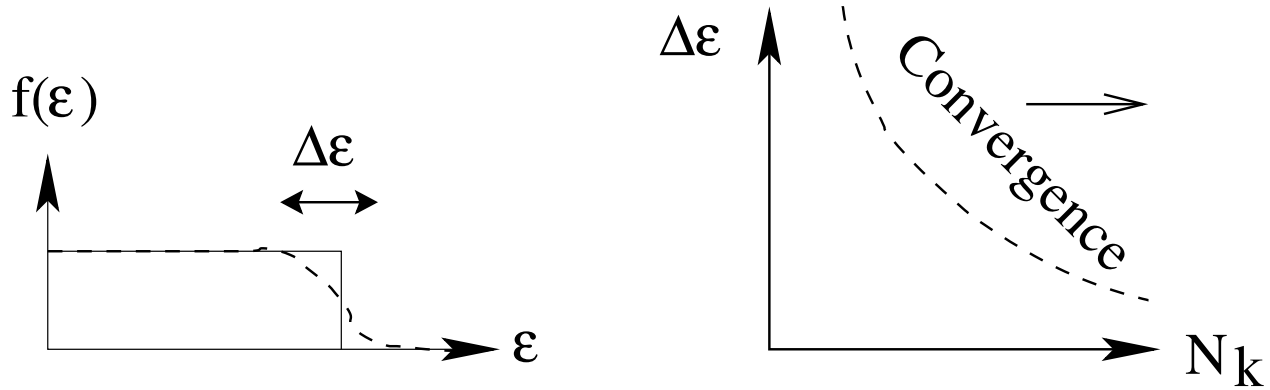
- However, a shift in this mesh restores its symmetry.

- an odd N_i M-P mesh maintains the hexagonal symmetry.

k-point sampling: Metals

Presence of a Fermi surface:
$\Rightarrow$ Discontinuities in occupation numbers f_{ik}:
eg. $\int_{BZ} d\vec{k} \epsilon_{i\vec{k}} f_{i\vec{k}}$
Smear or smoothen the occupation numbers:
scale $= \Delta\epsilon = k_B T$
Various schemes of smearing a delta function
($x = \frac{\epsilon - \epsilon_F}{\Delta\epsilon}$):

- Fermi-Dirac smearing: $0.25/cosh^2(x/2)$
- Gaussian smearing: $\exp(-x^2)/\sqrt{\pi}$



N_k for convergence of $E_{tot}(N_k, \Delta\epsilon)$ increseas with small $\Delta\epsilon$ and band gap.

$\vec{k}-$points: Practicalities

- Supercell (N_s unit cells) calculations:
  Brillouin zone is smaller: $N_k \propto 1/N_s$
  Number of PW is larger: $N_{pw} \propto N_s$
  Mapping for identical representation:

$$\vec{k}_s + \vec{G}_s = \vec{k}$$

- Perturbation calculations:
  perturbation with wave vector $\vec{q}_p$
  Ideally, for any $\vec{k}$,

$$\vec{k} + \vec{q}_p \in \{\vec{k}\}$$

  $\Rightarrow$ supercell commensurate with $\vec{q}_p$ has equivalent set of $\vec{k}-$points.

How to choose cutoffs?

- E_{cut}: *Ref. Eric's talk.*
  Convergence of energy of a single atom.

- Energy *differences* converge faster than *absolute* energies.

- $E_{kinetic,q>q_c} < 0.001\ E_{kinetic}$

- Which properties?
  Stresses, elastic moduli need higher E_{cut}.

- N_k:
  large if band gap is small. small for flat bands (eg. ionic insulators).

- Which properties?
  dielectric response: higher N_k (eg. Si).

Lab Exercise

Use multi-dataset inputs:

- Silicon, diamond structure (a=5.41 $\mathring{A}$):
  Use $E_{cut} = 8$ Ha, MP k-points (N×N×N), for N from 2 to 8 and *plot* E_{tot} *vs* N.
  - *with no shift (offset).*
  - *with a shift (offset), say 0.5 0.5 0.5.*

- Aluminium, FCC structure (a=4.04 Å):
  Use $E_{cut} = 8$ Ha, MP k-points (N×N×N), for N from 4 to 12 and $\Delta\epsilon = k_B T$ =0.02, 0.04, 0.08, 0.12, 0.16 eV.
  - *Plot* E_{tot} *as a function of* N_k.
  - *Plot* E_{tot} *as a function of* $\Delta\epsilon$.

Summary

- Plane wave cutoff E_{cut} controls the smallest length-scale
- $\vec{k}-$points control the longest length-scale
- $\vec{k}-$points applicable to electrons and phonons
- Various $\vec{k}-$point schemes for BZ sampling
- Number of $\vec{k}$-points should increase with decreasing band gap and smearing T.
- Use of symmetries allows treatment of only symmetry inequivalent $\vec{k}-$points and reduces computation.

References

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