Intro to DFT Part II

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k-Sampling

Hope you know:

- Reciprocal space

- Irreducible Brillouin zone (IBZ)

- Unit cell

Any point in the IBZ can represent a k-point, there are an infinite number of discrete k-vectors well qualified to be a wave function. The wave function and other properties vary smoothly over the IBZ, so we can just sample a finite number of k-points that represent each small region.

Choose k-points:

- Big system vs. small system

- Isolated molecule

- Symmetric system

Keynote for k-Point Sample

- Generate a grid of k-points spaced evenly throughout the Brillouin Zone (or along each reciprocal lattice vector).

- Any crystal structure can be represented in two spaces: real space (primitive cell or unit cell in x, y, z) and reciprocal space (Brillouin Zone in kx, ky, kz).

- Many physical properties of crystals as well as the geometry of the three-dimensional patterns resulting from a diffraction event (e.g., X-ray diffraction) are represented using the reciprocal lattice.

- Diffraction occurs in inverse proportion to the spacing between objects causing diffraction.

- Any point in the Brillouin Zone can represent a k-point, there are an infinite number of discrete k-vectors well qualified to be a wave function.

- The wave function and other properties (e.g., band structure) vary smoothly over the Brillouin Zone, so we can just sample a finite number of k-points that represent each small region.

- Each k-point contains rich information: Wavelength ($\lambda = 2\pi/k$), and kinetic energy ($E = k^2/2$); All the incoming energies on each k-point, it will form band structure.

- More k points lead to a more accurate simulation, but it costs more computational time.
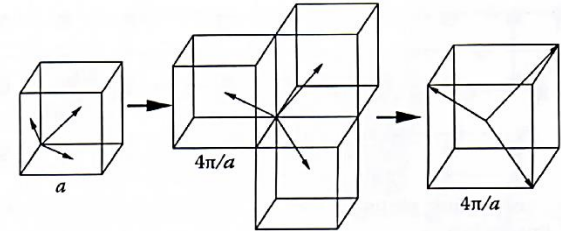

Figure 6.9 A face-centered cubic (FCC) lattice with a in the real space transforms to a body-centered cubic (BCC) lattice with $4\pi/a$ in the reciprocal space.
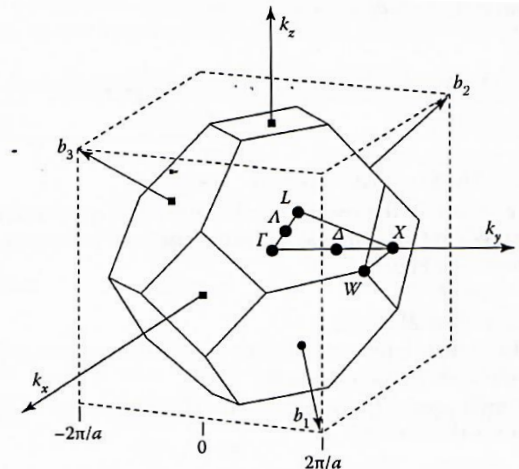

Figure 6.11 First Brillouin zone of FCC lattice showing some of the high symmetry lines and points.

| System	Symbol	Description
All	Γ	Center of the Brillouin zone
SC	H	Corner point joining four edges
(simple	N	Center of a face
cubic)	P	Corner point joining three edges
FCC	K	Middle of an edge joining two hexagonal faces
(face-	L	Center of a hexagonal face
centered	U	Middle of an edge joining a hexagonal and a square face
cubic)	W	Corner point
	X	Center of a square face
HCP	A	Center of a hexagonal face
(hexagonal	H	Corner point
close	K	Middle of an edge joining two rectangular faces
packed)	L	Middle of an edge joining a hexagonal and a rectangular face
	M	Center of a rectangular face

Each k-point contains rich information:

- k vector, wavelength ($\lambda = 2\pi/k$), and kinetic energy ($E = k^2/2$).

- All the incoming energies on each k-point, it will form band structure.
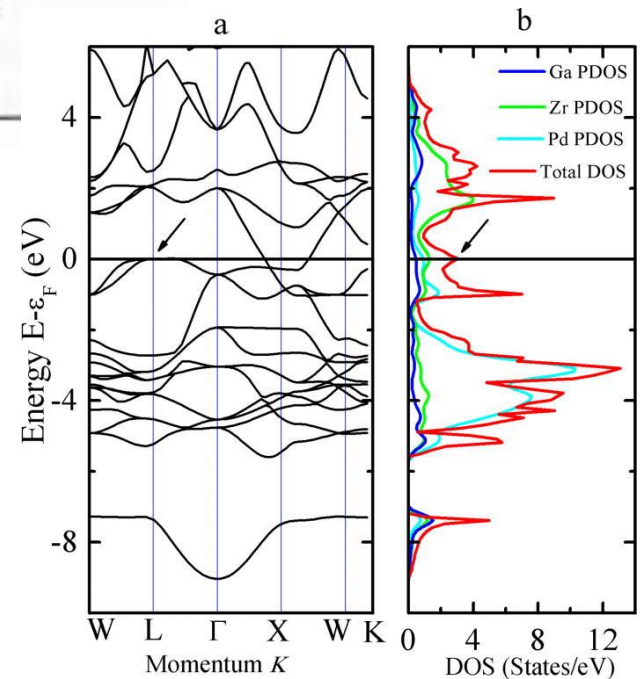
Band Structure of Graphene
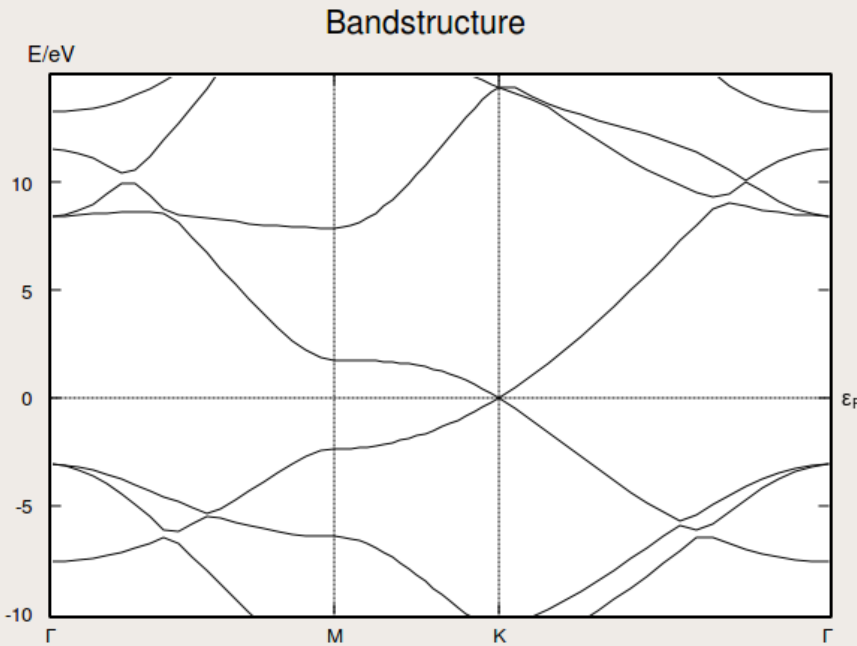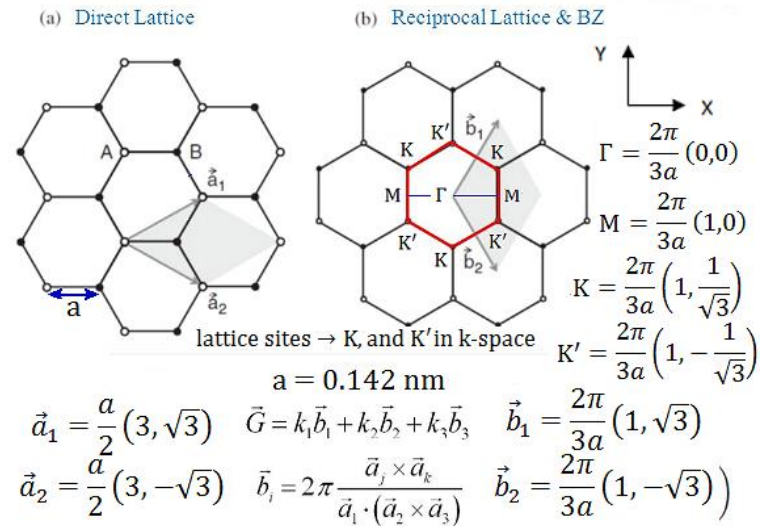
Bloch Theorem and Plane-Wave Basis Set

Atoms in most cases are arranged in a periodically repeating pattern in solids.

The potential acting on electrons is periodic and invariant with respect to the real lattice vector *R*.

$$U(r) = u(r + R)$$

$$R = n_1 a_1 + n_2 a_2 + n_3 a_3$$
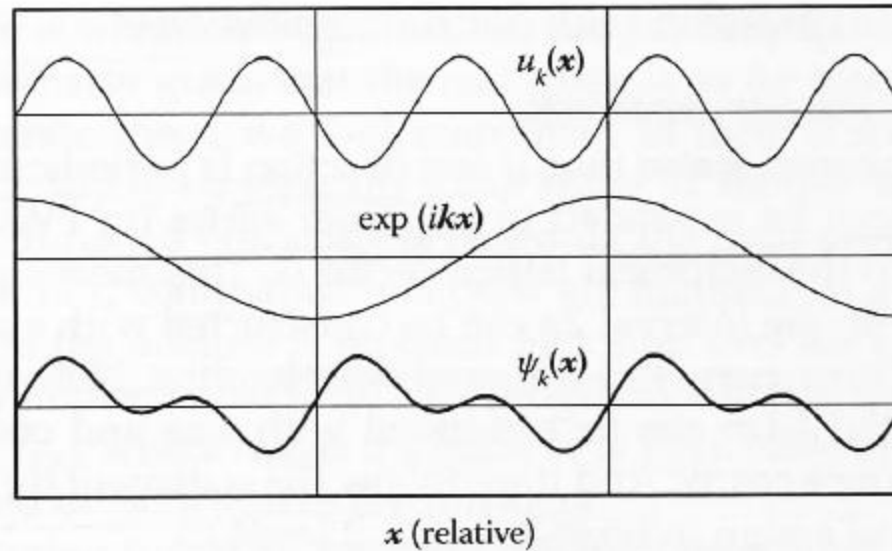
n_i = any integral number, a_i = unit cell vectors

Electron density in a periodic solid: $\rho(r) = \rho(r + R)$

Bloch expression: $\psi_k(r) = u_k(r) exp(ik \cdot r)$

$u_k(r)$ is a periodic function that has the same periodicity as the potential $u_k(r) = u_k(r + R)$.

$$\psi_k(r + R) = u_k(r + R)\exp[ik \cdot (r + R)] = \psi_k(r)\exp(ik \cdot R)$$

R is the real lattice vector.

Wave functions or KS orbitals, potentials, electron density or energies can be expressed in periodic forms in real space.

If any function is periodic within a finite real space, it can be expanded in a Fourier series with respect to the reciprocal lattice vector G.

$$u_k(r) = \sum_G c_k(G)\exp(iG \cdot r)$$

- $c_k(G)$ is the Fourier expansion coefficients.
- $\exp(iG \cdot r)$ is the phase factor at each G. It represents a PW traveling in space, perpendicular to the vector G.

Expression of a wave function in the reciprocal space with the introduction of G.

Periodicity of a wave function in the real space

Re-write wave function:

$$\psi_k(r) = u_k(r)exp(ik \cdot r) = \sum_G c_k(G)\exp(iG \cdot r)\exp(ik \cdot r) = \sum_G c_k(G)\exp[i(k + G) \cdot r]$$

A superposition of many PWs with wave vectors which differ by G.

The reciprocal space is the Fourier transformation of the real space.

In order to save computational time and transforming functions between different coordinates (kinetic energy and Hartree potential in the reciprocal space while the XC and external potentials in the real space), we need to use FFT. Charge density has to be computed in both spaces.

$u_k(x)$

$\exp(ikx)$

$\psi_k(x)$

x (relative)
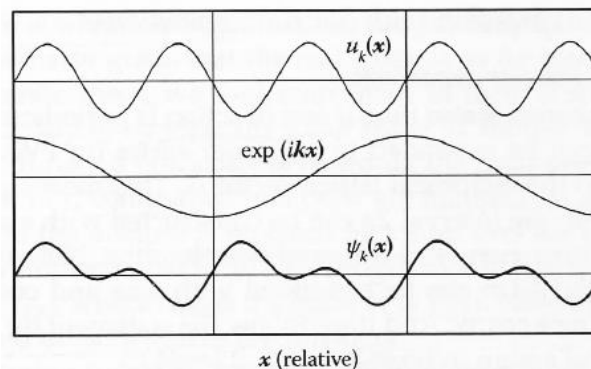
Plane-Wave Expansions

If we expand wave functions, densities, potentials, and energies in conjunction with a PW basis set, they satisfy Bloch theorem, meet the periodic boundary conditions, and are able to switch between the real and reciprocal spaces via FFT.

KS orbitals (wave functions) are approximated by basis sets.

- Wave function

$$\psi_k(r) = \sum_G c_k(G) \exp[i(k + G) \cdot r]$$

- Charge density obtained by squaring the expanded orbitals (wave functions):

$$\rho(r) = \sum_G \rho(G)\exp(iG \cdot r)$$

How Many Plane-Waves We Need - Cutoff Energy

We can make the size of the PW expansion finite by introducing a proper cutoff energy E_{cut}.

$$E_{cut} \geq \frac{1}{2}(k + G)^2$$

In a calculation, we only need to include PWs with kinetic energies smaller than this cutoff energy.

The Fourier expansion for the wave function becomes

$$\psi_k(r) = \sum_{|k+G|_{cut}} c_{k+G} \exp[i(k + G) \cdot r]$$

The k-vectors become finite by k-sampling in the IBZ and G-vectors become finite by energy cutoff.

DFT Application:
Density of States (DOS)

DOS defines the number of electronic states per unit energy range.

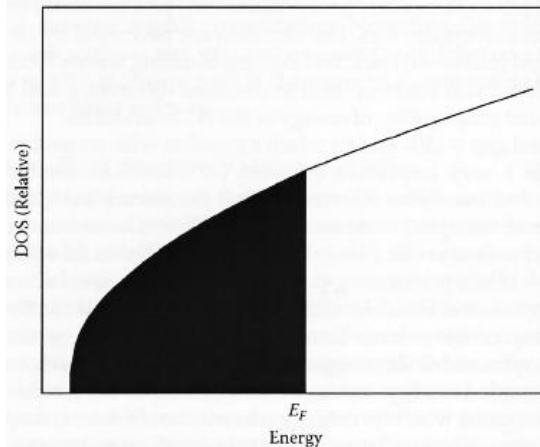For a free electron in one-dimension, the energy relation is

$$\varepsilon_k = \frac{\hbar^2}{2m} k^2 \quad \text{(obtained from Schrödinger's equation)}$$

The total number of states $n(\varepsilon)$

$$n(\varepsilon) = \frac{V}{3\pi^2} k_F^3 = \frac{V}{3\pi^2} \left(\frac{2m\varepsilon}{\hbar^2}\right)^{3/2}$$

The DOS is

$$D(\varepsilon) = \frac{dn}{d\varepsilon} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2} \propto \sqrt{\varepsilon}$$
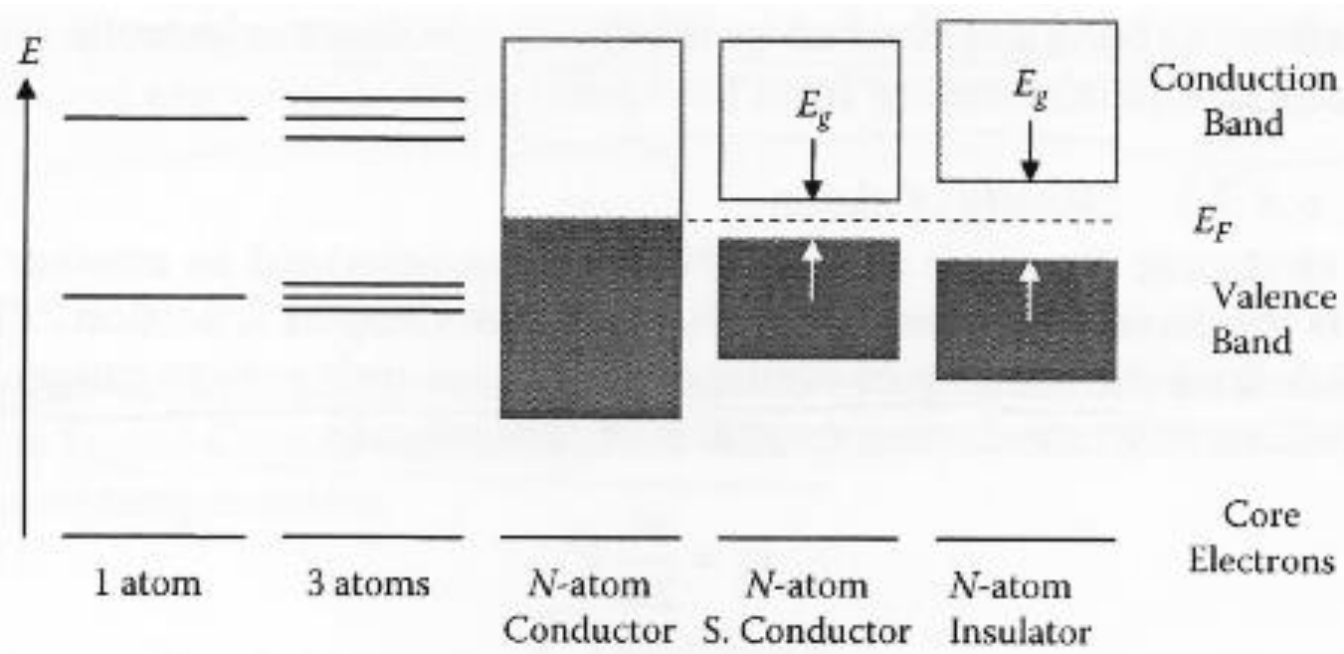

DOS (Relative)

E_F

Energy

The integral of DOS up to the Fermi level is the total number of electrons in the system:

$$\int_0^{E_F} D(\varepsilon)d\varepsilon = n$$

Whether any state is occupied by electron or not is decided by a distribution function, $f(\varepsilon)$ at nonzero temperatures:

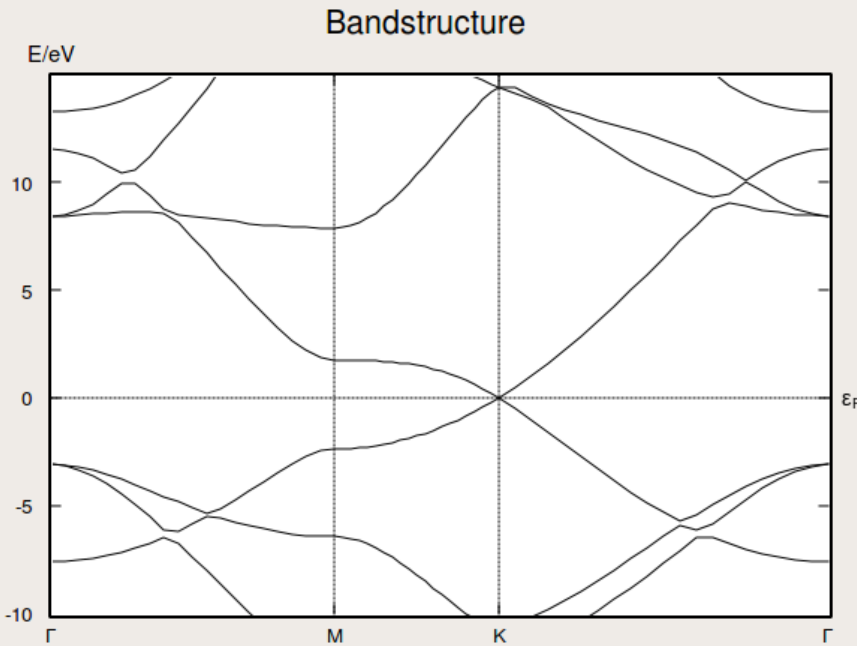$$\int_0^{\infty} D(\varepsilon)f(\varepsilon)d\varepsilon = n$$

DFT Application:
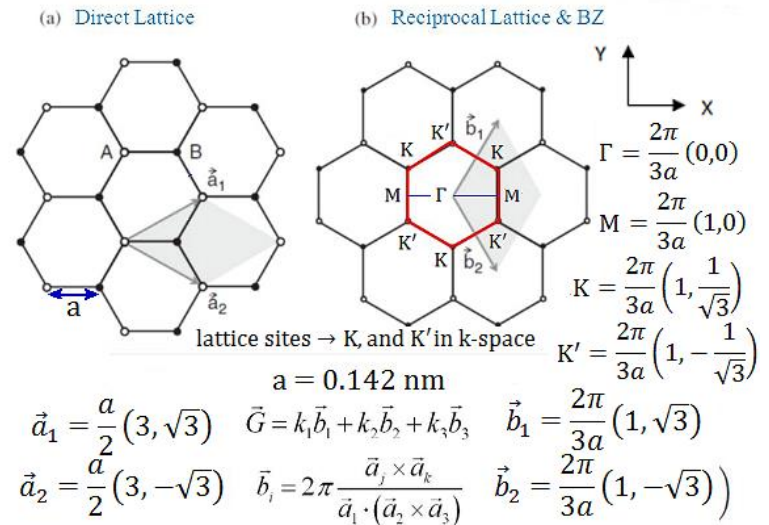# Band Structure of Electrons in Solids

The band structure of a solid:

- exhibits all ε_{nk} points at each band and k-point;

- identifies **each energy level of electrons** (eigenvalues); and

- describes the band gap formed by interactions between electrons and the periodic potentials coming from the core.

Band Structure of Graphene

Atomic Orbitals Basis Set

- Basis set is used to determine wave function.
- A linear combination of atomic orbitals basis set
- A larger or more complicated basis set leads to a more accurate simulation, but it takes a longer computational time.
- Basis functions have to be atomic-like (radial functions multiplied by spherical harmonics)

https://en.wikipedia.org/wiki/Radial_basis_function

- They must be of finite support, i.e., each orbital **becomes strictly zero** beyond some cutoff radius chosen by the user.

- Different from plane-wave basis set

- https://en.wikipedia.org/wiki/Basis_set_(chemistry)

$$\phi_i = \sum_r c_{ri} \chi_r$$

$$\phi_i = c_{1i}\chi_1 + c_{2i}\chi_2 + c_{3i}\chi_3 + \cdots + c_{ni}\chi_n$$
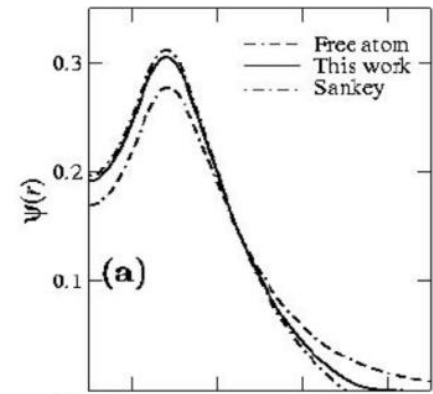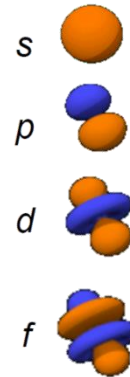
Strictly localised

(zero beyond cut-off radius)

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Quiz

- Review your notes and discuss with your group members
- Briefly explain 9 QM and DFT concepts:
    - Schrödinger equation
    - Wave function
    - Density functional theory
    - Kohn-Sham approach
    - Pseudopotential
    - LDA vs. GGA
    - k-sampling
    - Bloch theorem
    - Plane-wave vs. atomic orbital basis set