

Intro to DFT Part I

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Important Note from Last Lecture:

Kohn-Sham Method

$$\left[-\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_I^N \sum_i^n \frac{Z_I}{|r_{Ii}|} + \frac{1}{2} \sum_{i \neq j}^n \frac{1}{|r_{ij}|} \right] \Psi(r_i) = E \Psi(r_i)$$

- A major difficulty is the last term, the coupled interactions between n electrons.
- The last term contains various interactions that are difficult to formulate in calculable equations.

Kohn-Sham method:

- Map the n -electron system (interacting) on the one-electron system (noninteracting) under the given external energy.

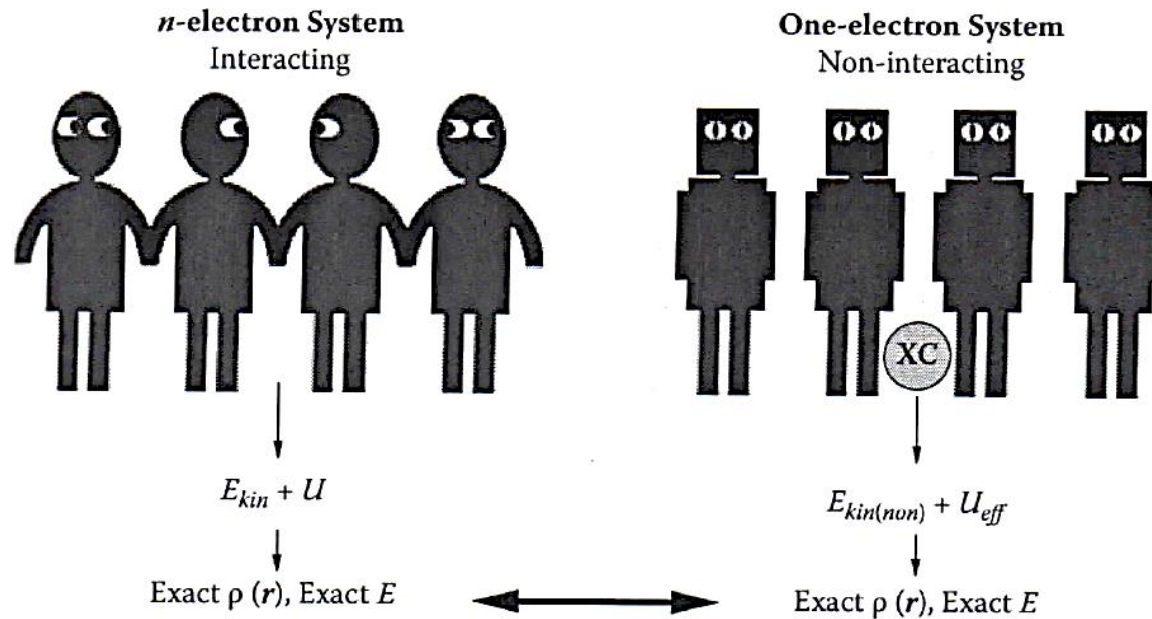


Figure 5.7 Schematic of the Kohn-Sham ansatz.

The corresponding Hamiltonian is

$$\hat{H}_{KS} = E_{kin}^{non} + U_{ext} + U_H + U_{xc} = -\frac{1}{2}\nabla^2 + U_{eff}$$

U_{eff} manipulates the ground-state electron density of the noninteracting system to be identical with that of the true interacting system.

Kinetic Energy

$$E = E_{kin}^{non} + E_{ext} + E_H + E_{xc}$$

In a **noninteracting system** of the KS scheme

$$E_{kin}^{non} = -\frac{1}{2} \sum_{i=1}^n \phi_i^*(r) \nabla^2 \phi_i(r)$$

The summation form with the KS orbitals ϕ_i

This noninteracting kinetic energy accounts for most of the total kinetic energy, and the neglected interacting kinetic energy is included in the XC term E_{xc} .

Assume a system of noninteracting and locally homogeneous electrons:

$$E_{kin}^{hom} = \int \varepsilon_{kin}^{hom}[\rho(r)] dr = C \int \rho^{\frac{5}{3}}(r) dr$$

C is a constant

External Energy

$$E = E_{kin}^{non} + E_{ext} + E_H + E_{xc}$$

External energy comes from the interaction **between an electron and other nuclei**.

$$E_{ext}[\rho(r)] = \int \phi^*(r) U_{ext}(r) \phi_i(r) dr = \int U_{ext}(r) \rho(r) dr$$

$E_{ext}[\rho(r)]$ is a functional, meaning that it is a function of $\rho(r)$, which in turn is a function of r (electronic coordinates).

A functional takes a function as input and outputs a number.

Hartree Energy

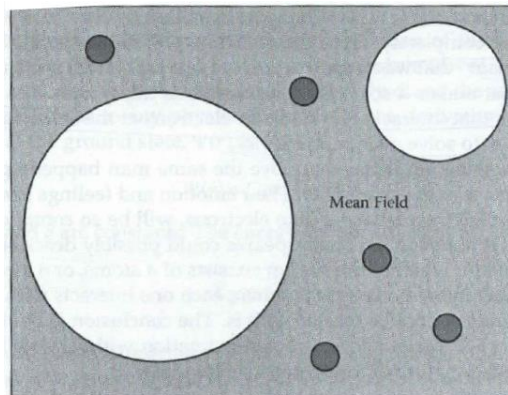
$$E = E_{kin}^{non} + E_{ext} + E_H + E_{xc}$$

In a noninteracting charge distribution, the Hartree potential comes from the interaction **between an electron at r and the mean electron density at r'** in a mean-field approximation:

$$U_H(r) = \int \frac{\rho(r')}{|r - r'|} dr'$$

The Hartree energy is expressed as:

$$E_H[\rho(r)] = \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr'$$



Exchange-Correlation Energy

$$E = E_{kin}^{non} + E_{ext} + E_H + E_{xc}$$

The XC term consists of all quantum effects and is approximated in terms of electron density.

$$E_{xc} = E_x + E_c$$

E_x is the exchange energy between electrons with **the same spin** (Pauli exclusion principle). – Antisymmetric nature of wave function

E_c is the correlation energy between electrons with **different spins**.

The resulting exchange energy is the sum of the four-center integrals as a function of the single-particle orbitals:

$$E_x = -\frac{1}{2} \sum_{ij}^n \int \int \frac{\phi_i^*(r) \phi_j^*(r') \phi_i(r') \phi_j(r)}{|r - r'|} dr dr'$$

In principle, E_x can be calculated exactly. For computational convenience, E_x is approximated.

E_c - electronic correlation effect between two electrons with different spins.

- Two electrons with different spin can **occupy the same orbital**, but they also **repel each other** because of the same negative charges they have.
- This is called electronic correlation, generating a small attractive energy.

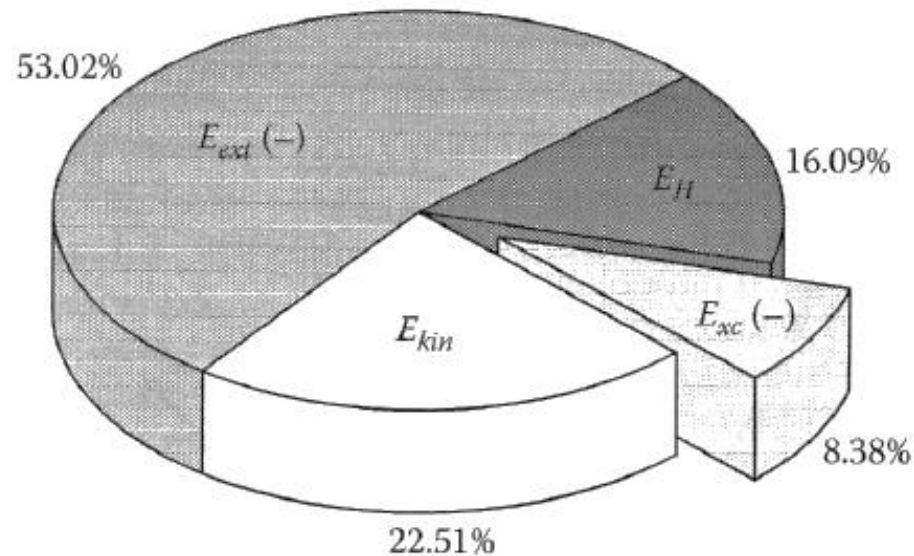
E_c is much smaller than E_x for materials at typical electron density. However, at very low electron density, E_c becomes very important since the E_x becomes less active in these sparse electron densities.

DFT has different methods to calculate E_{xc} , e.g., LDA and GGA. (more details later).

Magnitudes of Each Energy Term

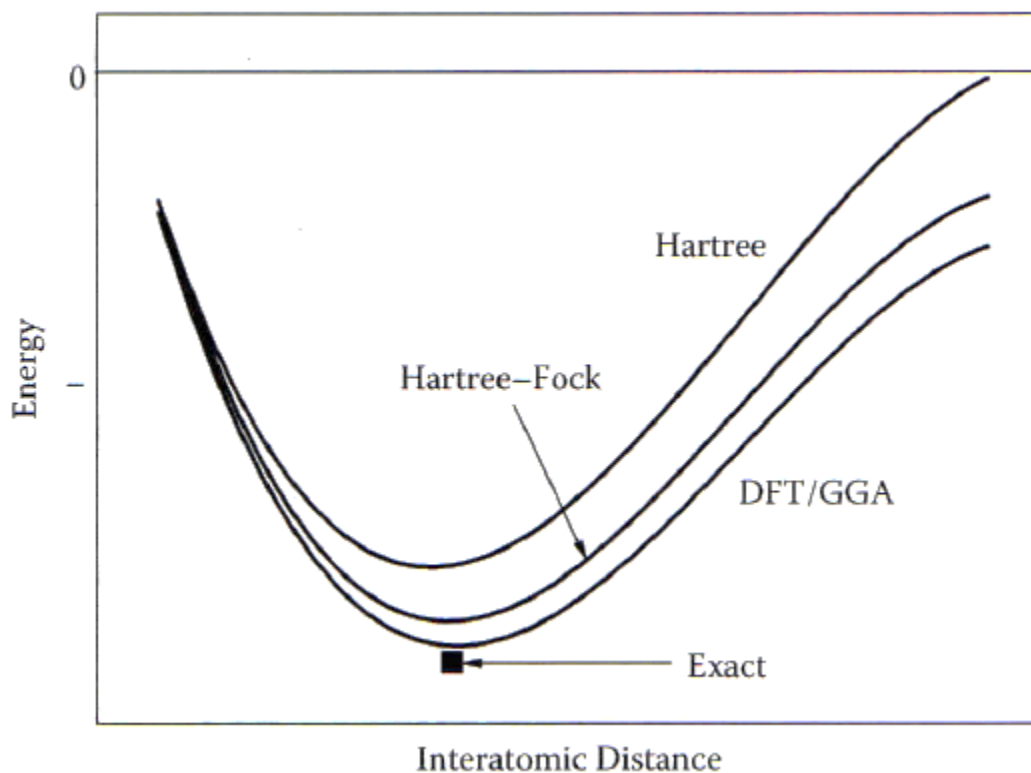
$$E = E_{kin}^{non} + E_{ext} + E_H + E_{xc}$$

Magnitudes of energy terms of an He atom



The XC energy is involved in the changes happening in the atomic, molecular, or solid system.

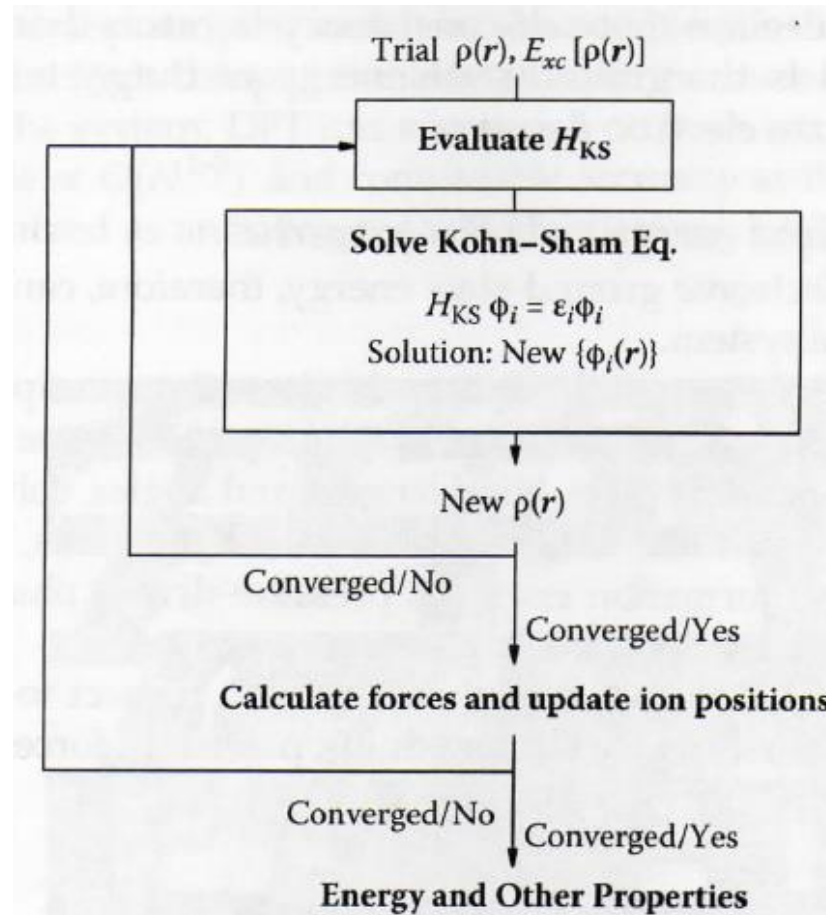
Even the XC energy term is small, it determines the accuracy of DFT.



The energy difference between the Hartree and HF methods represents E_x .
The energy difference between the HF and DFT methods represents E_c .

- Solve KS equations by direct diagonalization of KS Hamiltonian matrix
- Solutions, a set of KS orbitals ϕ_i

$$\rho(r) = 2 \sum_i^{occ} |\phi_i(r)|^2$$



Detailed Procedure

- 1) Construct the initial $\rho(r)$ of a material approximated by superimposing the electron densities of each atom in its isolated state as provided by the pseudopotential.
- 2) Calculate U_{xc} and other energy terms to evaluate $\hat{H}_{KS} = E_{kin}^{non} + U_{ext} + U_H + U_{xc}$.
- 3) Solve a set of KS equations by direct diagonalization in plane-wave-subset and obtain the solutions, a set of KS orbitals ϕ_i .
- 4) Use the new ϕ_i , calculate new $\rho(r)$ with mixing of previous and current densities, repeat the above steps.
- 5) Stop iteration when the energy E change of the system becomes less than a preset stopping criterion for the E change (e.g., $10^{-4} - 10^{-8}$ eV). Is E converged or not?
- 6) If converged, calculate forces and update ion positions.
- 7) Compare the calculated forces with a preset criterion for the forces (e.g. 0.01 eV/Å). If not converged in the forces, repeat the above steps.

What Can DFT Simulate?

- Bulk, surface and molecule (or solid, liquid and gas phases)
- Chemical reactions
- Phase diagram
- Materials properties
- Temperature and pressure effects
etc.

Key DFT Parameters

- Pseudopotential
- Exchange-correlation functional
- k-sampling
- Bloch theorem
- Plane-wave vs. atomic orbital basis set

Pseudopotential

Based on two conditions:

(1) Freezing core electrons. When atoms get together to form a solid, the core electrons stick tightly to their nucleus in a deep potential well and remain unchanged under most circumstances.

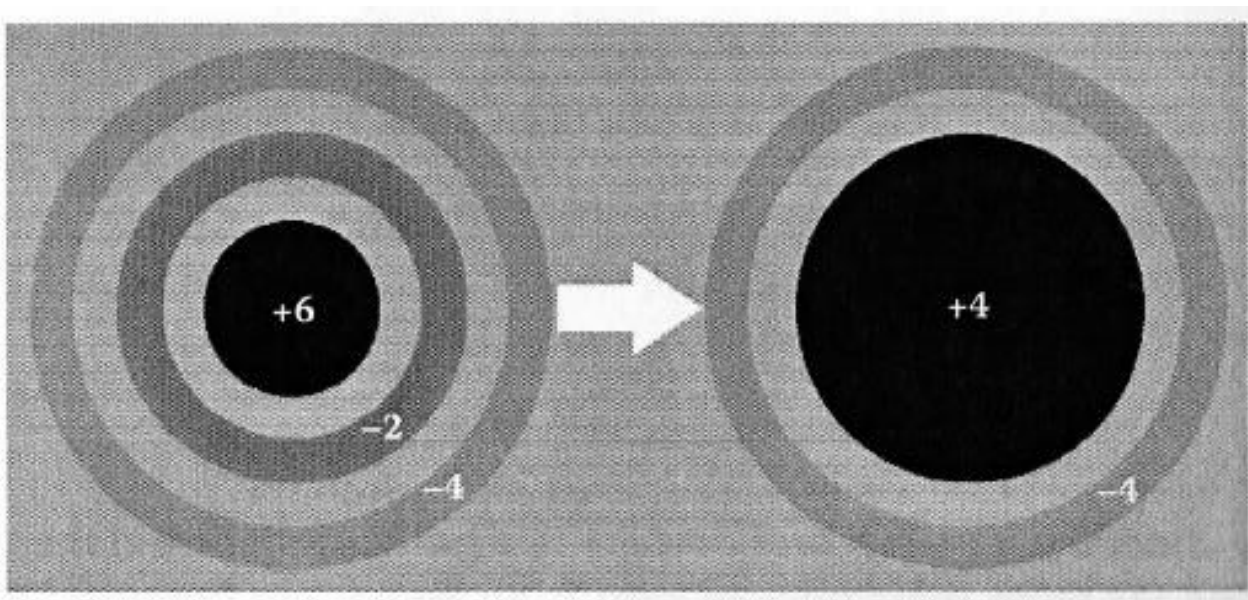
(2) Active and independent valence electrons. The valence electrons are far from the nucleus and stay high above the potential well.

- In metals, they can travel the whole solid like a plane wave.
- In covalent or ionic solids, they maintain in the solid, form bonds, and perform other atomic activities.

Frozen-core approach

Remove the nucleus and core electrons and only deal with the active valence electrons. For example, the frozen-core model for Pt only accounts for 10 valence electrons ($5d^9$ and $6s^1$) out of a total of 78 electrons.

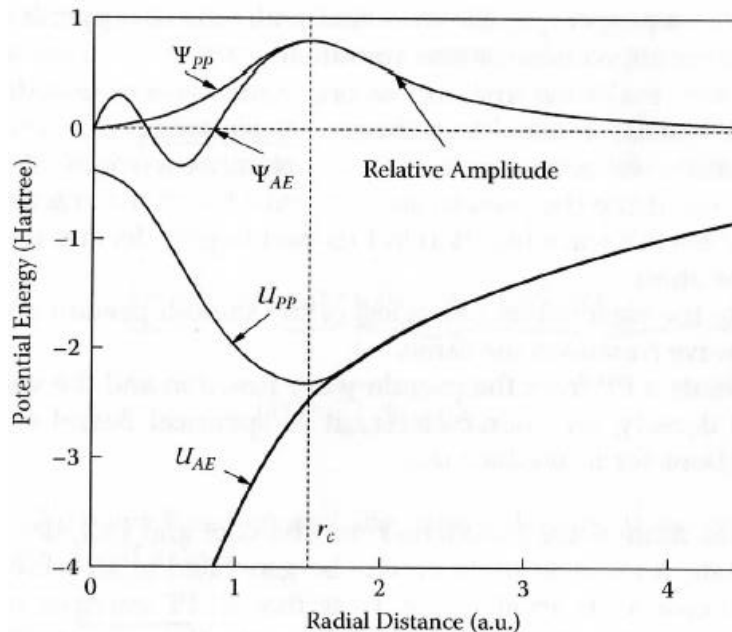
Atomic system of carbon, the frozen core and valence electrons for the construction of a pseudopotential



Pseudizing valence electrons

When a valence wave function ψ_i passes by the highly localized core region, it oscillates rapidly with many wiggles to be orthogonal to the core states. It is neither convenient to be expressed in a simple formula nor easy to be solved computationally.

With the frozen-core approximation, we can soften both the wave functions of the valence electrons and their potentials with ions.



Most DFT codes provide pseudopotentials for all isolated atoms in the period table. Its use in a solid is as simple as just adding them up, regardless of whether it is used for a single atom, molecule, or bulk solid.

$$\hat{H}_{KS} = E_{kin}^{non} + U_{ext} + U_H + U_{xc} = -\frac{1}{2}\nabla^2 + U_{eff}$$

U_{eff} manipulates the ground-state electron density of the noninteracting system to be identical with that of the true interacting system.



Re-write the KS equations with the PP (replacing the U_{eff}) and pseudized wave functions, which leads to a different electronic density:

$$\left[-\frac{1}{2}\nabla^2 + U_{pp}[\rho(r)] \right] \psi_i^{pp}(r) = \varepsilon_i \psi_i^{pp}(r)$$

$$\rho(r) = \sum_i |\psi_i^{pp}(r)|^2$$

Pseudopotential Examples

All are related to exchange-correlation function.

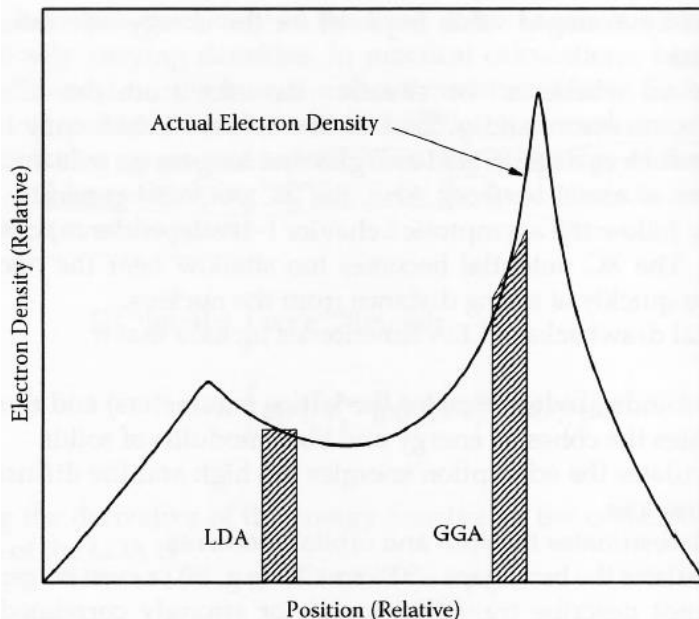
LDA – Local Density Approximation

PBE – Generalized Gradient Approximation
(GGA)

Exchange-Correlational Functional

$$E = -\frac{1}{2} \sum_i^n \int \phi_i^*(r) \nabla^2 \phi_i(r) dr + \int U_{ext}(r) \rho(r) dr + \frac{1}{2} \int \int \frac{\rho(r) \rho(r')}{|r-r'|} dr dr' + E_{xc}[\rho(r)]$$

- Local density approximation (LDA)
- Generalized gradient approximation (GGA)



$$E_{xc}^{LDA}[\rho(r)] = \int \rho(r) \varepsilon_{xc}^{hom}[\rho(r)] dr$$

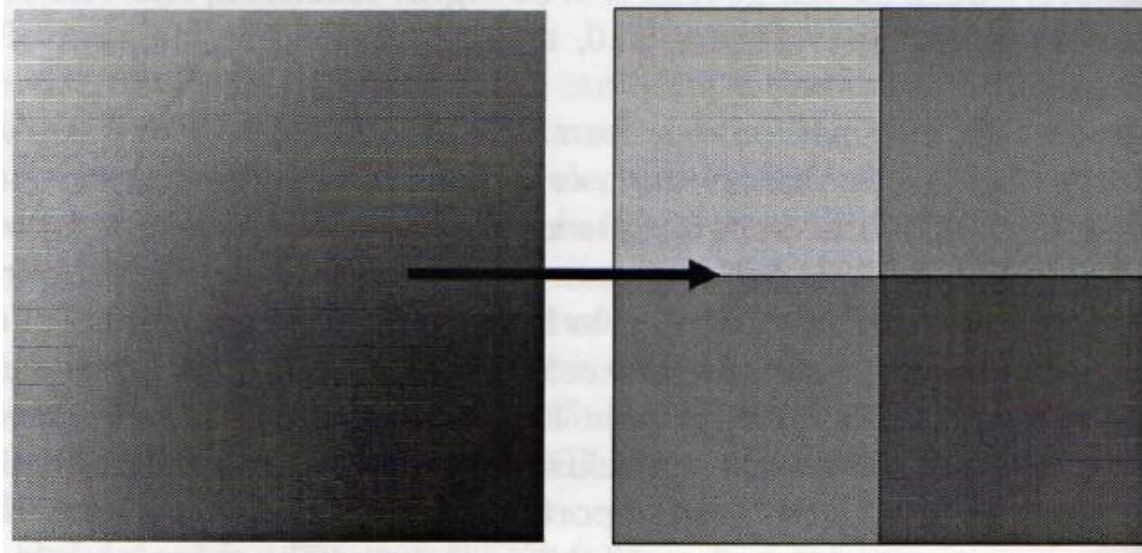
$$E_{xc}^{GGA}[\rho(r), s] = \int \rho(r) \varepsilon_{xc}^{LDA}[\rho(r)] F(s) dr$$

$$s = C \frac{|\nabla \rho(r)|}{\rho^{\frac{4}{3}}(r)}$$

Local Density Approximation

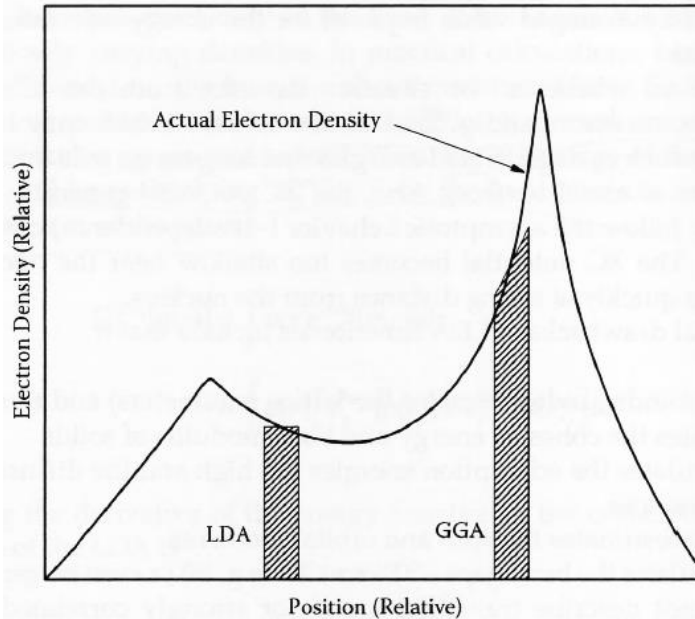
Basic principle of LDA:

Calculate the $E_{xc}[\rho(r)]$ for each electron with the electron density that is assumed to be **constant** in that piece. The **energy associated with these local elements** can be **summed up to total XC energy**.



The actual electron-density distribution is approximated by four local elements of uniform electron densities.

Generalized Gradient Approximation



$$E_{xc}^{GGA}[\rho(r)] = \int \rho(r) \varepsilon_{xc}^{GGA}[\rho(r), \nabla \rho(r)] dr$$

$$U_{xc}^{GGA}[\rho(r)] = \frac{\delta E_{xc}^{GGA}}{\delta \rho(r)} = \rho(r) \frac{d\varepsilon_{xc}^{GGA}[\rho(r)]}{d\rho(r)} + \varepsilon_{xc}^{GGA}[\rho(r)]$$

With spins

$$E_{xc}^{GGA}[\rho_{\uparrow}(r), \rho_{\downarrow}(r)] = \int \rho(r) \varepsilon_{xc}^{GGA}[\rho_{\uparrow}, \rho_{\downarrow}, \nabla \rho_{\uparrow}, \nabla \rho_{\downarrow}] dr$$

Unlike LDA, there is no simple functional form that correctly represents the GGA data, and thus the functional $E_{xc}^{GGA}[\rho(r)]$ is often expressed with a properly chosen form and is fitted to satisfy various physical constraints.

$$E_{xc}^{GGA}[\rho(r), s] = \int \rho(r) \varepsilon_{xc}^{LDA}[\rho(r)] F(s) dr$$

s depends on both electron density and its gradient:

$$s = C \frac{|\nabla \rho(r)|^{\frac{4}{3}}}{\rho^{\frac{4}{3}}(r)}$$

The typical range of electron density is $s=0-3$. In this range, the enhancement factors $F(s)$ vary from 1.0 to 1.6.

Many different forms of GGA have been proposed, depending on DFT codes.

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

K Points

Reciprocal space:

<https://www.youtube.com/watch?v=DFFU39A3fPY>

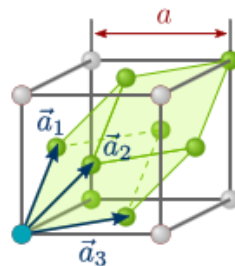
Crystal systems in real space

System	Conventional cell axes and angles	Number of lattices
<i>Cubic</i>	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	3
<i>Hexagonal</i>	$a = b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	1
<i>Triclinic</i>	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	1
<i>Trigonal</i>	$a = b = c$ $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$	1
<i>Monoclinic</i>	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	2
<i>Tetragonal</i>	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	2
<i>Orthorhombic</i>	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	4

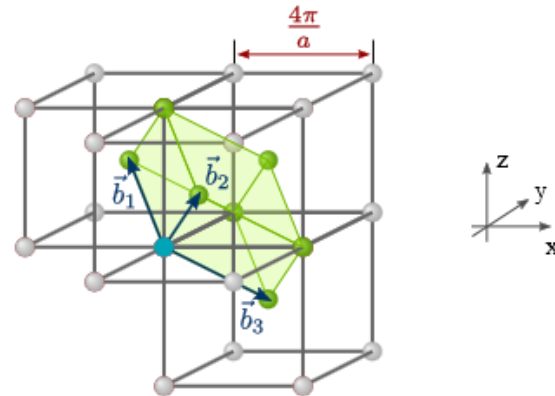
Real Space vs. Reciprocal Space

Real	Reciprocal
Simple cubic	Simple cubic
FCC	BCC
BCC	FCC
HCP	HCP

direct lattice:
fcc with edge length a



reciprocal lattice:
bcc with edge length $4\pi/a$



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 k_x, k_y, k_z).
- 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.**

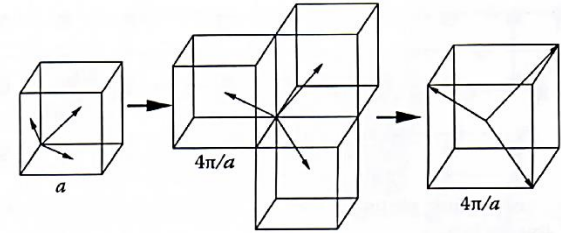


Figure 6.9 A face-centered cubic (FCC) lattice with a in the real space transforms to a body-centered cubic (BCC) lattice with $4\pi/a$ in the reciprocal space.

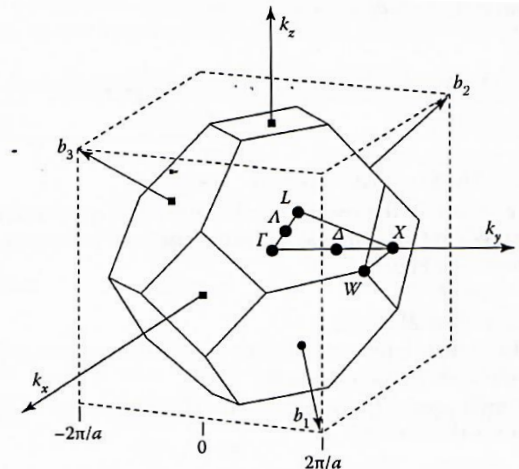


Figure 6.11 First Brillouin zone of FCC lattice showing some of the high symmetry lines and points.

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

