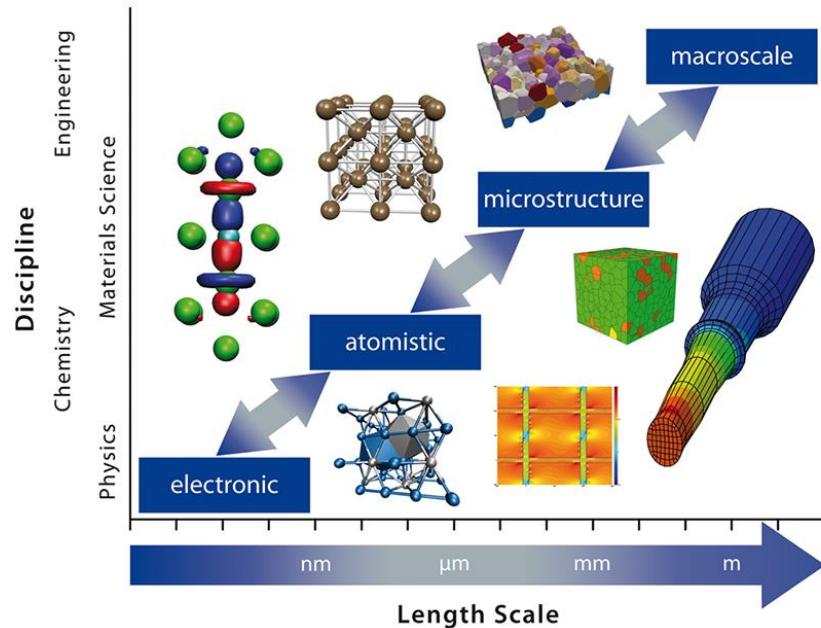


MLL213: Materials Modelling

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Density Functional Theory

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Definitions

- The wave function in quantum mechanics describes the quantum state of a single particle.
- Operator → does a mathematical operation on a variable
- Quantum mechanical operator → Any observable (physically measurable) in quantum mechanics is represented by an operator.

$$E_i^{\text{kin}} = -\frac{\hbar^2}{2m} \sum_i^n \nabla_i^2 = -\frac{1}{2} \sum_i^n \nabla_i^2$$

- Ground state: lowest energy state (stable state of the system)

$$\hat{\mathcal{H}}\psi = E\psi$$

- $\hat{H} = \hat{T} + \hat{V}_{\text{Coloumb}}$, \hat{T} = K.E. operator and \hat{V}_{Coloumb} = P.E operator

Many body problem

Born-Oppenheimer approximation:

- As $M_{\text{nucleii}} \gg m_{\text{electron}}$, the dynamics of nuclei and electrons are very different
- Their wave functions can be decoupled → Effectively the many body problem to electronic Hamiltonian.

$$\left[\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V(\mathbf{r}_i) + \sum_{i=1}^N \sum_{j < i} U(\mathbf{r}_i, \mathbf{r}_j) \right] \psi = E\psi$$

Kinetic energy of electrons Interaction energy between the electron and collection of nuclei Interaction between the electrons

$$\psi = \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \psi_1(\mathbf{r})\psi_2(\mathbf{r}), \dots, \psi_N(\mathbf{r}) \rightarrow \text{Hartree Product}$$

Zn: 30 electrons, 3 spatial coordinates for each electron → 90-dimensional problem

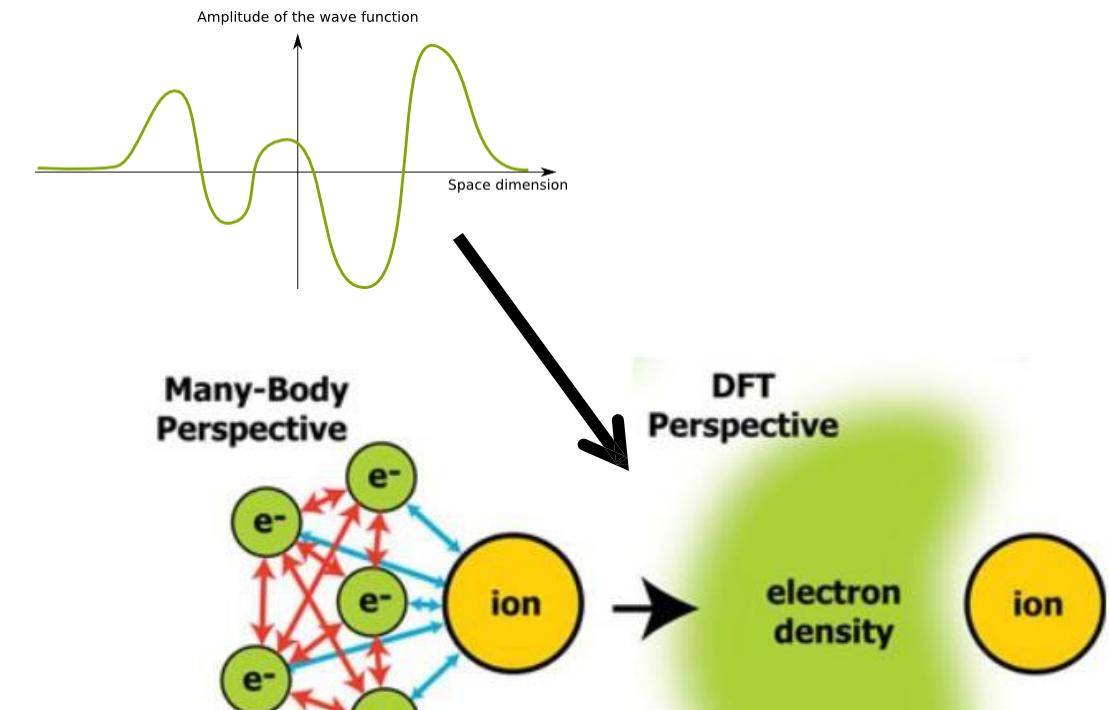
Density functional theory

Wavefunctions to electron density

- The quantity that can be measurable is the probability

$$\psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N)\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

- We cannot distinguish the electrons in the system. Therefore, the electronic density, $n(r)$ can be written as a summation that goes over all the individual electron wavefunctions
- The factor ‘2’ appears due to the spin associated with the electrons and Pauli’s exclusion principle states that the individual state can be occupied by two electrons provided they have different spins



$$n(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$$

$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$

Function of $3N$ variables

$n(\mathbf{r})$

Function of 3 variables

Hohenberg and Kohn Theorems (DFT Origins)

Theorem 1

- The ground-state energy from Schrödinger's equation is a unique functional of the electron density, $n(r)$

$$E = E [n(r)]$$

Theorem 2

- The electron density, $n(r)$ that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.

$$E[n(r)] > E_0[n_0(r)]$$

$$F[f] = \int_1^1 f(x) dx$$
$$f(x) = x^2 + 1$$

Energy terms in DFT

Known:

- Electron kinetic energies
- Coulomb interactions between the electrons and the nuclei
- Coulomb interactions between pairs of electrons
- Coulomb interactions between pairs of nuclei

$$E[\{\psi_i\}] = E_{\text{known}}[\{\psi_i\}] + E_{\text{XC}}[\{\psi_i\}]$$

Unknown:

- Everything else is E_{XC}
- Includes all the quantum mechanical terms → needs approximations

$$\begin{aligned} E_{\text{known}}[\{\psi_i\}] = & \frac{\hbar^2}{m} \sum_i \int \psi_i^* \nabla^2 \psi_i d^3 r + \int V(\mathbf{r}) n(\mathbf{r}) d^3 r \\ & + \frac{e^2}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' + E_{\text{ion}}. \end{aligned}$$

Kohn Sham method

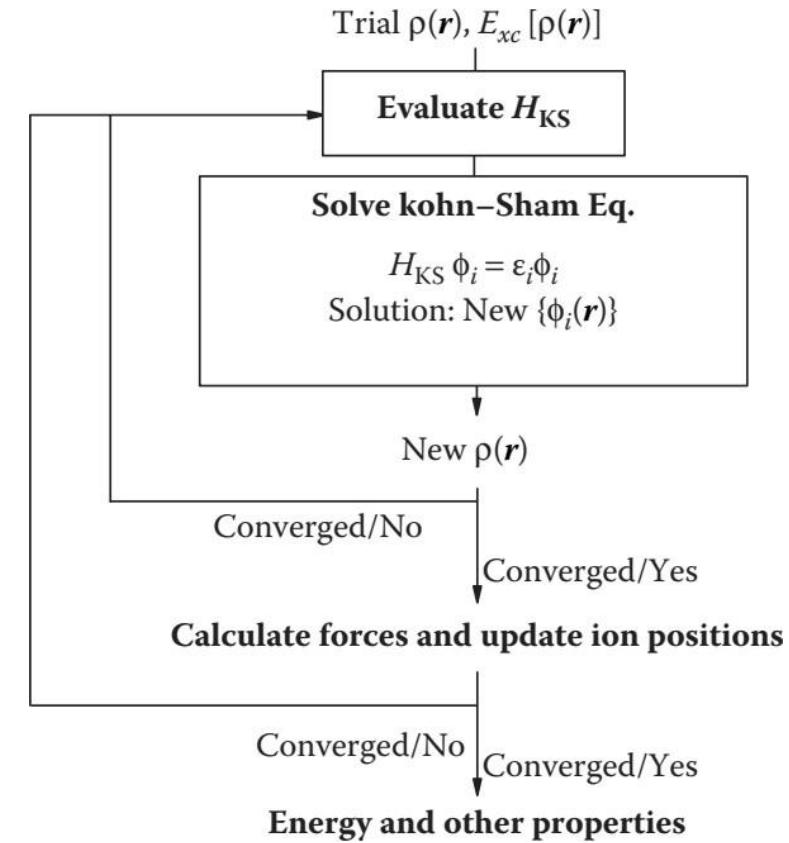
$$\left[\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

- Kohn and Sham showed that finding the correct electron density $n(r)$ involves solving a set of equations (each involving a single electron)
- V_{XC} → the exchange-correlation potential
 - Exchange energy: A quantum mechanical effect due to the indistinguishability of electrons.
 - Correlation energy: The correlation energy accounts for the repulsion and tendency of electrons to avoid each other because of their electrostatic charge

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}(\mathbf{r})}{\delta n(\mathbf{r})}$$

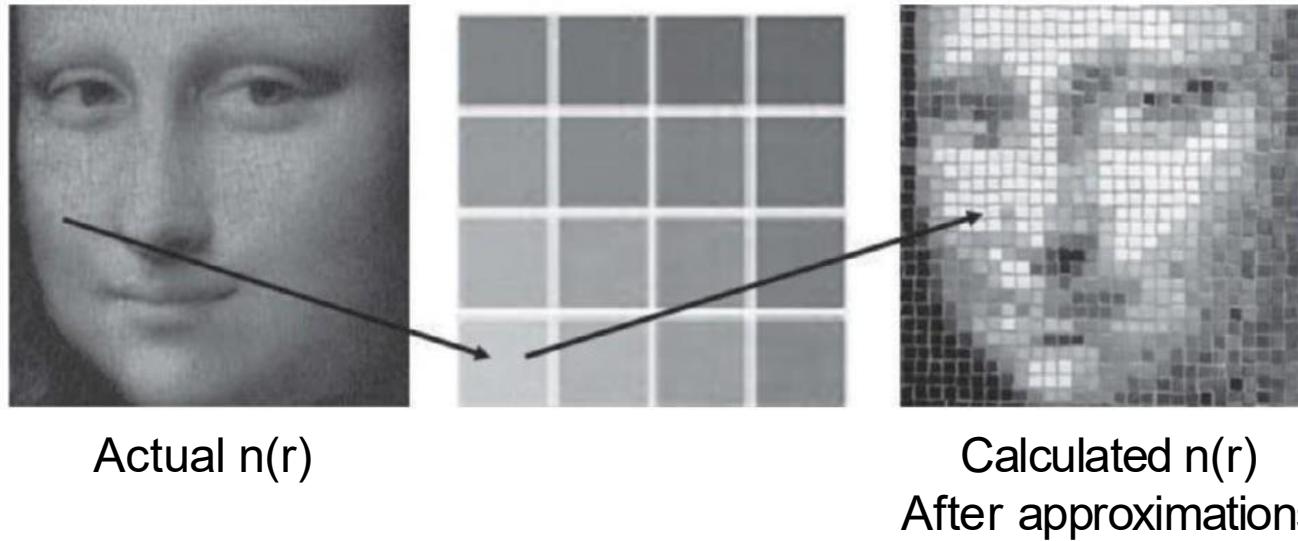
Kohn Sham scheme

1. Define the initial trial electron density, $n(r)$
2. Solve the Kohn-Sham equations using the trial electron density to find the single particle wave functions, $\psi_i(r)$
3. Calculate the electron density defined by the Kohn-Sham single particle wave functions from step 2 , $n_{KS}(r) = 2 \sum_i \psi_i^*(r)\psi_i(r)$
4. Compare the calculated electron density $n_{KS}(r)$ with the trial electron density
→ If they are identical, it is the true ground state
→ otherwise update the trial electron density and begin again at step 2



Depending on the textbook,
 ψ and ϕ are used interchangeably for wavefunctions
 n and ρ are used interchangeably for electron density

Local Density Approximation (LDA)



$$V_{XC}(\mathbf{r}) = V_{XC}^{\text{electron gas}}[n(\mathbf{r})]$$

- The complex system can be transformed into many pieces of uniform electron density, with different values, so that the XC energy for each electron can be calculated with the electron density that is assumed to be constant in that piece.
- The energies associated with these local elements can be summed up to equal the total XC energy. This is the local density approximation (LDA)
- Underestimates lattice parameters, overestimates cohesive energies and bulk modulus

Generalized Gradient approximation

- Real systems are evidently not homogeneous and have a varying density landscape around electrons
- To generate more accurate XC functionals, the generalized gradient approximation (GGA) captures both the local and semilocal information: the electron density and its gradient at a given point
- Most commonly used GGA functionals
 - Perdew-Wang: PW91
 - Perdew-Burke-Ernzerhof: PBE

Lattice constants by PAW/PBE calculations

| Materials | Lattice constants (Å) (cal./exp.) |
|--------------|--------------------------------------|
| Al | 4.040/4.032 |
| BN | 3.626/3.616 |
| C | 3.574/3.567 |
| Si | 5.469/5.430 |
| SiC | 4.380/4.358 |
| β -GaN | 4.546/4.520 |
| GaP | 5.506/5.451 |
| GaAs | 5.752/5.648 |
| MgO | 4.258/4.207 |
| Cu | 3.635/3.603 |
| Rh | 3.830/3.798 |
| Pd | 3.943/3.881 |
| Ag | 4.147/4.069 |

Source: Paier, J. et al., *J. Chem. Phys.*, 124(15), 154709–154721, 2006

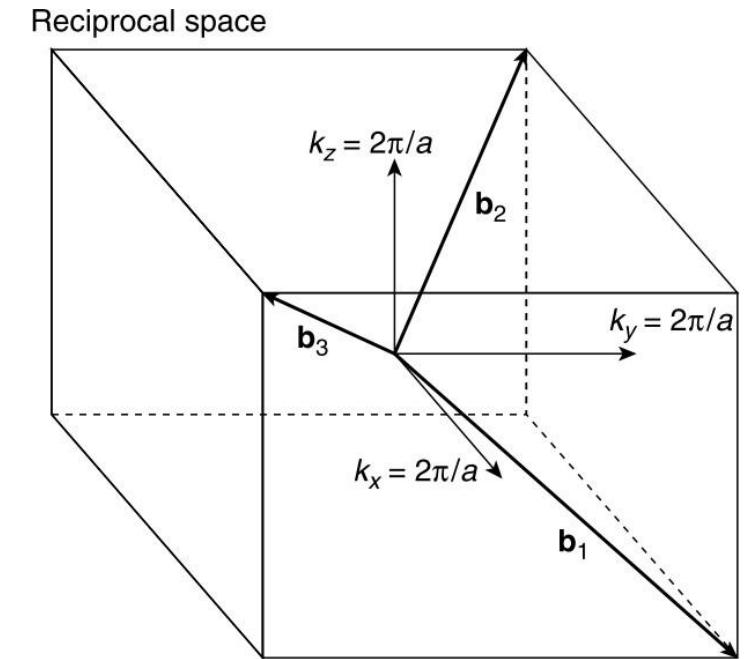
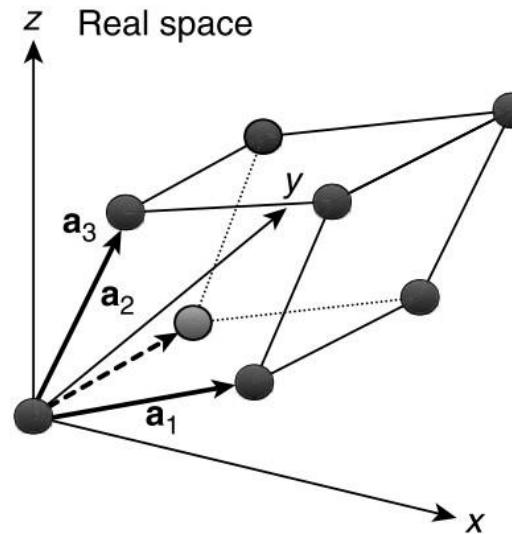
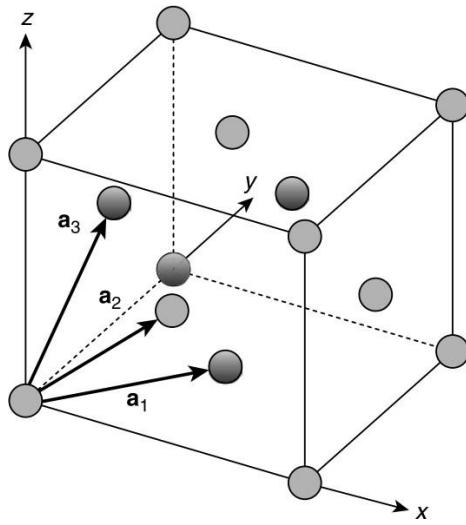
GGA and beyond

- GGA works very well with almost all systems, giving most structural properties within a 1%–3% error
- GGA corrects most of the over binding problems of LDA, producing an increase in lattice constants and a decrease in cohesive energies, and improving activation barriers.

Table 5.2 Typical XC functionals commonly used in DFT calculations

| Classification | Examples | Remarks |
|----------------|----------|-----------------------------------------------------------------------------------------------------------------------------------------------------|
| Local | LDA | $\rho_{\uparrow}, \rho_{\downarrow}$ |
| Semilocal | GGA | $\rho_{\uparrow}, \rho_{\downarrow}, \nabla \rho_{\uparrow}, \nabla \rho_{\downarrow}$ |
| Seminonlocal | Meta-GGA | $\rho_{\uparrow}, \rho_{\downarrow}, \nabla \rho_{\uparrow}, \nabla \rho_{\downarrow}, \nabla^2 \rho_{\uparrow}, \nabla^2 \rho_{\downarrow}$, etc. |
| Hybrid | B3LYP | GGA + HF |

Reciprocal lattice

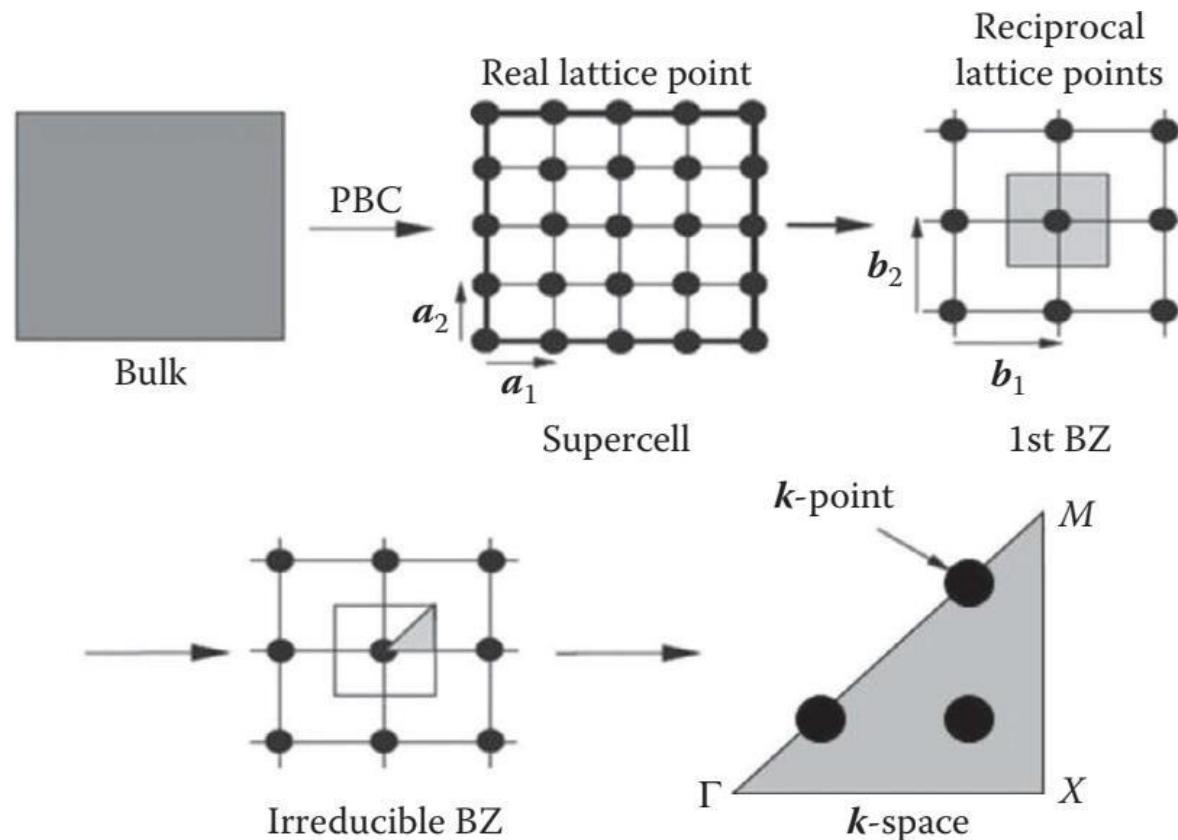
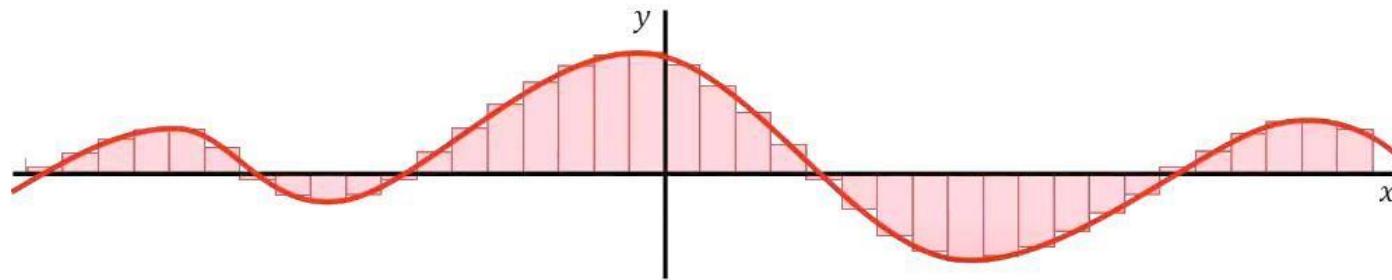


$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V}, \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{V}, \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{V}$$

- In a practical DFT calculation, dealing with Brillouin zone reduces the work on evaluating integrals of this form

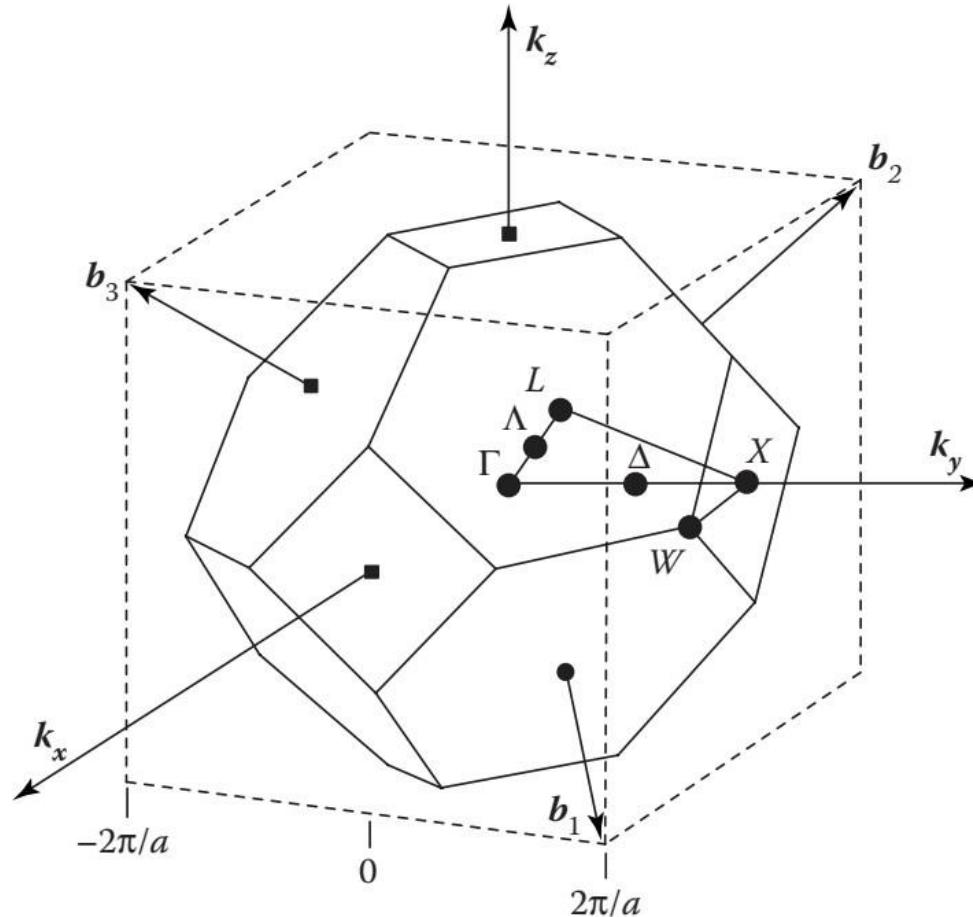
$$V_{\text{BZ}} = \frac{(2\pi)^3}{V_{\text{cell}}} \quad g = \frac{V_{\text{cell}}}{(2\pi)^3} \int_{\text{BZ}} g(\mathbf{k}) d\mathbf{k}$$

Treating crystals



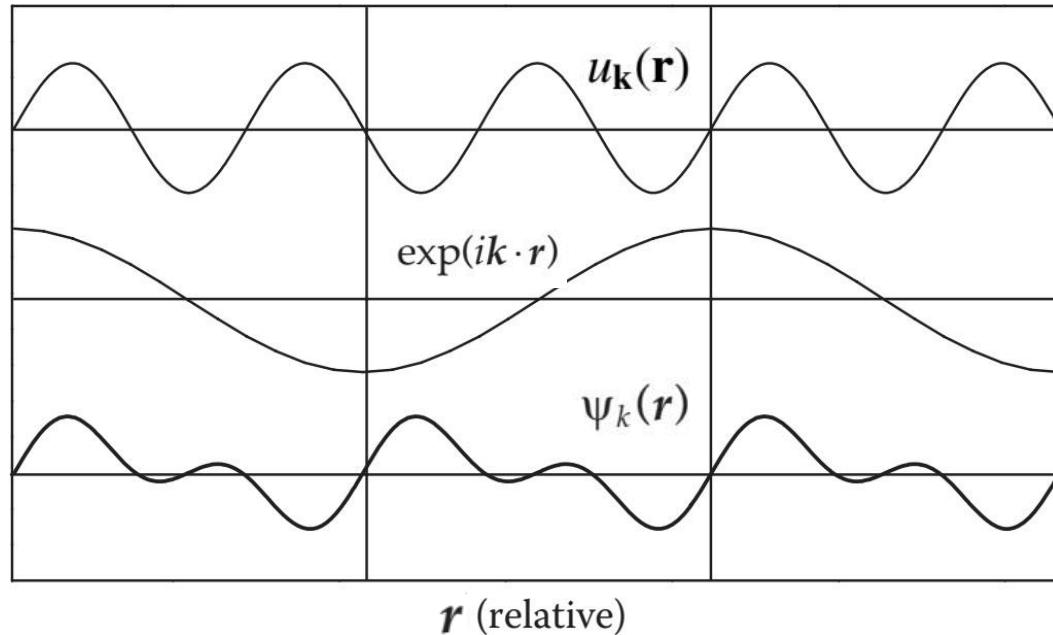
Brillouin Zone

First Brillouin zone of FCC lattice



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

Bloch's Theorem



Bloch noticed that the wavefunction differs from the Plane wave of free electrons only by a periodic modulation

$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3$$

Each plane wave in the sum has kinetic energy

$$E = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2$$

Wavefunctions as Plane Wave

$$\psi(\mathbf{r}) = C \exp(i\mathbf{k} \cdot \mathbf{r})$$

Bloch solved the problem of mapping on to the structurally repeating pattern of a crystal.

$$\psi_k(\mathbf{r}) = u_k(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r})$$

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}]$$

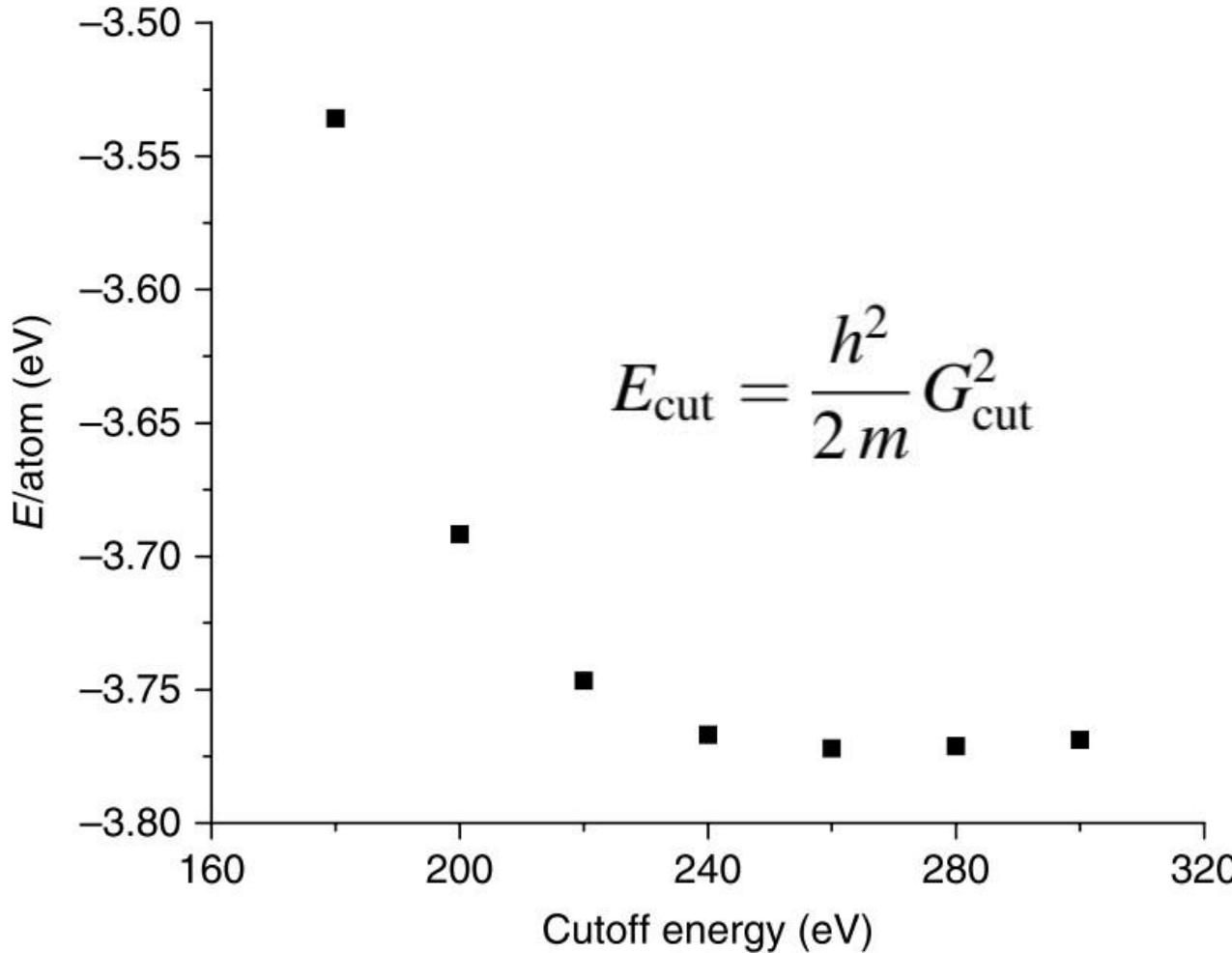
$$\psi_k(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}]$$

Sum of plane waves

Real vs Reciprocal lattices

| Characteristics | Real lattice | Reciprocal lattice |
|---------------------|-----------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|
| Description | Bravais lattice for particles | Fourier transform of the real lattice for waves |
| Cell shape and size | SC: a BCC: a FCC: a HCP: a, c | SC: $2\pi/a$ FCC: $4\pi/a$ BCC: $4\pi/a$ 30°-rotated HCP ($4\pi/\sqrt{3}a, 2\pi/c$) |
| Coordinates | x, y, z | k_x, k_y, k_z |
| Lattice vector | $\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$ | $\mathbf{G} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3$ |
| Lattice parameter | \mathbf{a}_i | \mathbf{b}_i |
| Lattice volume | $V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$ | $\Omega = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)$ |
| Function | $f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R})$ | $f(\mathbf{G}) = \sum_G c(\mathbf{G}) \exp(i\mathbf{G} \cdot \mathbf{r})$ |

Energy Cutoff



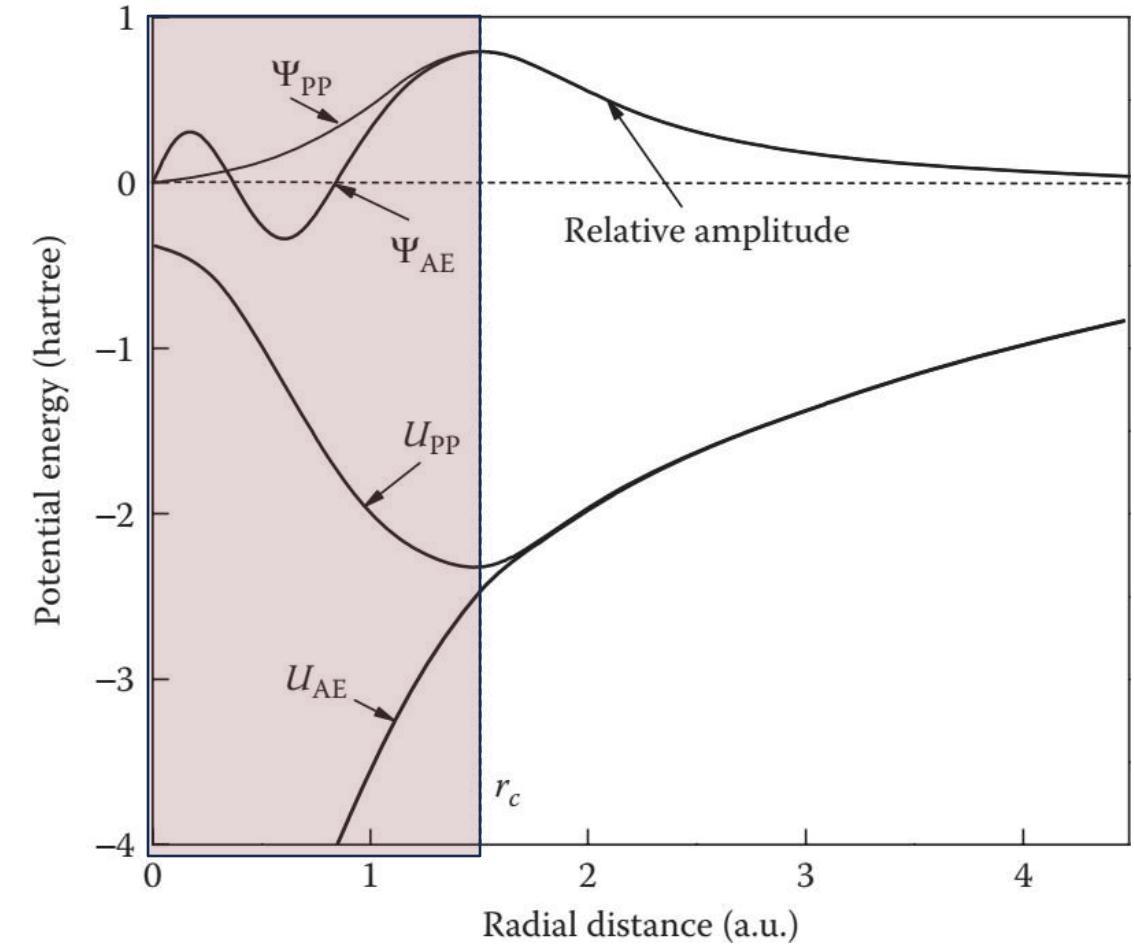
- It is reasonable to expect that the solutions with lower energies are more physically important than solutions with very high energies

$$\psi_k(\mathbf{r}) = \sum_{|\mathbf{G}+\mathbf{k}| < G_{\text{cut}}} c_{\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G})\mathbf{r}]$$

- Whenever DFT calculations for multiple systems are compared to calculate energy differences, the same energy cutoff should be used in all calculations

Pseudopotentials

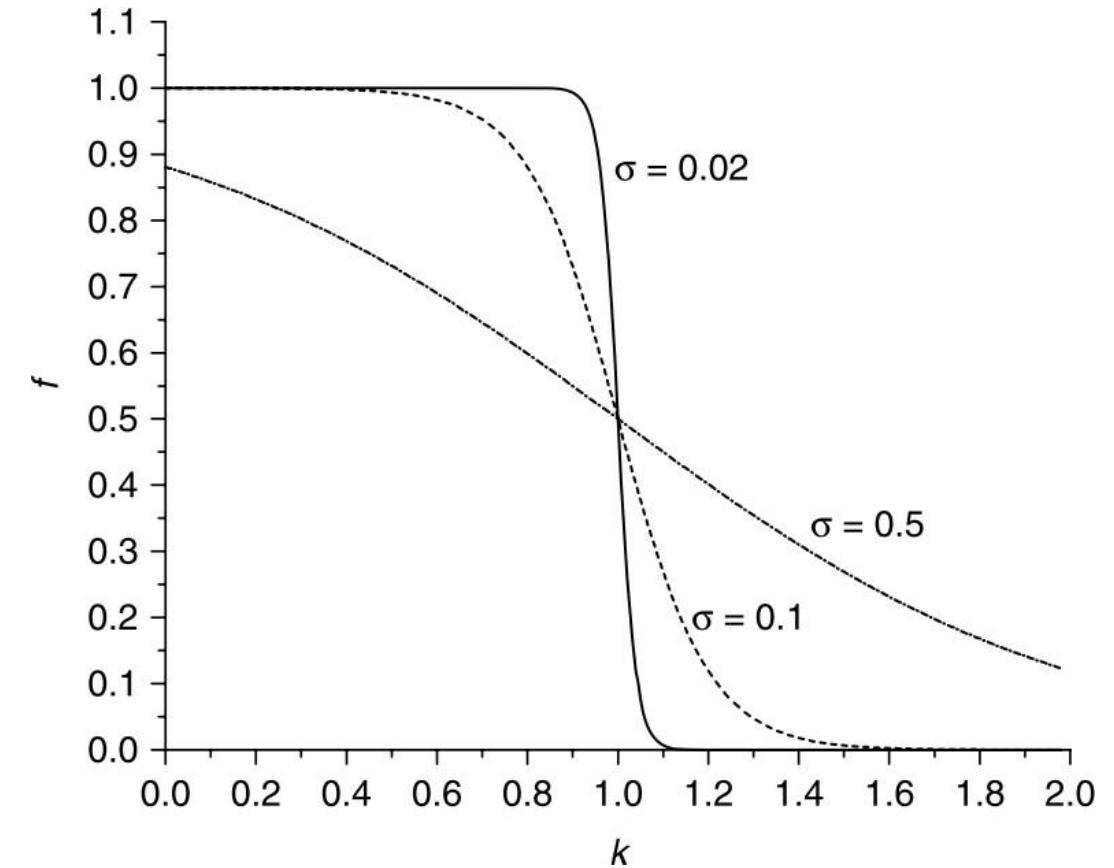
- Large energy cutoffs must be used to include plane waves that oscillate on short length scales in real space
- This is problematic because the tightly bound core electrons in atoms are associated with wave functions with exactly this kind of oscillation
- However, core electrons are not especially important in defining chemical bonding and other physical characteristics of materials; these properties are dominated by the less tightly bound valence electrons



Frozen core approximation

Considerations in Implementation

- Geometry
- DFT Solver
- Pseudopotential
- K-points description
- Energy cutoff
- Smearing : occupations of electrons
- Metals → divided into occupied and unoccupied regions (Fermi surface is the one that separates these two is discontinuous)



abc

Software

| Packages | Description | Remarks |
|------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------|
| Quantum Espresso | <ul style="list-style-type: none">• Best for classrooms• Best for CPMD• Limited built-in PP | Free and open code |
| VASP | <ul style="list-style-type: none">• The leading package• Best for serious calculations | Purchase required |
| MedeA-VASP | <ul style="list-style-type: none">• VASP with GUI• Many convenient tools including flow diagrams• Best for all users for faster results | Purchase required |

Typical input file in Quantum Espresso

```
/  
ATOMIC_SPECIES  
  Si 28.086 Si.pbe-rrkj. UPF      # name, mass, PP  
ATOMIC_POSITIONS (alat)          # direct x, y, z  
  Si 0.0 0.0 0.0  
  Si 0.25 0.25 0.25  
K_POINTS (automatic)            # MP method  
  6 6 6 1 1 1                  # Nk1, Nk2, Nk3, shift1,  
                                shift2, shift3  
                                # 0; no shift, grid from  
                                0 to Nk  
                                # 1; shift, grids shifted  
                                by half a grid
```