Electronic structure calculation methods using the Density Functional Theory-II

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Outline

- Recap of HK theorems and KS equations
- The physical meaning of the XC energy
- Solution of a one-particle Schroedinger equation
- Pseudo Potentials
- The nitty-gritty of an actual KS calculation
  - For molecules
  - For solids
- DFT software packages

The HK theorems

- **HK Th 1:** *The external potential , and hence the total energy, is a unique functional of the electron density*

- **HK Th 2:** *The density that minimizes the total energy is the exact ground state density.*

Kohn-Sham equations

$$\text{If} \quad \rho(\mathrm{r}) = \sum_{\lambda}^{\text{occupied}} |\psi_\lambda(\mathrm{r})|^2 \quad \text{then}$$

$$\text{Minimizing } \mathrm{E}[\rho] = \mathrm{T} + \mathrm{E}_{\mathrm{ee}} + \mathrm{E}_{\mathrm{ext}} \quad \text{wrt } \rho$$

$$\text{leads to} \quad \mathrm{H}_{\mathrm{KS}}[\rho]\,\psi_\lambda = \varepsilon_\lambda\,\psi_\lambda \quad \text{where}$$

$$\mathrm{H}_{\mathrm{KS}}[\rho] = -\frac{\hbar^2\nabla^2}{2\mathrm{m}} + \mathrm{v}_{\mathrm{ext}}(\mathrm{r}) + \mathrm{v}_{\mathrm{Coulomb}}[\rho(\mathrm{r})] + \mathrm{v}_{\mathrm{xc}}[\rho(\mathrm{r})]$$

$$\text{Solve self} - \text{consistently}$$

$$\mathrm{H}_{\mathrm{KS}}[\rho]\,\psi_\lambda = \varepsilon_\lambda\,\psi_\lambda \;;\; \rho(\mathrm{r}) = \sum_{\lambda}^{\text{occupied}} |\psi_\lambda(\mathrm{r})|^2$$

What can be calculated from E_o?

> Magnetization and magnetic susceptibility

> EA, IP, Chemical potential, Band gap

> Forces and Elastic constants

> **Generalized Forces** and **Response Functions**, which can be expressed as: $\frac{\partial E}{\partial A}, \frac{\partial^2 E}{\partial A \partial B}$

> Using the KS wavefunctions, other properties can also be calculated…

Shortcomings of DFT

» Overestimates binding energies (≈ by 15%)

» Underestimates the gap (≈ by 40%)

» "Good" for solids but "bad" for molecules

Overscreens, since functionals are taken from Jellium model

But surprisingly successful in predicting the correct crystal structure and elastic constants (<5% error) for a large variety of systems.

Improvements to DFT

» Generalized Gradients Approximation **(GGA/MGGA)**: to handle non-uniformity in charge density (good for metals, still local):

$$E_{XC} = E_{XC}^{GGA}[\rho, |\nabla\rho|] \text{ or } E_{XC}^{MGGA}[\rho, |\nabla\rho|, \Delta\rho, \ldots]$$

» Hybrid functionals (Exc=a*Exc[DFT]+b*Ex[HF]) to remedy the bandgap problem

» More advanced and general functionals

> **non-local**

> **orbital-dependent**

The physical meaning of the Exchange-correlation Energy

- Pauli principle forbids two electrons to get too close to each other.
- => Their Coulomb repulsion becomes weaker!
- Coulomb interaction is overestimated by the electrostatic interaction ($E_{xc} < 0$)

Two-body terms

If $\rho(\mathrm{r}) = < \sum_{\mathrm{i}} \delta(\mathrm{r} - \mathrm{r_i}) >$ and

$\rho(\mathrm{r}_1, \mathrm{r}_2) = < \sum_{\mathrm{i,j,i \neq j}} \delta(\mathrm{r}_1 - \mathrm{r_i})\,\delta(\mathrm{r}_2 - \mathrm{r_j}) >$ then

Self-interaction term

$$< \sum_{\mathrm{ij,i \neq j}} \mathrm{f}(\mathrm{r_i}, \mathrm{r_j}) > = \int \mathrm{dr_1 dr_2}\ \rho(\mathrm{r}_1, \mathrm{r}_2)\,\mathrm{f}(\mathrm{r}_1, \mathrm{r}_2)$$

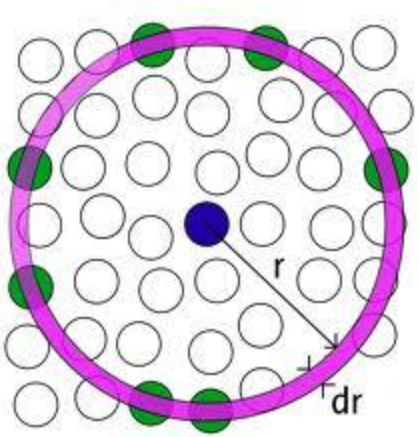
In the uncorrelated limit, $\rho(\mathrm{r}_1, \mathrm{r}_2) = \rho(\mathrm{r}_1)\rho(\mathrm{r}_2) - \rho(\mathrm{r}_2)\delta(\mathrm{r}_1 - \mathrm{r}_2)$

In the correlated limit,

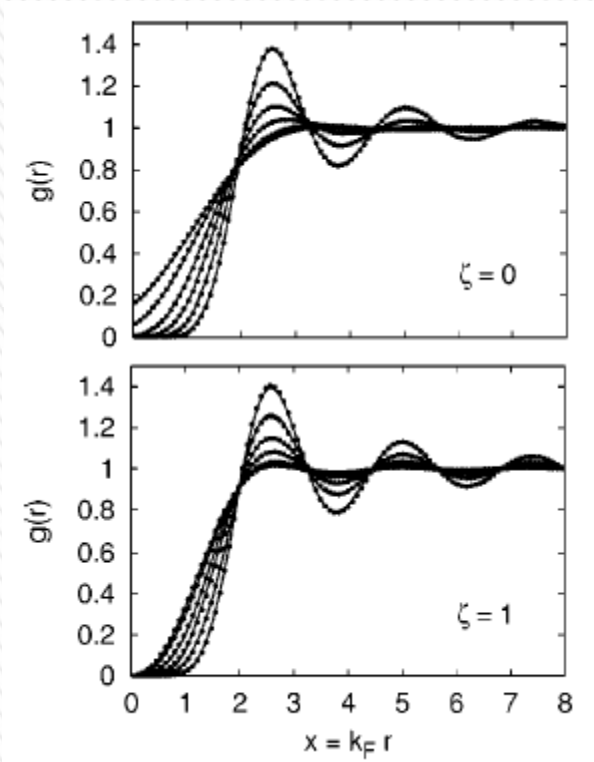
$$g(r) = \frac{V}{4\pi r^2 N^2} \langle \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \rangle$$

$$\rho(\vec{\mathrm{r}}_1, \vec{\mathrm{r}}_2) = \rho(\vec{\mathrm{r}}_1)\,\rho(\vec{\mathrm{r}}_2)\,\mathrm{g}(\vec{\mathrm{r}}_1, \vec{\mathrm{r}}_2)$$

g is called the pair correlation function and is only known for the Jellium model: $\mathrm{g_{hom}}(\mathrm{r}, \rho)$



Electron correlations



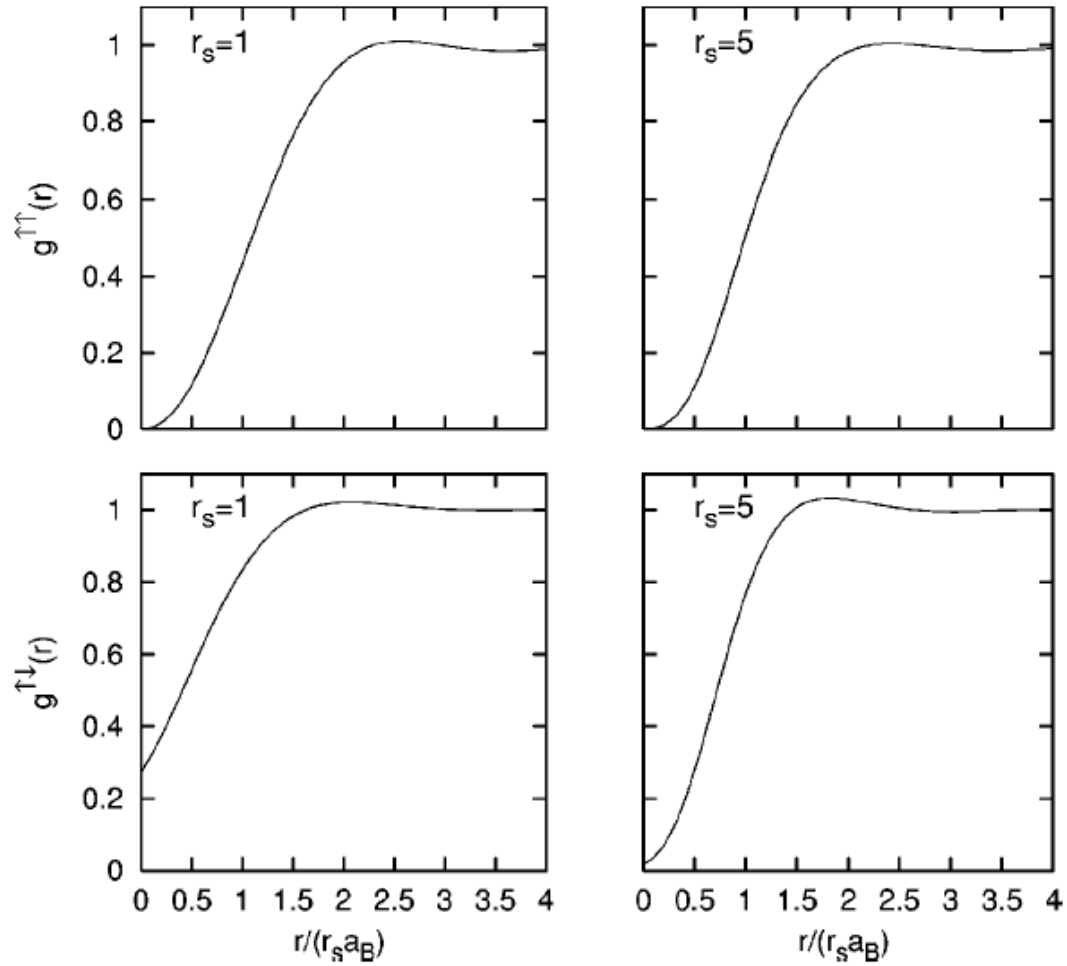
GORI-GIORGI, MORONI, AND BACHELET

PHYSICAL REVIEW B **70**, 115102 (2004)

2DEG For rs=1,2,5,10,20

High density

Low density



B. DAVOUDI, M. POLINI, R. ASGARI, AND M. P. TOSI

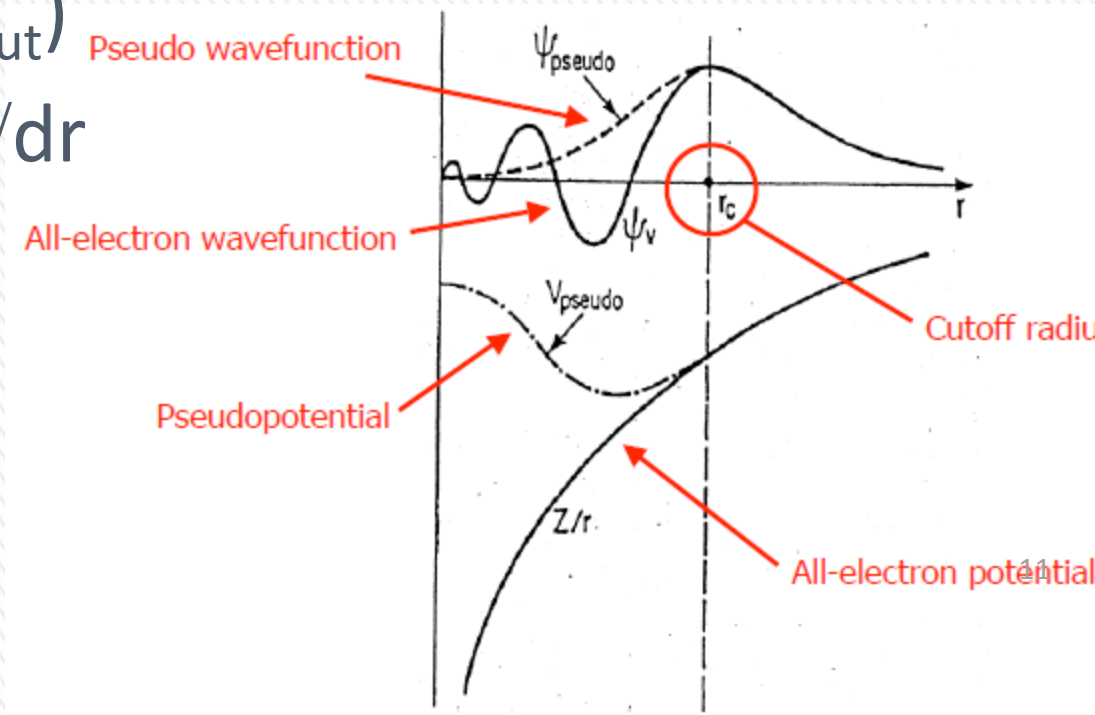
PHYSICAL REVIEW B **66**, 075110 (2002)

Pseudo-potentials

Core electrons do not contribute=>heavy calculations

Replace (V_{ion} + core electrons) by V_{pseudo}

- $\psi_{pseudo} = \psi_{exact}\ (r > r_{cut})$
- Scattering: d Log ψ_E/dr
- Norm conservation
- Smoothness



How to solve a one-particle Schrodinger's equation?

» **SPECTRAL METHODS:**

» Consider the proper boundary conditions

» Choose **accordingly** a basis set ϕ_i :

$$H_{KS}[\rho] = \frac{p^2}{2m} + v_{ext}(r) + v_{Coulomb}[\rho(r)] + v_{xc}[\rho(r)]$$

$$H|\psi_\lambda> = \varepsilon_\lambda |\psi_\lambda> \quad ;\text{expand } \psi_\lambda \text{ on a complete basis set:}$$

$$|\psi_\lambda> = \sum_j C_{\lambda j} |\varphi_j>$$

Multiplying the eigenvalue equation on the left by φ_i leads to:

$$\sum_j H_{ij} C_{\lambda j} = \varepsilon_\lambda \sum_j S_{ij} C_{\lambda j}$$

with $H_{ij} = <\varphi_i|H|\varphi_j>$ and $S_{ij} = <\varphi_i|\varphi_j>$

How to solve a one-particle Schrodinger's equation?...

» Construct the Hamiltonian and overlap MATRIX

$$H_{ij} = <\phi_i | H[\rho] | \phi_j >; S_{ij} = <\phi_i | \phi_j >$$

» Solve Det [H-ES] = 0 (Generalized eigenvalue problem)

» Get the density from the eigenstates:

$$\rho(r) = \sum_{\lambda}^{\text{occupied}} |\psi_\lambda(r)|^2$$

» Make it **self-consistent** since H depends itself on ρ

Flowchart of ES calculation algorithm

1) read coordinates of atoms from input file

2) Initialize the input charge density

3) Construct the H-matrix and overlap Matrix

4) Solve Det[H-ES]=0

Obtain the new charge density from the occupied eigenstates

Eventually mix the charge density with old ones

If converged calculate the ground state energy
else
go back to step 3 and use this density to calculate H-

Plane Wave basis for crystals

$$\varphi_k(r) = \frac{1}{\sqrt{\Omega}} e^{ikr}$$

$$< \varphi_k \mid H \mid \varphi_{k'} >= \frac{\hbar^2 k^2}{2m} \delta_{k,k'} + V(G)\delta_{k-k',G}$$

k only couples to k+nG => G-periodicity in k-space

$\Rightarrow$It is enough to keep k in the **First Brillouin Zone**

$$< \varphi_k \mid H \mid \varphi_{k+G} >= V(G) \;\; ; \;\; < \varphi_k \mid H \mid \varphi_k >= \frac{\hbar^2 k^2}{2m}$$

Number of plane waves decided by the choice of Ecut, usually leads to a large Hamiltonian matrix : $O(n_{occ} x N_{PW}^2)$

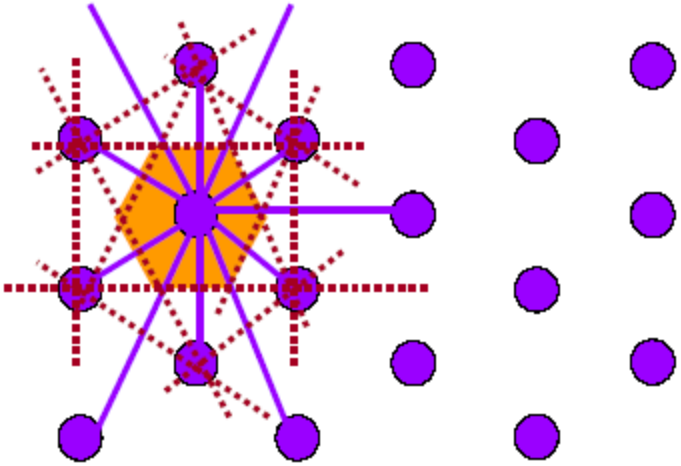
Structure of the Hamiltonian matrix in a PW scheme

$$
\begin{array}{c}
\begin{array}{ccccccccc} G_1 & G_2 & G_3 & G_1 & G_2 & G_3 & G_1 & G_2 & G_3 \end{array} \\
\begin{bmatrix}
\begin{bmatrix} & & \\ & H(k_1) & \\ & & \end{bmatrix} & 0 & 0 \\
0 & \begin{bmatrix} & & \\ & H(k_2) & \\ & & \end{bmatrix} & 0 \\
0 & 0 & \begin{bmatrix} & & \\ & H(k_3) & \\ & & \end{bmatrix}
\end{bmatrix}
\end{array}
$$

Eigenvalues and eigenfunctions are periodic in the reciprocal space

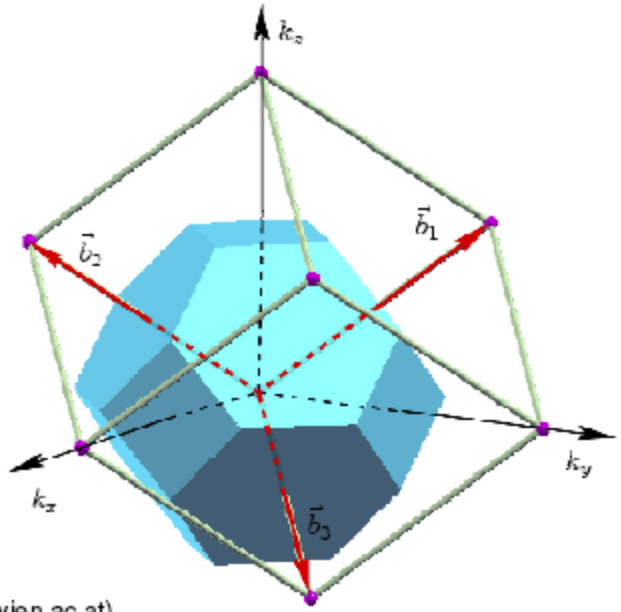
First Brillouin Zone

- Wigner-Seitz cell in reciprocal space.



(Or could choose to use parallelepiped defined by $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$)

e.g., 1st BZ for FCC lattice →



(www.iue.tuwien.ac.at)

Atomic Orbital basis for crystals

$$\text{Bloch Basis}: \psi_{k\alpha}(r) = \frac{1}{\sqrt{N}} \sum_{R} e^{ikR} \phi_{\alpha}(r - R)$$

Where α and β are atom or orbital indices within the unit cell (α,β)={1,... ,n}

$$H_{\alpha\beta}(k) = < \psi_{k\alpha} \mid H \mid \psi_{k\beta} >$$

is a rather small matrix: (n,n) for each k in the FBZ, where n is the number of orbitals per unit cell

Next Step: download, install and get familiar with a program

» Many Programs available:

> Gaussian

> SIESTA (free)

> Wien2k

> ELK (free)

> VASP

> ABINIT (free)

> Quantum Espresso (free)

> …. Check the Web

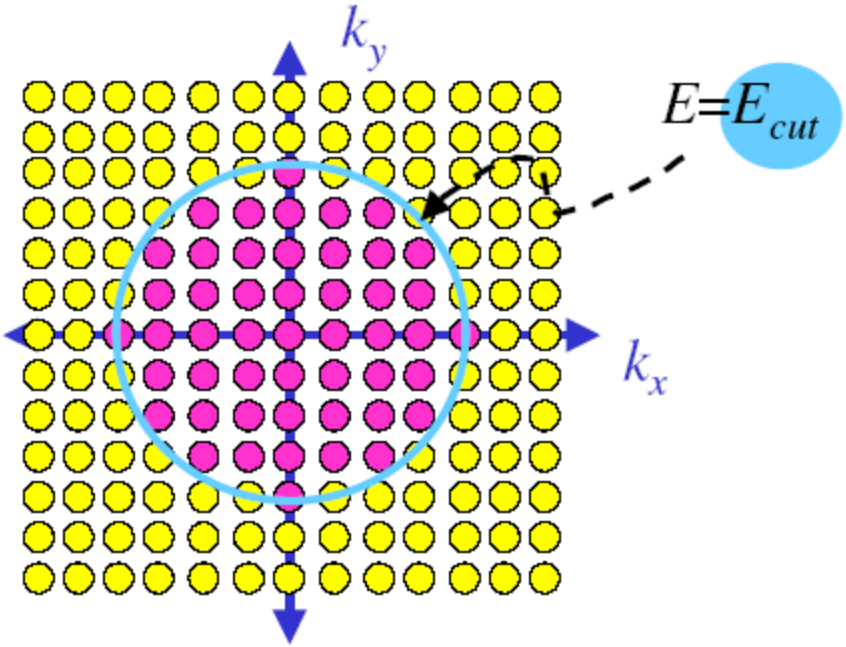
PW Calculation setup

- INPUTS:
  - Atomic coordinates
  - Unit cell
  - DFT functional (LDA, LSDA, GGA …)
  - Cutoff Energy
  - Kpoints mesh
  - Diagonalization, mixing and Convergence threshold preferences
- 3 calculations required for a band structure & DOS
  - A SC with kpoints in the IBZ
  - A non-SC with chosen kpoints along symmetry directions (BS)
  - A finer kpoint mesh in the IBZ (DOS)
- OUTPUT:
  - Single total energy and forces on all atoms
  - Electronic eigenstates and eigenvalues, charge &spin density

Truncating the Plane Wave Expansion

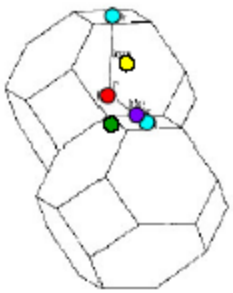
- In practice, the contribution from higher Fourier components (large |**k**+**G**|) is small.
- So truncate the expansion at some value of |**k**+**G**|.
- Traditional to express this cut-off in energy units:

$$\frac{\hbar^2 |\mathbf{k}+\mathbf{G}|^2}{2m} \leq E_{cut}$$

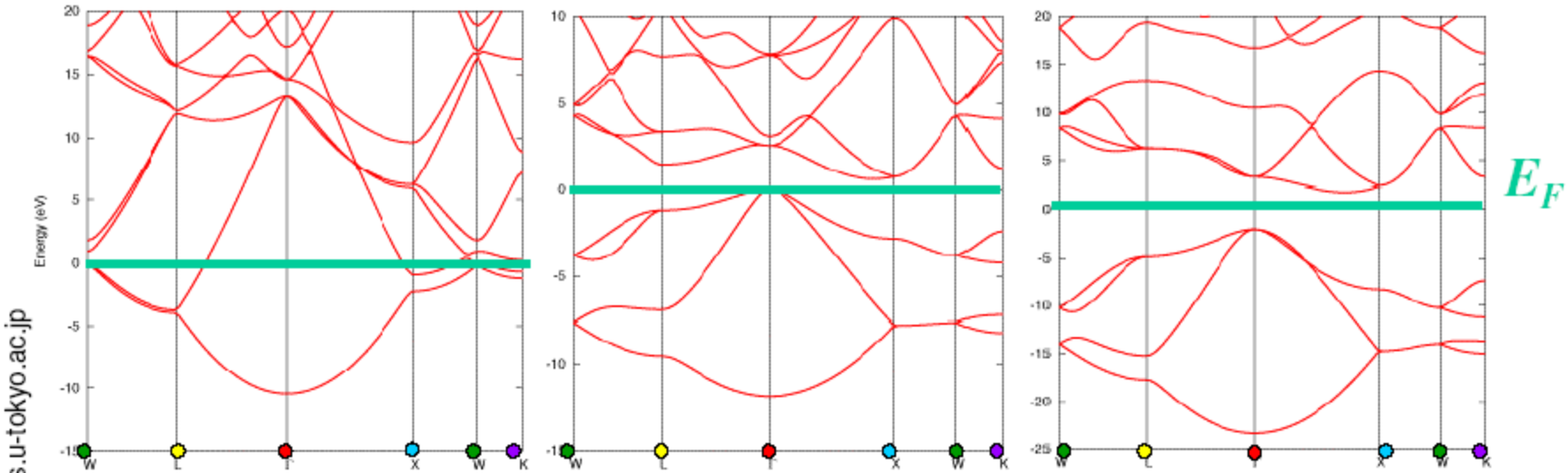


Input parameter **ecutwfc**

Band Structure



- "Band structure" (graph of ε_n vs. $\mathbf{k}$): what states are available for electrons.
- At T=0, all states that lie below/above Fermi level are occupied/empty.



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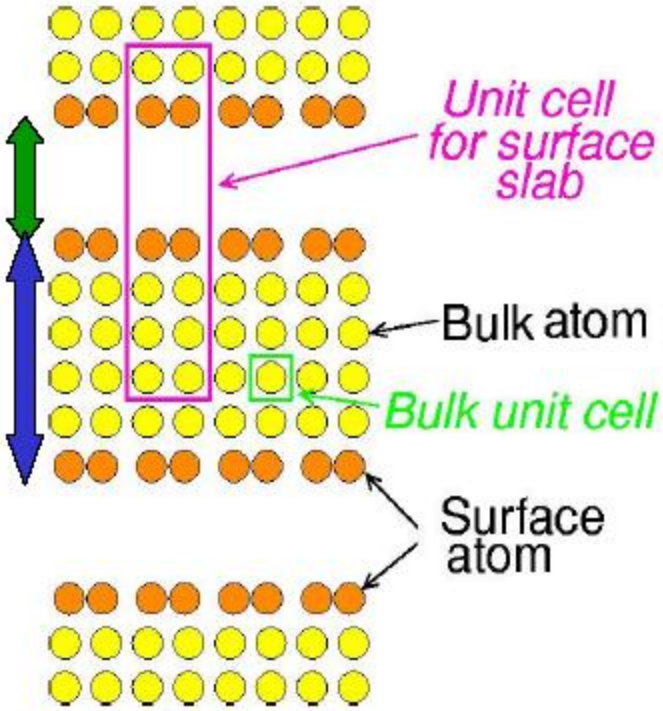
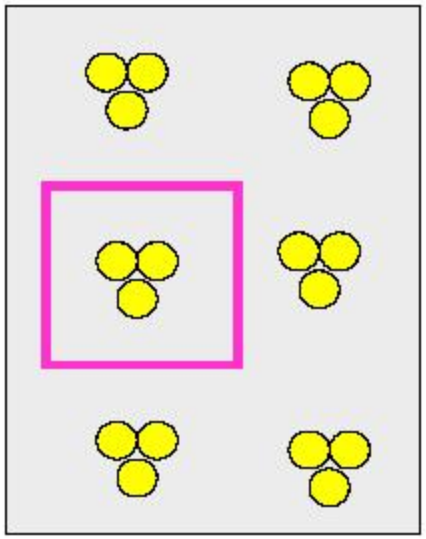
Al (metal) | Si (semiconductor) | C (diamond) (insulator)

Artificially Periodic 'Supercells'

- Introduce 'vacuum' along the direction(s) where translational symmetry broken to get supercell:





etc.

Brillouin Zone Sums

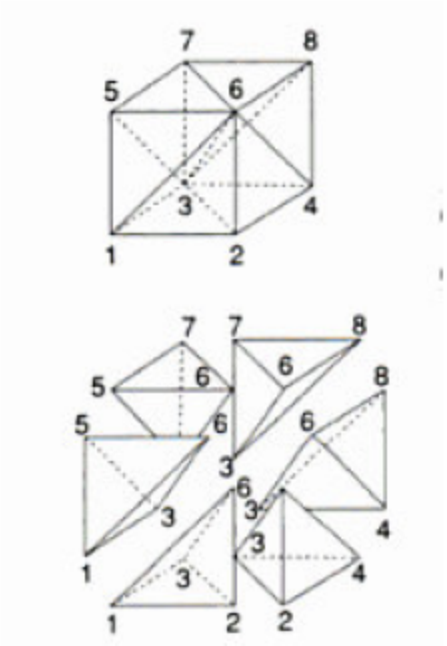
- Many quantities (e.g., density, total energy) involve integrals over **k:**

$$\langle P \rangle = \frac{\Omega}{(2\pi)^3} \sum_{n\ occ} \int_{BZ} P_n(\mathbf{k}) d^3k$$

- $\mathbf{k}$ (wave-vector) is in the first Brillouin zone,
- n (band index) runs over occupied manifold.
- In principle, need infinite number of $\mathbf{k}$'s.
- In practice, sum over a finite number: BZ "Sampling".

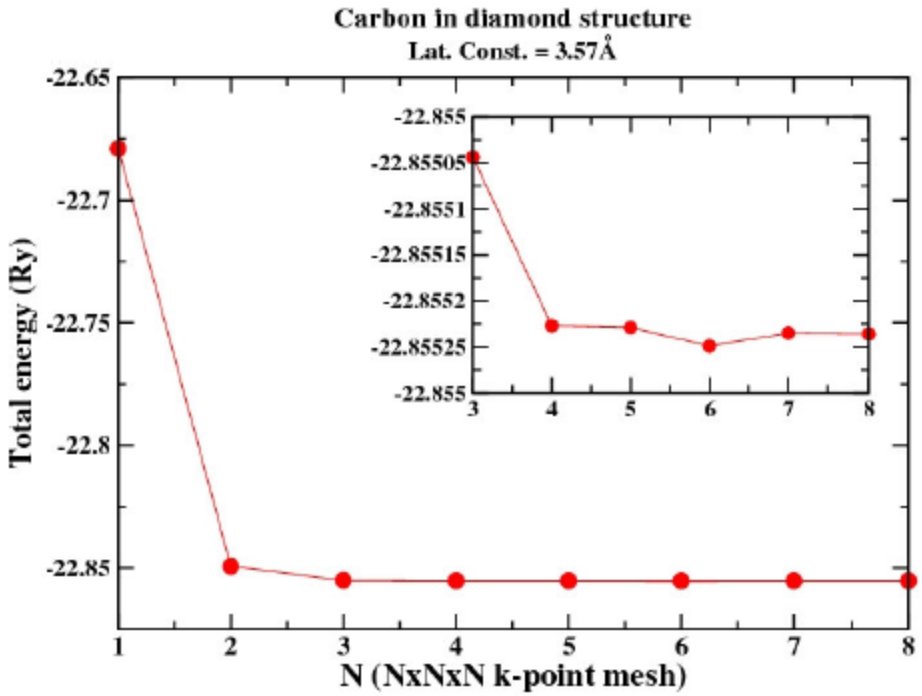
Interpolating between k-points

- In order to get sharp features in the DOS (e.g., van Hove singularities) correctly, use a method that interpolates between k-points.
- e.g., the Linear Tetrahedron method.
- Tetrahedra can be used to fill all space for any grid.
- Linear interpolation between values at vertices.



Bloechl, Jepsen & Andersen

Convergence wrt BZ sampling



Madhura Marathe

Note: Differences in energy usually converge faster than absolute value of total energy because of error cancellation (if supercells & k-points are identical or commensurate).

Convergence checks

- Energy cutoff
- Number of kpoints
- Diagonalization
- Self-consistency (mixing schemes)

Analyzing the output

» Self-consistent electronic charge
» Magnetization distribution
» Total energy (stability)
» Band structure or energy levels (approximate)

Using post-processing tools, can also compute :

> Optical properties:dielectric matrix, optical conductivity
> Mechanical properties: elastic constants
> Chemical properties (hardness, IP, EA)
> Phonons
> Molecular dynamics: relaxation, reaction paths…