Fundamentals and Applications of FLAPW Method: HiLAPW Code

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CMD Workshop

FLAPW Method

- The FLAPW is among the most precise and efficient first-principles methods which are able to solve density-functional-theory Kohn-Sham equations with the periodic boundary conditions.

- FLAPW =

  Full-potential **L**inearized **A**ugmented **P**lane **W**ave

- A great number of applications to a variety of solid systems

1. OUTLINE

- Fundamentals of FLAPW Method
  - One-electron equations and Bloch function
  - Augmented Plane Wave method
  - Linear method
  - Full-potential method
- FLAPW Codes
  - Packages open to public
  - HiLAPW code and some applications

2. OUTLINE

- **Practical Aspects of FLAPW Methods**
  - **First-Principles Calculation – Kohn-Sham Eqs.**
  - **Crystal Structure and Atomic Position**
  - **Lattice – Primitive Translation Vector**
  - **Space Group**
  - **Reciprocal Lattice – Brillouin Zone**
  - **k-point Integration**
  - **Eigenvalue Problem**
  - **Self-Consistent Field**
  - **Mixing of Electron Density**

Kohn-Sham Equations

$$\mathcal{H}\psi_j(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + v_{\mathrm{eff}}(\mathbf{r})\right]\psi_j(\mathbf{r}) = \varepsilon_j\psi_j(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_j |\psi_j(\mathbf{r})|^2$$

$$v_{\mathrm{eff}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + e^2\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \mu_{\mathrm{xc}}(n(\mathbf{r}))$$

★ One-electron Kohn-Sham equations are given within the local density approximation (generalized gradient approximation) to the density functional theory.

Band Theory

How to solve the one-electron equations for particular condensed-matter systems

Periodic system → Band theory

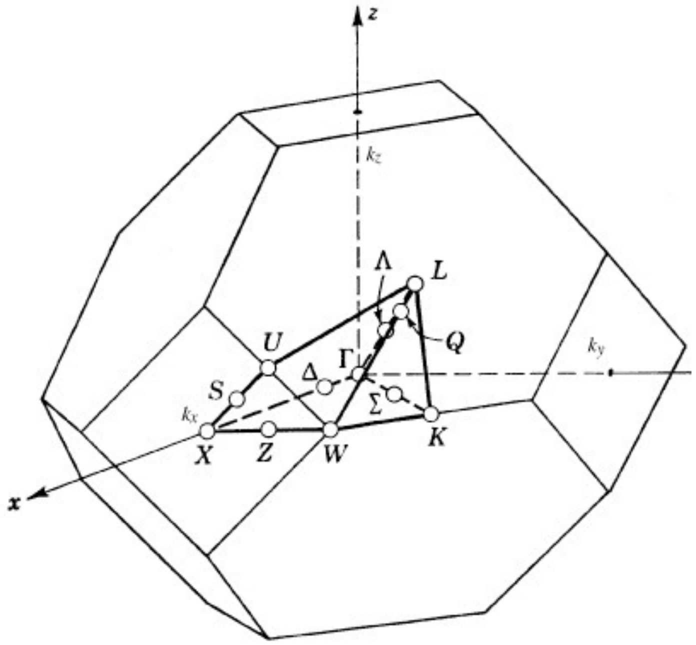
Bloch Theorem

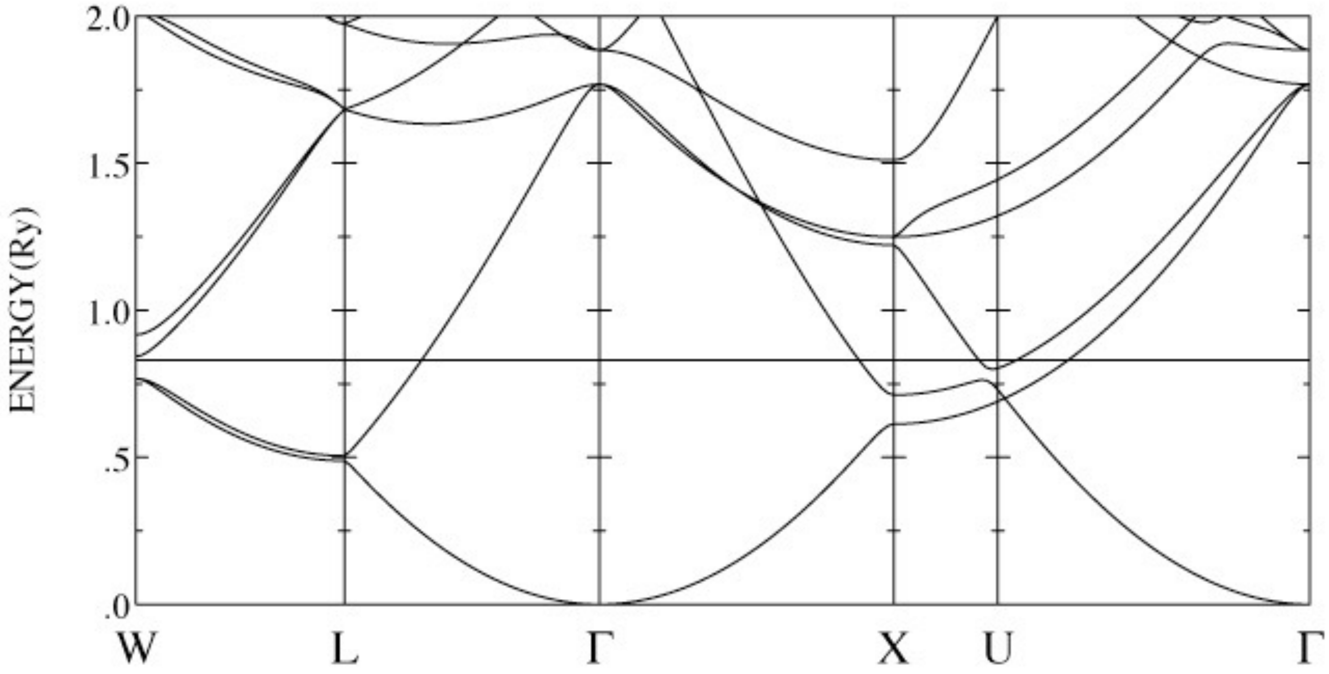
- **A quantum-mechanical state in a periodic system can be specified with a wave number k**

$$\mathcal{H}\psi_j^{\mathbf{k}}(\mathbf{r}) = \varepsilon_j^{\mathbf{k}}\psi_j^{\mathbf{k}}(\mathbf{r})$$

Dispersion relation: band structure

Brillouin Zone and Bands





BZ of fcc lattice

Band structure of fcc Al

independent quantum number

Bloch Function

$$\psi_j^{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_j^{\mathbf{k}}(\mathbf{r})$$ **: Bloch theorem**

$$\psi_j^{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_j^{\mathbf{k}}(\mathbf{r})$$

$$u_j^{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_j^{\mathbf{k}}(\mathbf{r})$$ **: periodic function represented in a Fourier form**

$$\psi_j^{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\sum_{\mathbf{K}} a_{j,\mathbf{K}}^{\mathbf{k}} e^{i\mathbf{K}\cdot\mathbf{r}}$$

$$= \sum_{\mathbf{K}} a_{j,\mathbf{K}}^{\mathbf{k}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}$$

K: reciprocal lattice vector

Bloch Function

- **Normalized in a macroscopic volume Ω**
- **k points in BZ are independent and sufficient**

$$\psi_j^{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{K}} a_j^{\mathbf{k}+\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}$$

⇓

$$\mathcal{H}\psi_j^{\mathbf{k}}(\mathbf{r}) = \varepsilon_j^{\mathbf{k}} \psi_j^{\mathbf{k}}(\mathbf{r})$$

Secular Equation

$$\sum_{\mathbf{K}} \langle \mathbf{k}+\mathbf{K}' | \mathcal{H} - \varepsilon_j^{\mathbf{k}} | \mathbf{k}+\mathbf{K} \rangle a_j^{\mathbf{k}+\mathbf{K}} = 0$$

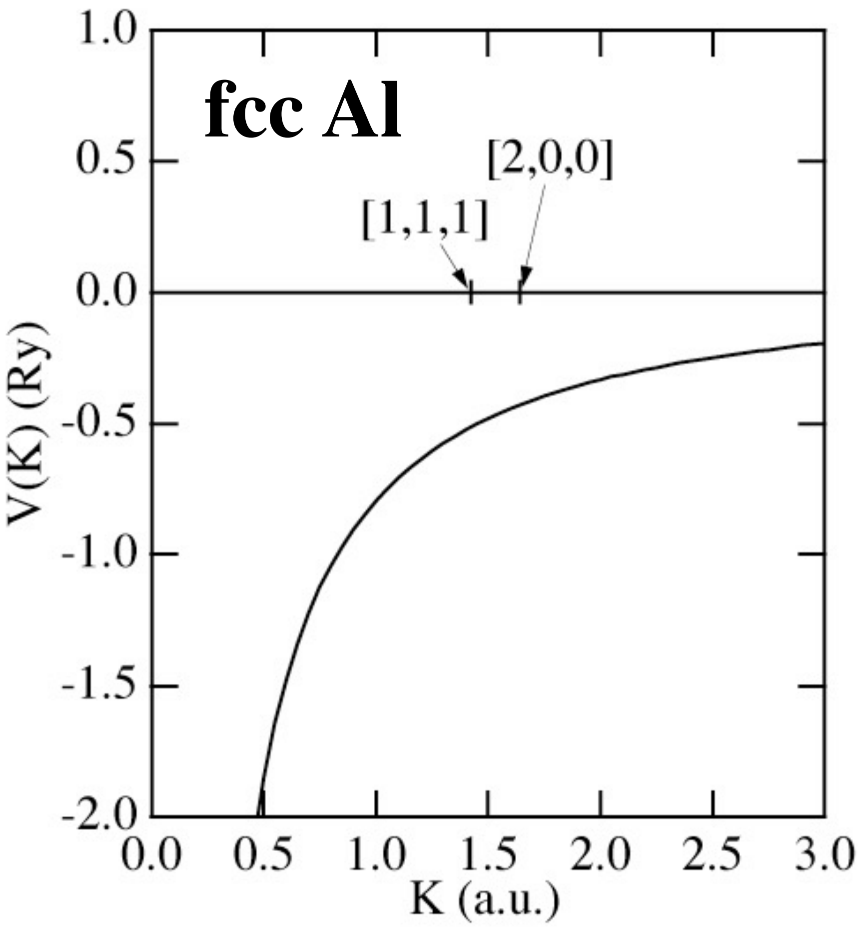
Matrix elements

$$\langle \mathbf{k}+\mathbf{K}' | \mathcal{H} | \mathbf{k}+\mathbf{K} \rangle = \frac{\hbar^2}{2m} |\mathbf{k}+\mathbf{K}|^2 \delta_{\mathbf{K}',\mathbf{K}} + V(\mathbf{K}'-\mathbf{K})$$

$$V(\mathbf{K}'-\mathbf{K}) = \frac{1}{\Omega} \int d\mathbf{r} e^{-i(\mathbf{K}'-\mathbf{K})\cdot\mathbf{r}} v(\mathbf{r})$$

Fourier Transform of Potential

$$V(\mathbf{K}' - \mathbf{K}) = \frac{1}{\Omega} \int d\mathbf{r} e^{-i(\mathbf{K}'-\mathbf{K})\cdot\mathbf{r}} v(\mathbf{r})$$



$$v(\mathbf{r}) \approx \sum_{\mathbf{R}} v_{\text{atom}}(|\mathbf{r} - \mathbf{R}|)$$

Very slow convergency of FT due to Coulombic behavior requires a large number of K vectors.

Orthogonalization to Core Functions

$$\langle \mathbf{k}+\mathbf{K}|\phi_{\mathrm{core}}\rangle = \frac{1}{\Omega}\int d\mathbf{r} e^{-i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}\phi_{\mathrm{core}}(\mathbf{r})$$

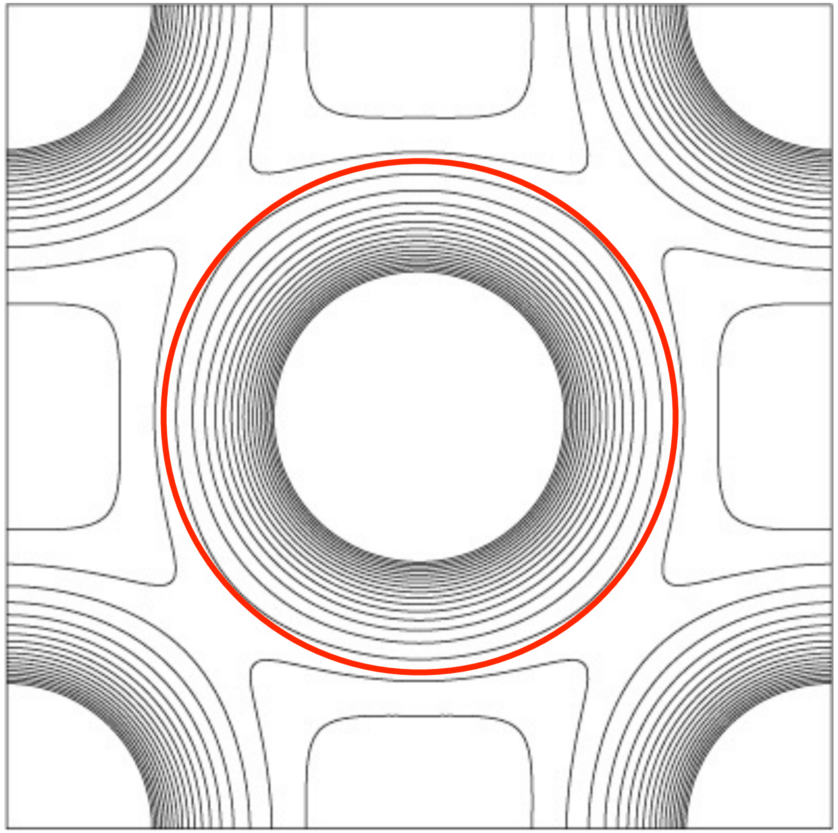
Very slow convergency of the core functions because of localized nature.

How to Solve the Problems

1. **Contributions from core (nucleus and core electron potentials, and orthogonality to core electron states) are replaced by a soft (easily Fourier transformed) potential.**
   → pseudopotential
2. **PW basis functions are augmented with localized functions.**
   → augmented basis
3. **Green's functions are used as a multiple scattering problem.**
   → Korringa-Kohn-Rostoker method

Muffin-tin Potential Approximation

Crystal Potential



FCC Cu

- **Spherical around atoms**
- **Constant in the interstitial**

$$v(\mathbf{r}) = \begin{cases} v(|\mathbf{r}-\mathbf{R}|) & |\mathbf{r}-\mathbf{R}| \in S \\ v_{\mathrm{MTZ}} & |\mathbf{r}-\mathbf{R}| \ni S \end{cases}$$

Slater's Idea

Phys. Rev. <u>51</u>(1937)846.

Plane waves $|\mathbf{r}-\mathbf{R}| \ni S$

$$\phi^{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}$$

Augmentation waves $|\mathbf{r}-\mathbf{R}| \in S$

$$\phi^{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{lm} i^l a_{lm}^{\mathbf{k}+\mathbf{K}} R_l(|\mathbf{r}-\mathbf{R}|;E) Y_{lm}(\mathbf{r}-\mathbf{R})$$

$R_l(r;E)$ **: radial function for energy *E***

$Y_{lm}(\mathbf{r})$ **: spherical harmonics**

Augmented Plane Wave

Secular Equation

$$\det ||\langle \mathbf{k}+\mathbf{K}'|\mathcal{H}-E|\mathbf{k}+\mathbf{K}\rangle|| = 0$$

$$\langle \mathbf{k}+\mathbf{K}'|\mathcal{H}-E|\mathbf{k}+\mathbf{K}\rangle = \left\{\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{K}|^2 - E\right\}\delta_{\mathbf{K}',\mathbf{K}}$$

$$+\Gamma^{\mathrm{APW}}_{\mathbf{K}',\mathbf{K}}(E)$$

Matrix elements have non-linear energy dependence due to logarithmic derivatives of the radial functions.

Problems in APW Method

1. **Energy dependence of the matrix elements $\Gamma^{\mathrm{APW}}_{\mathbf{K}',\mathbf{K}}(E)$ requires searching poles of the determinants**
   → Linear Method by Andersen (1975) and
   Koelling-Arbman (1975)
   LAPW
2. **Muffin-tin potential approximation doesn't work for less-packing or low-symmetry systems**
   → Full-potential Method by Weinert (1981)
   FLAPW

Linear Method

O.K. Andersen, PRB 12(1975)3060.
D.D. Koelling and G.O. Arbman, JPF 5(1975)2041.

- **Remove the energy dependence of radial functions**

  using Tayler expansion

$$R_l(r;E) \approx R_l(r;E_0) + (E-E_0)\dot{R}_l(r;E_0) + \cdots$$

$$\dot{R}_l(r;E_0) = \left.\frac{d}{dE}R_l(r;E)\right|_{E=E_0}$$

- **Use radial function at E_0 and its energy derivative to represent a radial function with any logarithmic derivative**

$$R_l(r;D) = R_l(r;E_0) + \omega(D)\dot{R}_l(r;E_0)$$

Linear Method

- **APW → LAPW**

- **KKR → MTO → LMTO**

  KKR: Korringa-Kohn-Rostoker

  MTO: Muffin-Tin Orbital

  LMTO: Linear Muffin-Tin Orbital

LAPW Method

Augmentation basis

$$\phi^{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{lm} i^l \phi_{lm}^{\mathbf{k}+\mathbf{K}}(|\mathbf{r}-\mathbf{R}|) Y_{lm}(\mathbf{r}-\mathbf{R})$$

$$\phi_{lm}^{\mathbf{k}+\mathbf{K}}(r) = A_{lm}^{\mathbf{k}+\mathbf{K}} R_l(r; E_l) + B_{lm}^{\mathbf{k}+\mathbf{K}} \dot{R}_l(r; E_l)$$

$\left\{ \begin{array}{l} A_{lm}^{\mathbf{k}+\mathbf{K}} \\ B_{lm}^{\mathbf{k}+\mathbf{K}} \end{array} \right.$ **determined from the boundary conditions**

E_l **energy parameter usually taken at the center of the occupied partial band**

Why the Linear Method Works Well?

Orthogonality to maximize the variational degree

$$\int_0^S R_l(r;E_l)\dot{R}_l(r;E_l)r^2dr = 0$$

Orthogonality to the core functions

$$\int_0^S R_l(r;E_l)R_{\rm core}(r;E_{\rm core})r^2dr = 0$$

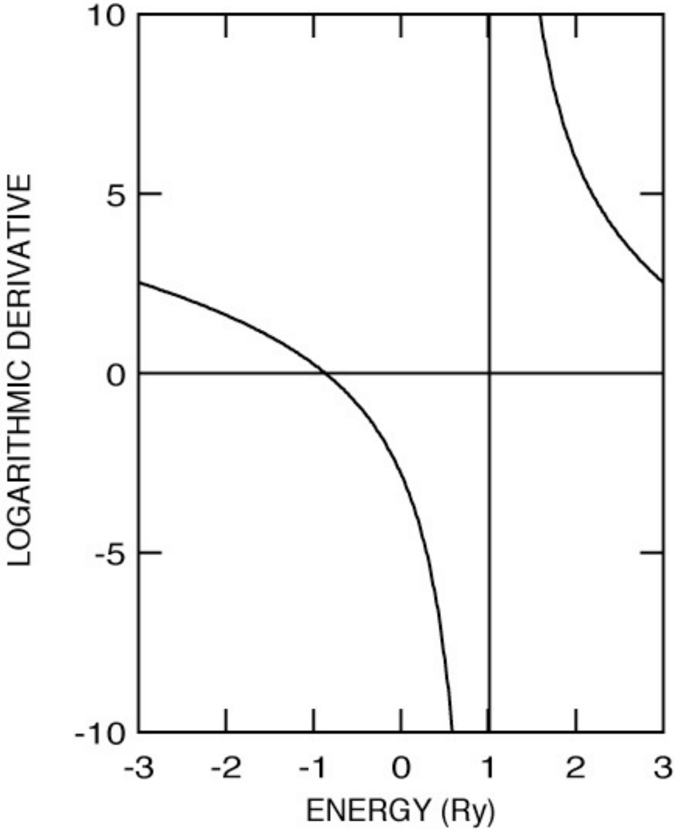
$$\int_0^S \dot{R}_l(r;E_l)R_{\rm core}(r;E_{\rm core})r^2dr = 0$$

Why the Linear Method Works Well?

Energy expectation value of the orbital with the exact logarithmic derivative

$$\langle E(D)\rangle = \frac{\langle \phi_l(D)|\mathcal{H}|\phi_l(D)\rangle_S}{\langle \phi_l(D)|\phi_l(D)\rangle_S}$$

$$= E + \mathcal{O}(E - E_l)^4$$



Coulomb Potential

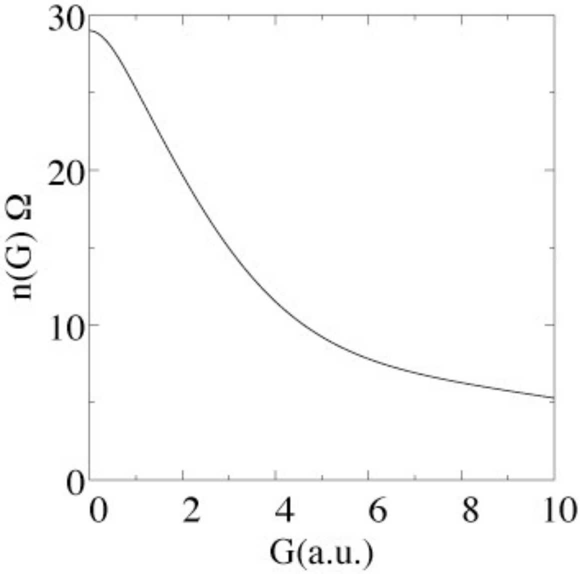
- **Coulomb potential for smooth density distribution**

$$n(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} n_{\mathbf{G}} \qquad \nabla^2 v^{\mathrm{C}}(\mathbf{r}) = 4\pi e^2 n(\mathbf{r})$$

$$v^{\mathrm{C}}(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} v^{\mathrm{C}}_{\mathbf{G}} \qquad v^{\mathrm{C}}_{\mathbf{G}} = \frac{4\pi e^2 n_{\mathbf{G}}}{G^2}$$

- **Realistic distribution**

$$n_{\mathbf{G}} = \frac{1}{\Omega}\int e^{-i\mathbf{G}\cdot\mathbf{r}} n(\mathbf{r}) d\mathbf{r}$$



Full Potential Method

M. Weinert, J. Math. Phys. 22 (1981) 2433.

- **Electron density inside the sphere is replaced by a smoothed density with the exact multipole moments.**

$$
n(\mathbf{r}) = \begin{cases} \tilde{n}(\mathbf{r}) & |\mathbf{r}-\mathbf{R}| \in S \\ n(\mathbf{r}) & |\mathbf{r}-\mathbf{R}| \ni S \end{cases}
$$

- **Potential outside the sphere is given with the smoothed density.**
- **Potential inside the sphere can be solved with the sphere boundary conditions.**

Full Potential Method

- **Electron density inside the sphere**

$$n(\mathbf{r}) = \sum_{lm} n_{lm}(r) Y_{lm}(\mathbf{r})$$

- **Potential function inside the sphere**

$$v(\mathbf{r}) = \sum_{lm} v_{lm}(r) Y_{lm}(\mathbf{r})$$

- **Matrix element of potential**

$$\Delta H_{\mathbf{K}',\mathbf{K}} = \langle \mathbf{k}+\mathbf{K}' | \Delta v | \mathbf{k}+\mathbf{K} \rangle$$

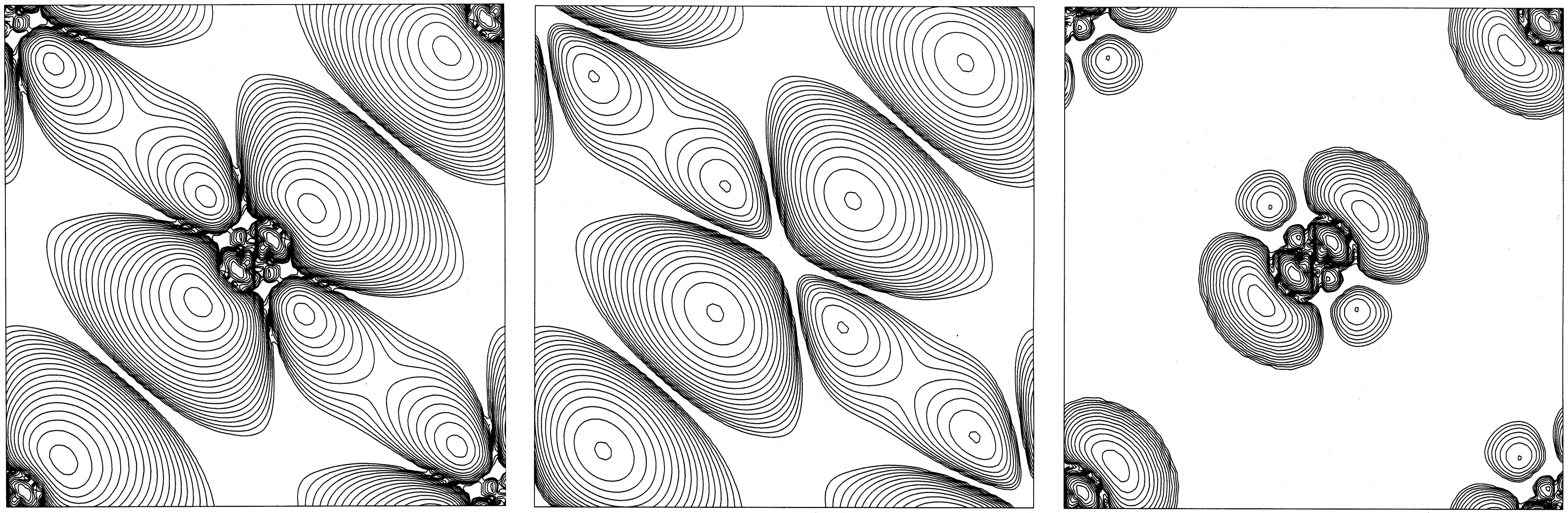
non-spherical part

FLAPW Method

- Two-dimensional slab models
  - E. Wimmer, H. Krakauer, M. Weinert and A. J. Freeman, PRB 24, 864 (1981).
  - M. Weinert, E. Wimmer and A. J. Freeman, PRB 26, 4571 (1982).
- Three-dimensional systems
  - H. J. F. Jansen and A. J. Freeman, PRB 30 , 561 (1984).

FLAPW Packages Open to Public

$$\psi_j^{\mathbf{k}} = \tilde{\psi}_j^{\mathbf{k}} + \sum_{\nu} \left[\psi_{\nu j}^{\mathbf{k}} - \tilde{\psi}_{\nu j}^{\mathbf{k}} \right]$$



- **ABCAP**
- **HiLAPW**
- **KANSAI**
- **FLEUR**
- **QMD-FLAPW**
- **WIEN**

HiLAPW

- 100% Original Code
  - LAPW basis functions
  - LSDA, GGA, Hubbard-*U*
  - Scalar relativity, Spin-orbit coupling
  - All-electron SCF full-potential scheme
  - BZ integration with tetrahedron method
  - Group theory
  - Crystal structure & element database
  - Total E, forces, DOS, ...
  - XAS, Berry phase, ...

optional functionalities

HiLAPW

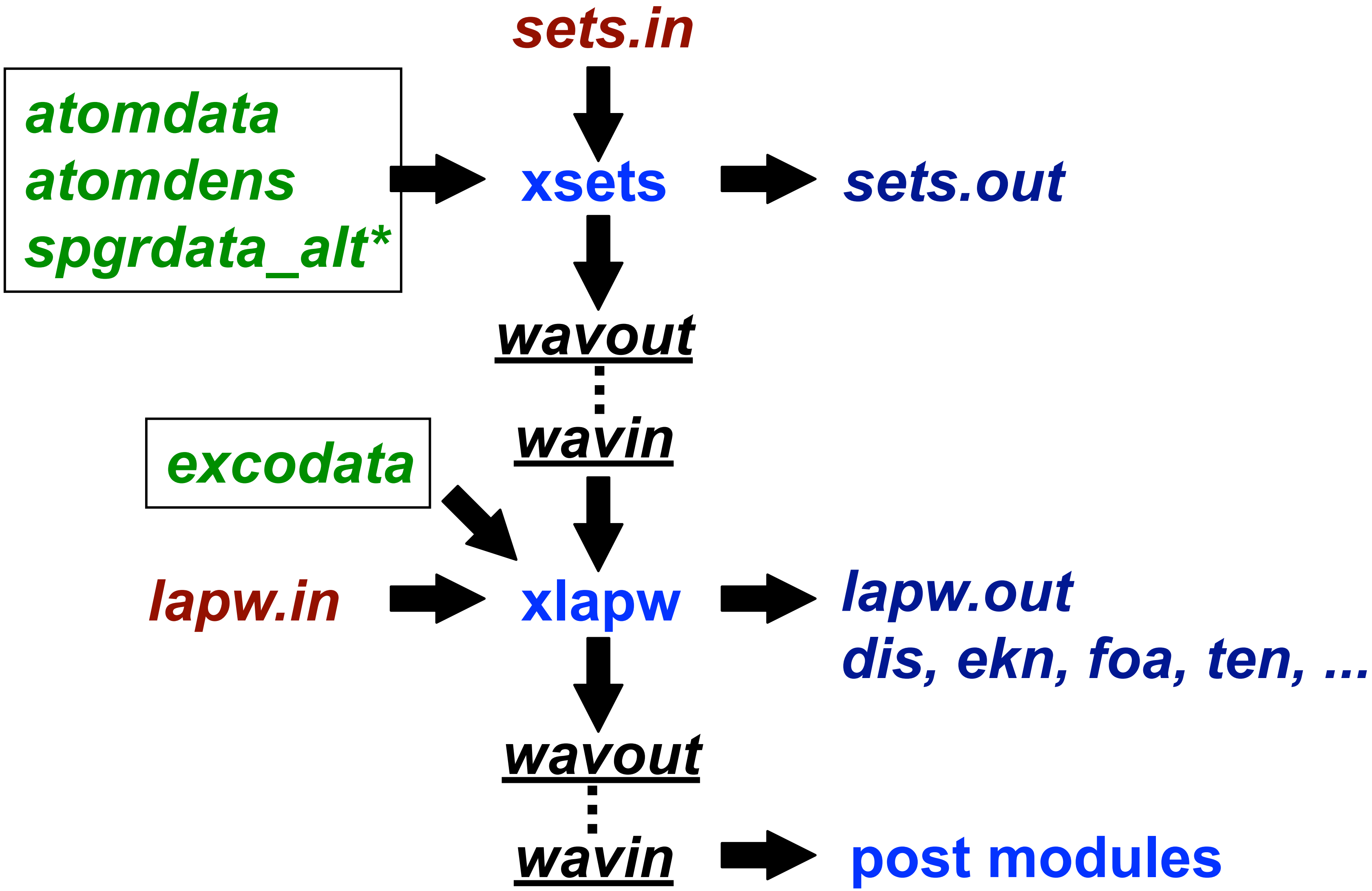
- 100% Original Code
  - Modular executables
  - fortran90
    - dynamical memory allocation
  - BLAS and LAPACK libraries
  - PSP : PostScript Plot routines
  - MPI parallelization

- Manuals and some useful data
  - www.cmp.sanken.osaka-u.ac.jp/~oguchi/HiLAPW/

HiLAPW – Executables

executables	contents
xsets	initialization
xlapw	SCF calculation
xdoss	DOS
xnewa	modification k-point data
xwbox	electron density on 3D mesh
xpbox	potential on 3D mesh
xspin	addition of spin polarization
xsymm	irreducible representation extract
xrept	rearrangement of eigenvalues

HiLAPW – Executables



sets.in

atomdata
atomdens
*spgrdata_alt**

xsets

sets.out

wavout

wavin

excodata

lapw.in

xlapw

lapw.out
dis, ekn, foa, ten, …

wavout

wavin

post modules

*:spgrdata_alt: spgrdata is used in old versions

2. OUTLINE

- Practical Aspects of FLAPW Methods
  - First-Principles Calculation – Kohn-Sham Eqs.
  - Crystal Structure and Atomic Position
  - Lattice – Primitive Translation Vector
  - Space Group
  - Reciprocal Lattice – Brillouin Zone
  - k-point Integration
  - Eigenvalue Problem
  - Self-Consistent Field
  - Mixing of Electron Density

First-Principles Calculation

- **Local Density Approximation to Density Functional Theory — Kohn-Sham Equations**

$$\mathcal{H}\psi_j^{\mathbf{k}}(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r})\right]\psi_j^{\mathbf{k}}(\mathbf{r}) = \varepsilon_j^{\mathbf{k}}\psi_j^{\mathbf{k}}(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{j,\mathbf{k}}^{\text{occ.}} |\psi_j^{\mathbf{k}}(\mathbf{r})|^2$$

$$v(\mathbf{r}) = -e^2\sum_{\nu}\frac{Z_\nu}{|\mathbf{r}-\mathbf{R}_\nu|} + e^2\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \mu_{\text{xc}}(n(\mathbf{r}))$$

basic input

Crystal Structure and Atomic Position

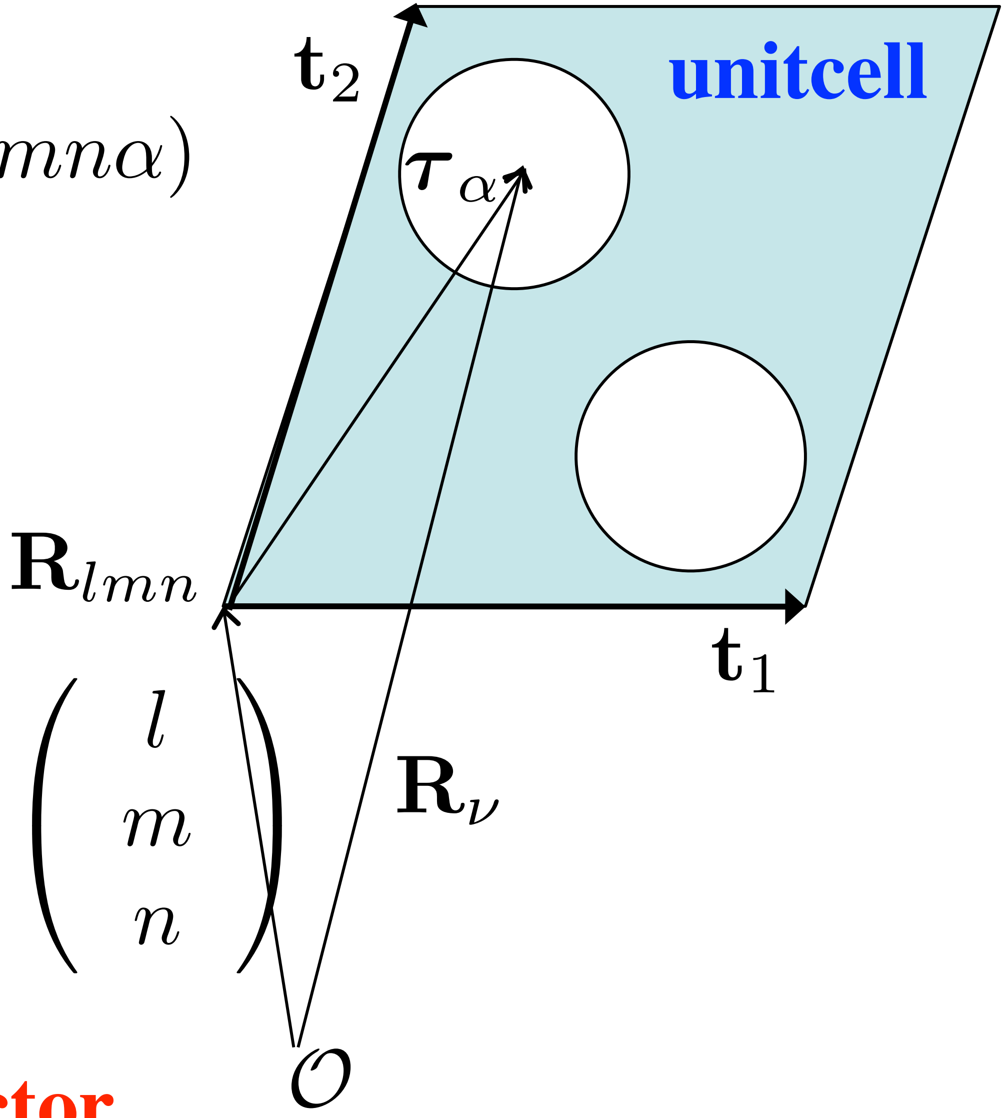
$$\mathbf{R}_\nu = \mathbf{R}_{lmn} + \boldsymbol{\tau}_\alpha \qquad \nu = (lmn\alpha)$$

- **Lattice Vector**

$$\mathbf{R}_{lmn} = l\mathbf{t}_1 + m\mathbf{t}_2 + n\mathbf{t}_3$$

$$\begin{pmatrix} R^x_{lmn} \\ R^y_{lmn} \\ R^z_{lmn} \end{pmatrix} = \underbrace{\begin{pmatrix} t^x_1 & t^x_2 & t^x_3 \\ t^y_1 & t^y_2 & t^y_3 \\ t^z_1 & t^z_2 & t^z_3 \end{pmatrix}}_{} \begin{pmatrix} l \\ m \\ n \end{pmatrix}$$

Primitive translation vector



Lattice Translation Vector

- **Primitive Translation Vector (Bravais lattice)**

$$\begin{pmatrix} t_1^x & t_2^x & t_3^x \\ t_1^y & t_2^y & t_3^y \\ t_1^z & t_2^z & t_3^z \end{pmatrix} = \begin{pmatrix} a_1^x & a_2^x & a_3^x \\ a_1^y & a_2^y & a_3^y \\ a_1^z & a_2^z & a_3^z \end{pmatrix} \begin{pmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{pmatrix}$$

- **Conventional Translation Vector**

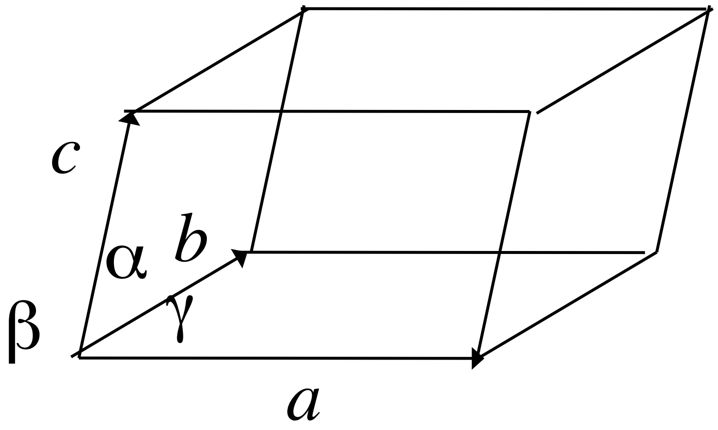
$$\begin{pmatrix} a_1^x & a_2^x & a_3^x \\ a_1^y & a_2^y & a_3^y \\ a_1^z & a_2^z & a_3^z \end{pmatrix} \Leftarrow (a, b, c, \alpha, \beta, \gamma)$$

Lattice constants

Lattice: System and Type

- Lattice system

$$\begin{pmatrix} a_1^x & a_2^x & a_3^x \\ a_1^y & a_2^y & a_3^y \\ a_1^z & a_2^z & a_3^z \end{pmatrix} \Leftarrow (a, b, c, \alpha, \beta, \gamma)$$



system	a	b	c	α	β	γ	type
cubic	a	a	a	90	90	90	P,I,F
tetragonal	a	a	c	90	90	90	P,I
orthorhombic	a	b	c	90	90	90	P,I,F,C
hexagonal	a	a	c	90	90	120	P
trigonal	a	a	a	α	α	α	R
(trigonal	a	a	c	90	90	120	P)
monoclinic	a	b	c	90	90	γ	P,B
triclinic	a	b	c	α	β	γ	P

Lattice: System and Type

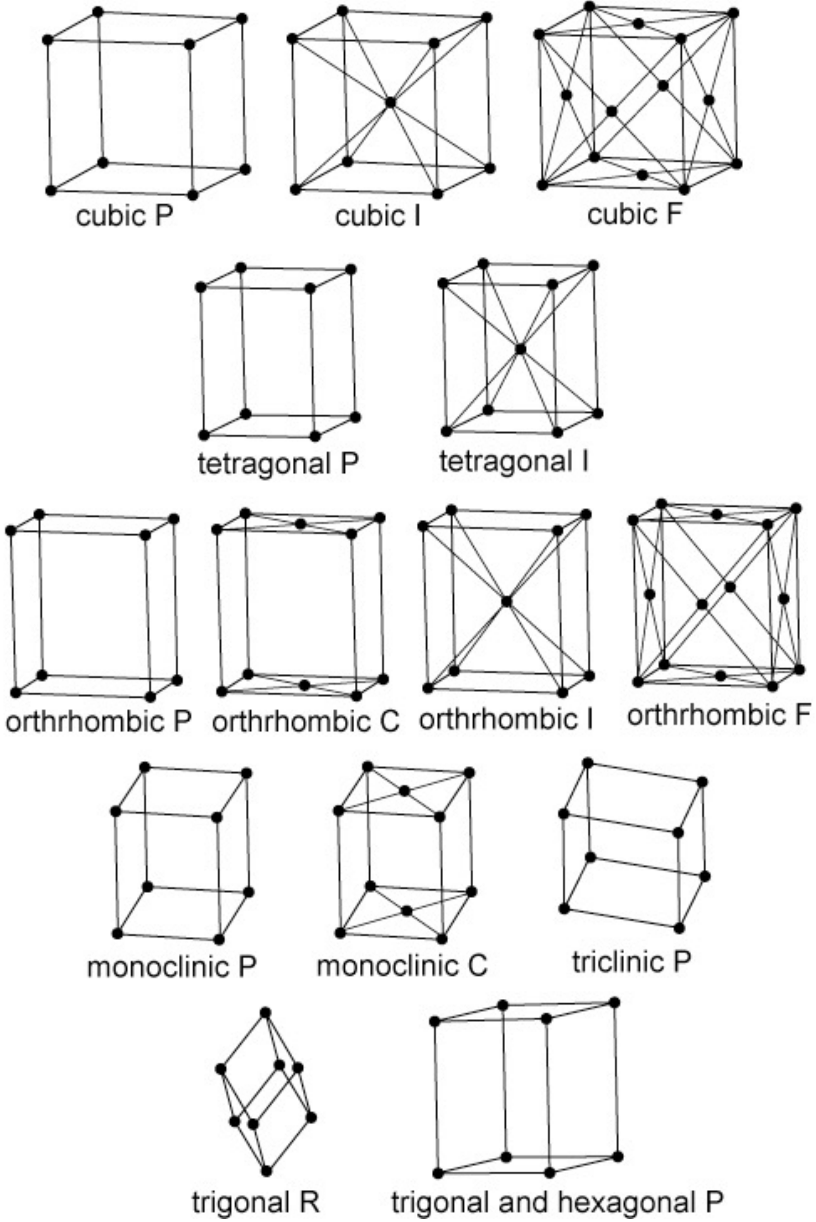
- **Lattice type**

$$P = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad F = \begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}$$

$$I = \begin{pmatrix} -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \end{pmatrix} \qquad A = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & -\frac{1}{2} & \frac{1}{2} \end{pmatrix}$$

$$B = \begin{pmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \qquad C = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

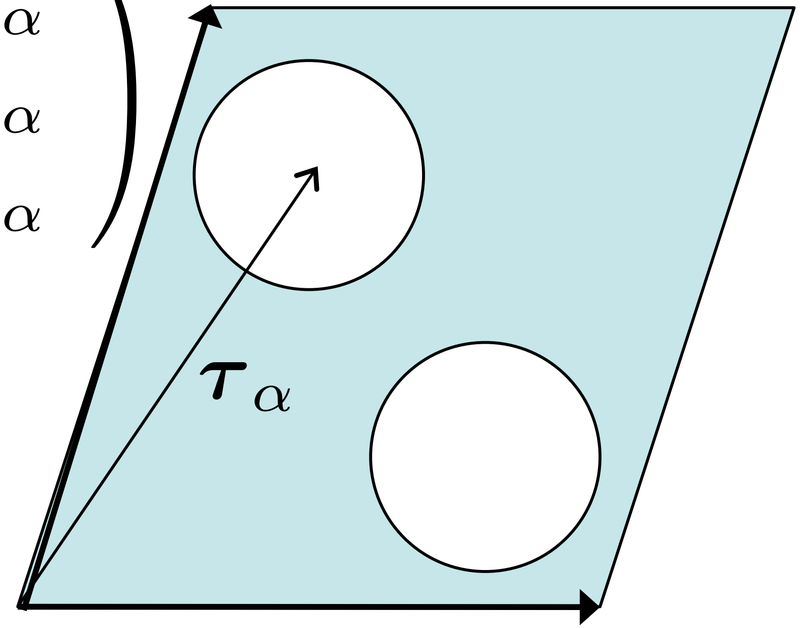
Lattice: System and Type



- **Number of mathematically independent lattice is 14 called Bravais Lattice.**
- **For example, a face-centered tetragonal lattice can be represented as body-centered tetragonal.**
- **Some of trigonal systems are represented as rhombohedral R or hexagonal P.**

Atomic Position in a Unitcell

$$\begin{pmatrix} \tau_\alpha^x \\ \tau_\alpha^y \\ \tau_\alpha^z \end{pmatrix} = \begin{pmatrix} a_1^x & a_2^x & a_3^x \\ a_1^y & a_2^y & a_3^y \\ a_1^z & a_2^z & a_3^z \end{pmatrix} \begin{pmatrix} \tau_{1\alpha} \\ \tau_{2\alpha} \\ \tau_{3\alpha} \end{pmatrix}$$



Atomic positions are represented on the basis of the conventional lattice vectors.

Space Group

- **Symmetry operation** $\{\beta|\mathbf{v}_\beta + \mathbf{R}_{lmn}\}$

$$\{\beta|\mathbf{v}_\beta\}\,\mathbf{r} = \beta\mathbf{r} + \underline{\mathbf{v}_\beta}$$

non-primitive translation vector

$$= \begin{pmatrix} \beta_{11} & \beta_{12} & \beta_{13} \\ \beta_{21} & \beta_{22} & \beta_{23} \\ \beta_{31} & \beta_{32} & \beta_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} v_\beta^x \\ v_\beta^y \\ v_\beta^z \end{pmatrix}$$

Example: Diamond Structure

- fcc $a=b=c$, $\alpha=\beta=\gamma=90^\circ$
- space group Fd-3m (#227)

  generators $C_4[001]$ + (1/4,1/4,1/4)

  $C_3[111]$

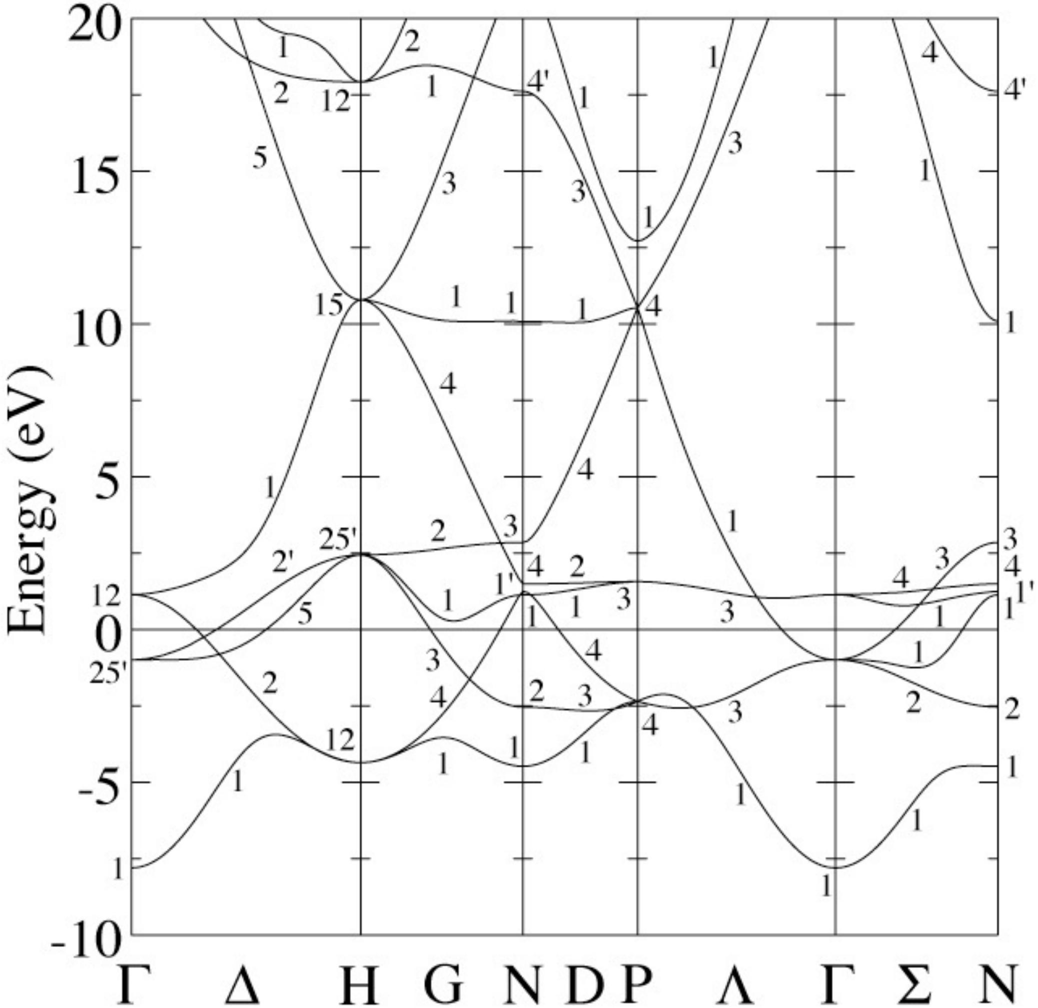
  I + (1/4,1/4,1/4)
- atomic positions (0,0,0); (1/4,1/4,1/4)

International Tables for Crystallography

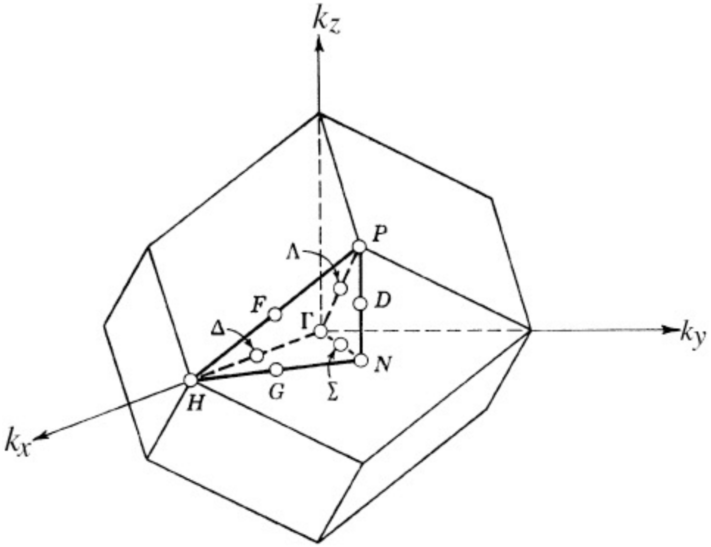
k Group

$$\beta\mathbf{k} = \mathbf{k} + \mathbf{K}$$

The Bloch wave function belongs to an irreducible representation of the k group.



bcc Cr



Space Group Symbol

1,2,3,4,6：rotation axis

m：mirror plane

2_1：twofold screw with v=1/2

4_2：fourfold screw with v=2/4

a, b, c：axial glide with v=1/2 along each axis

n：diagonal glide

d：diamond glide

-：inversion

4/m：fourfold axis and mirror plane perpendicular to it

4/n：fourfold axis and n-glide plane perpendicular to it

Reciprocal Lattice

- **Definition**

$$\underline{\mathbf{R}} \cdot \mathbf{K} = 2\pi I \qquad \boldsymbol{I}\text{ : any integer}$$

lattice vector

$$\mathbf{K}_{lmn} = l\mathbf{b}_1 + m\mathbf{b}_2 + n\mathbf{b}_3$$

$$\mathbf{b}_i = 2\pi \frac{\mathbf{t}_j \times \mathbf{t}_k}{\mathbf{t}_i \cdot (\mathbf{t}_j \times \mathbf{t}_k)}$$

- **Brillouin zone (BZ) = unitcell of reciprocal lattice**
- **States with k inside BZ are independent**

→ State sum = k-integration inside BZ

Brillouin Zone

Unitcell of reciprocal lattice

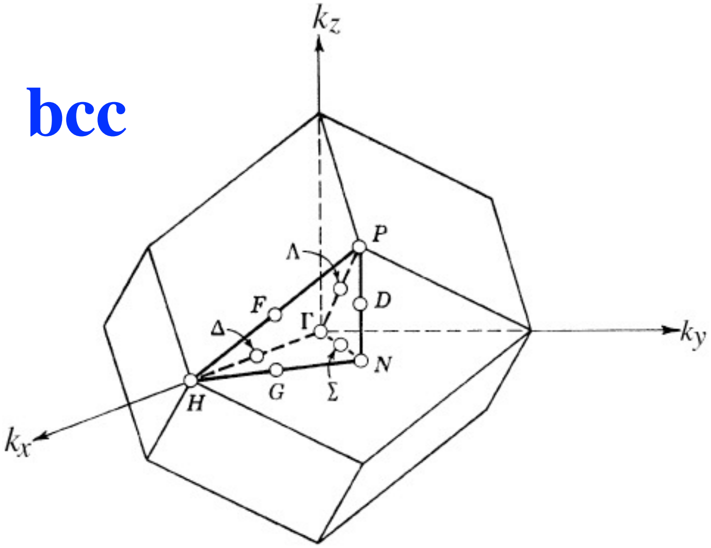
- **parallelepiped** $(\mathrm{b}_1, \mathrm{b}_2, \mathrm{b}_3)$

  easy to treat numerically

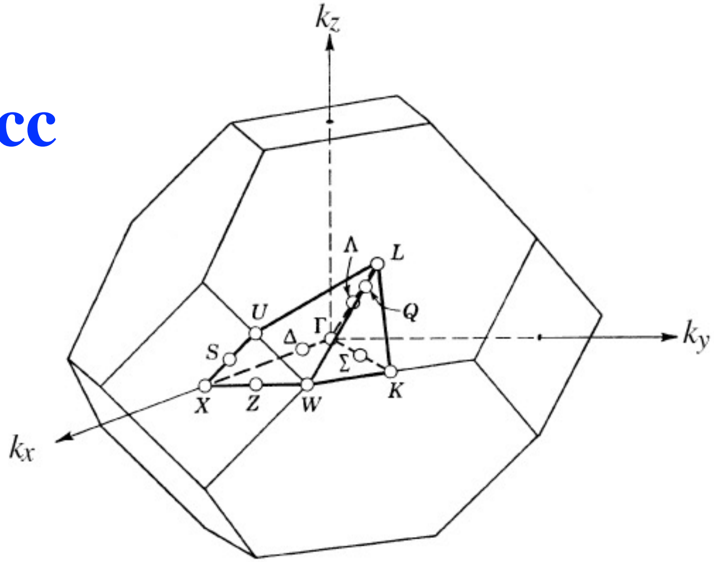
- **Voronoi Polyhedron**

  Wigner-Seitz cell

bcc



fcc

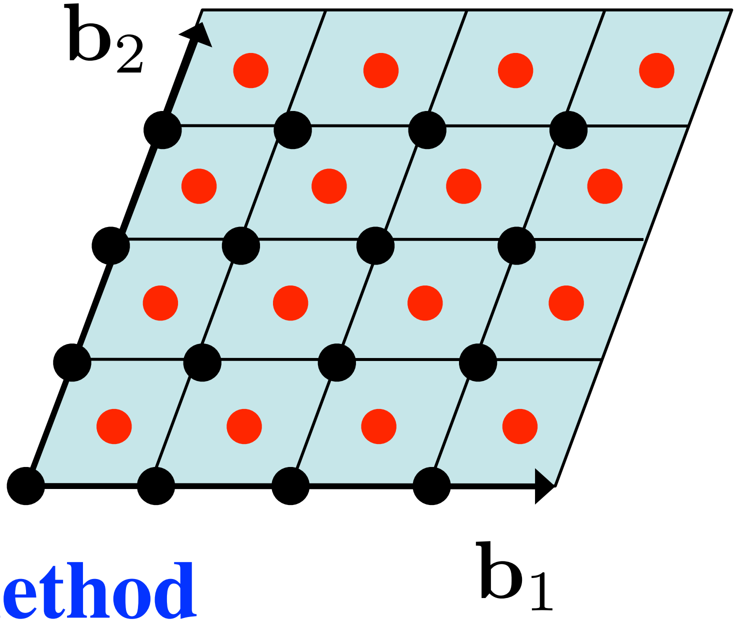


k Integration

k-point mesh

(N_1, N_2, N_3) **division of parallelepiped BZ**

$$n(\mathbf{r}) = \sum_{j,\mathbf{k}}^{\text{occ.}} |\psi_j^{\mathbf{k}}(\mathbf{r})|^2$$



- **Linear Tetrahedron method**
- **Broadening method**

Eigenvalue Problem

- **Basis function expansion**

$$\psi_j^{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{i}} \phi_i^{\mathbf{k}} C_{ij}^{\mathbf{k}}$$

- **Secular equation**

$$\mathbf{HC} = \mathbf{SC}E$$

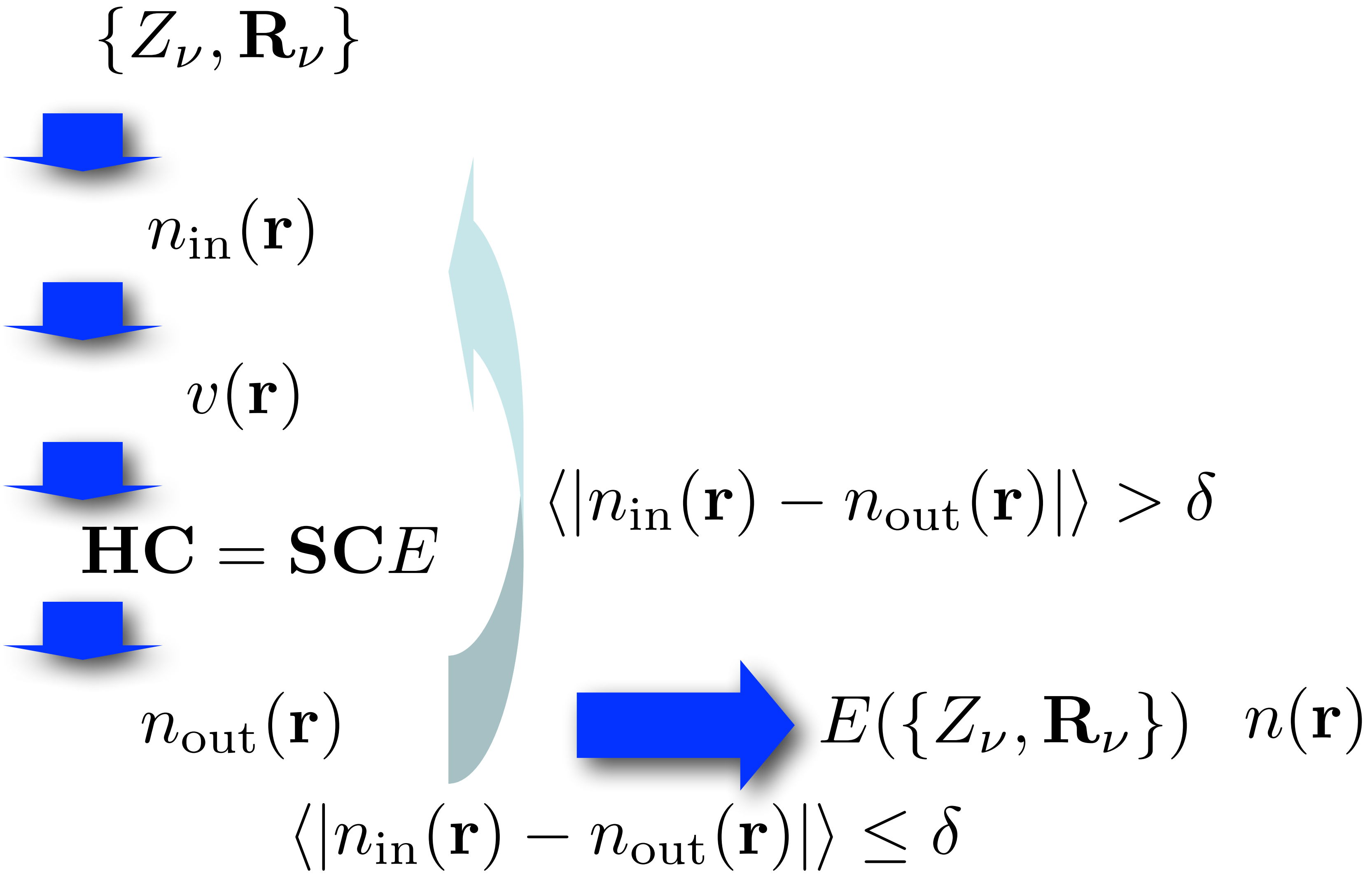
- **Matrix elements**

$$H_{ij} = \langle \phi_i^{\mathbf{k}} | \mathcal{H} | \phi_j^{\mathbf{k}} \rangle \qquad S_{ij} = \langle \phi_i^{\mathbf{k}} | \phi_j^{\mathbf{k}} \rangle$$

Basis Functions

- Plane waves
  - pseudopotential
  - simple, fast, extendable, transferability
- Plane waves + Augmentation functions
  - all-electron scheme
  - robust, precise, complicated
- Local orbitals
  - minimal
  - real space → O(N)

Self-Consistent Field



$$\{Z_\nu, \mathbf{R}_\nu\}$$

$$n_{\text{in}}(\mathbf{r})$$

$$v(\mathbf{r})$$

$$\mathbf{HC} = \mathbf{SC}E$$

$$n_{\text{out}}(\mathbf{r})$$

$$\langle | n_{\text{in}}(\mathbf{r}) - n_{\text{out}}(\mathbf{r}) | \rangle > \delta$$

$$E(\{Z_\nu, \mathbf{R}_\nu\}) \quad n(\mathbf{r})$$

$$\langle | n_{\text{in}}(\mathbf{r}) - n_{\text{out}}(\mathbf{r}) | \rangle \leq \delta$$

Mixing of Electron Density

- **Simple Method**

$$n_{\mathrm{in}}^{(i+1)} = (1-\alpha) n_{\mathrm{in}}^{(i)} + \alpha n_{\mathrm{out}}^{(i)}$$

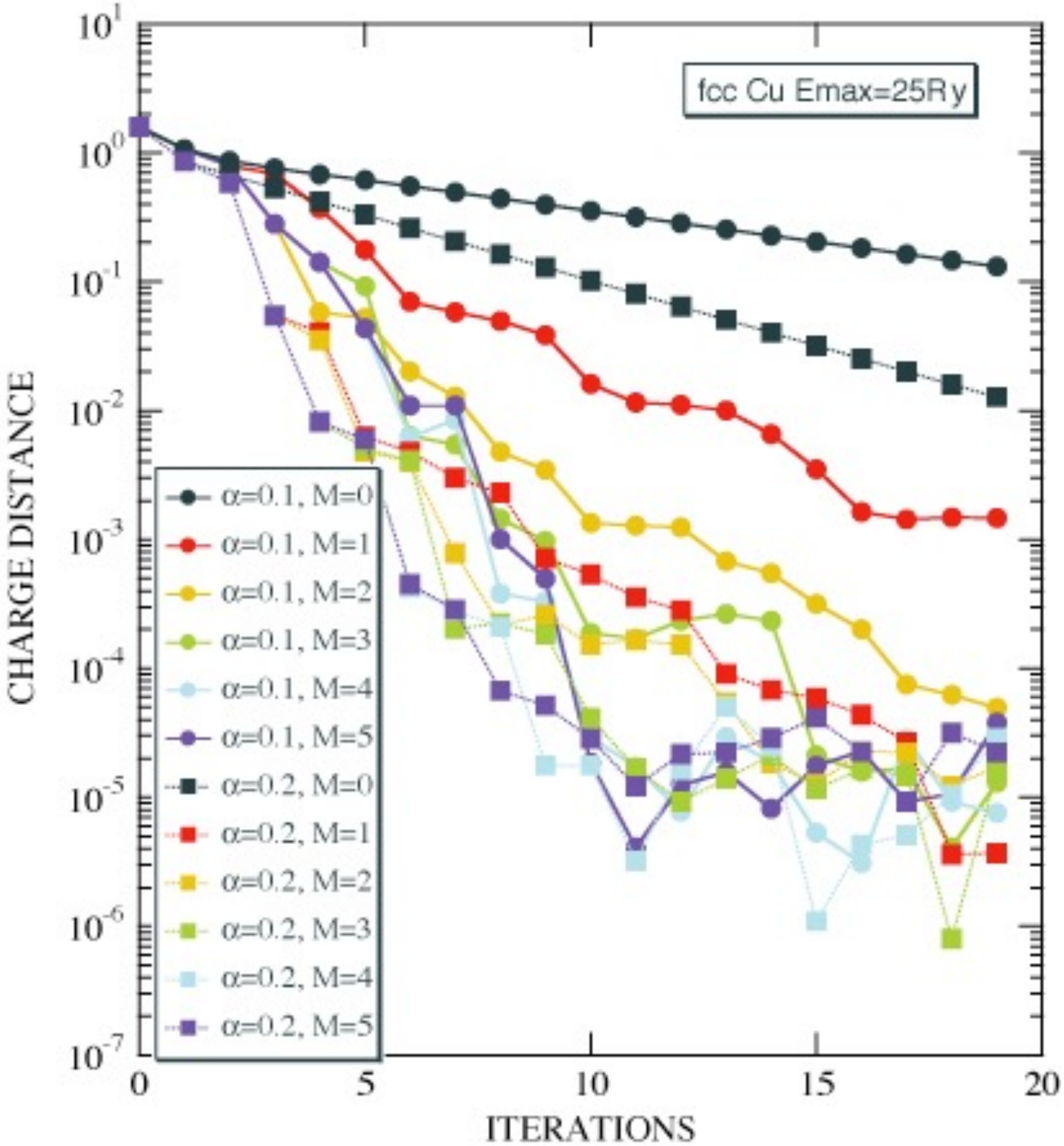
- **Extended Anderson Method**

$$n_{\mathrm{in}}^{(i+1)} = (1-\alpha) \bar{n}_{\mathrm{in}}^{(i)} + \alpha \bar{n}_{\mathrm{out}}^{(i)}$$

$$\bar{n}_{\mathrm{in}}^{(i)} = \sum_{j=i-M}^{i} \beta^{(j)} n_{\mathrm{in}}^{(j)} \qquad \bar{n}_{\mathrm{out}}^{(i)} = \sum_{j=i-M}^{i} \beta^{(j)} n_{\mathrm{out}}^{(j)}$$

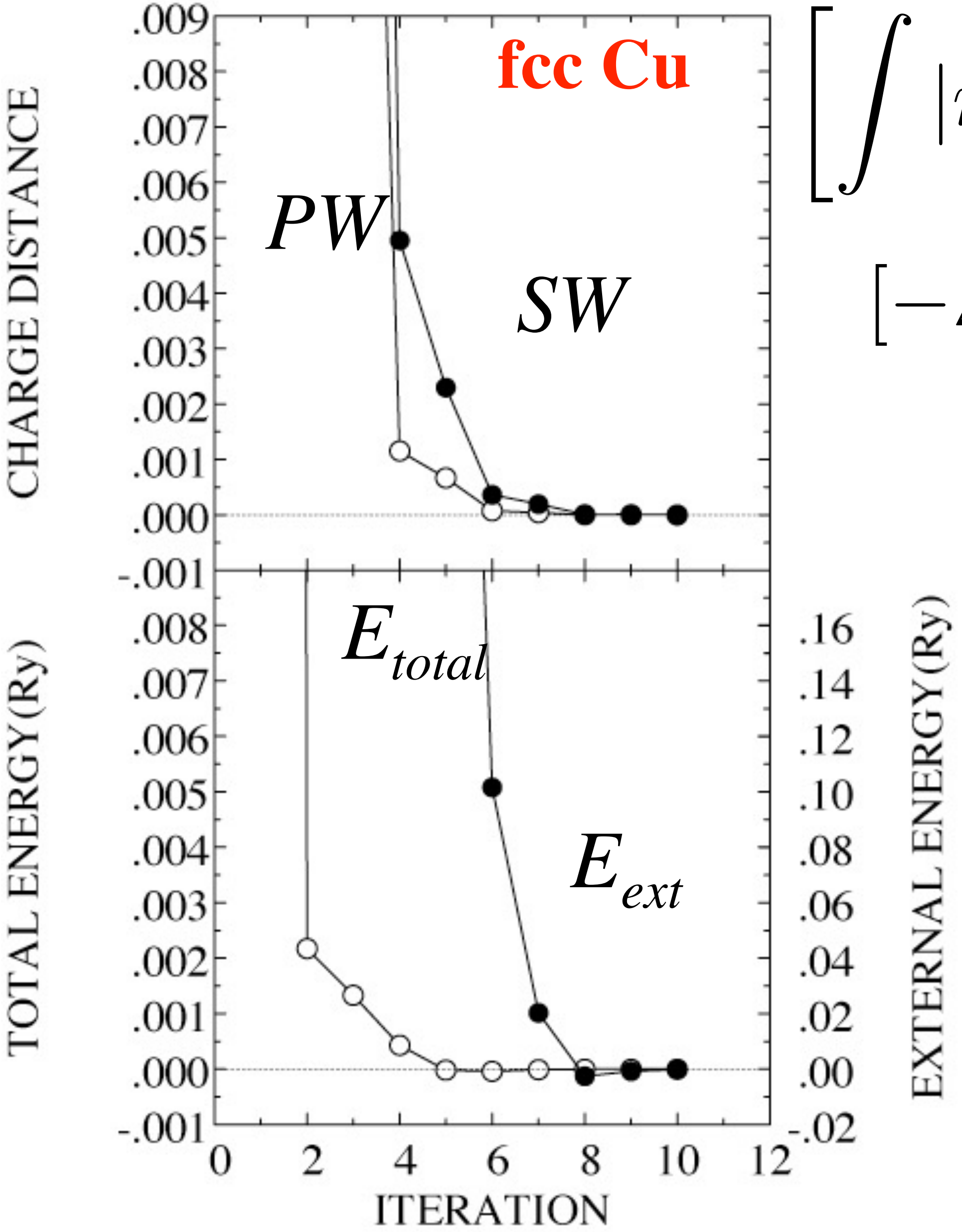
$$\min_{\beta} \int \left(\bar{n}_{\mathrm{in}}^{(i)} - \bar{n}_{\mathrm{out}}^{(i)} \right)^2 d\mathbf{r} \qquad \sum_{j=i-M}^{i} \beta^{(j)} = 1$$

Mixing of Electron Density



$$\left[\int |n_{\text{in}} - n_{\text{out}}|^2 d\mathbf{r}\right]^{1/2}$$

Convergency to SCF



$$\left[\int |n_{\mathrm{in}}(\mathbf{r}) - n_{\mathrm{out}}(\mathbf{r})|^2 d\mathbf{r}\right]^{1/2}$$

$$\left[-\Delta + v[n_{\mathrm{in}}]\right] \psi_j^{\mathbf{k}}(\mathbf{r}) = \varepsilon_j^{\mathbf{k}} \psi_j^{\mathbf{k}}(\mathbf{r})$$

$$n_{\mathrm{out}} = \sum_{j,\mathbf{k}}^{\mathrm{occ.}} |\psi_j^{\mathbf{k}}|^2$$

$$\left[-\Delta + v[n_{\mathrm{out}}] + v_{\mathrm{ext}}\right] \psi_j^{\mathbf{k}}(\mathbf{r}) = \varepsilon_j^{\mathbf{k}} \psi_j^{\mathbf{k}}(\mathbf{r})$$

$$v_{\mathrm{ext}} = v[n_{\mathrm{in}}] - v[n_{\mathrm{out}}]$$

$$E_{\mathrm{ext}} = \int v_{\mathrm{ext}} n_{\mathrm{out}} d\mathbf{r}$$

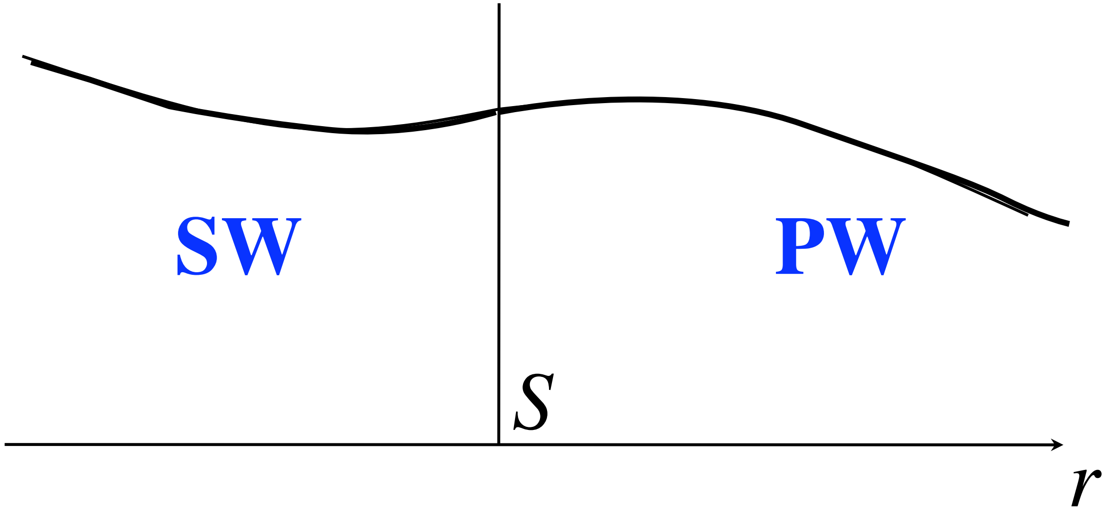
Appendix

- Logarithmic Derivatives
- Density of States
- Precision of FLAPW
- All-Electron vs. Pseudopotential
- Murnaghan’s Equation of State

Logarithmic Derivative

$$L_l(E) = \frac{R_l'(S;E)}{R_l(S;E)} = \frac{d}{dr} \ln R_l(r;E)\Big|_{r=S}$$

The APW eigenfunction satisfies the boundary conditions (logarithmic derivatives) on the spheres among the general solutions.



Single-MT Problem

Radial Equation in Rydberg units

$$\left[-\frac{d^2}{dr^2}-\frac{2}{r}\frac{d}{dr}+\frac{l(l+1)}{r^2}+v(r)-E\right]R_l(r;E)=0$$

Normalization $$\int_0^S R_l^2(r;E)r^2dr=1$$

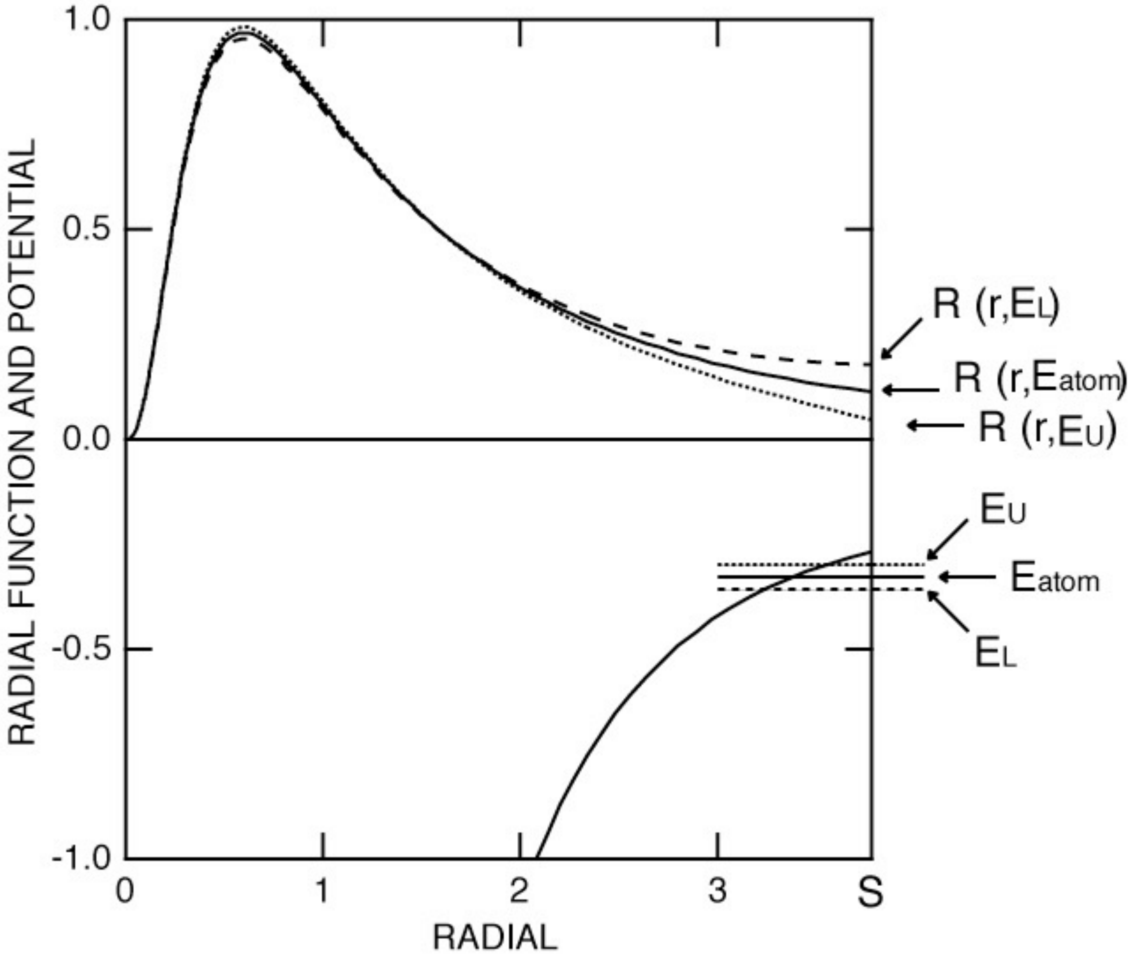
Radial function $$P_l(r;E)=rR_l(r;E)$$

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+v(r)-E\right]P_l(r;E)=0$$

$$\int_0^S P_l^2(r;E)dr=1$$

Energy Dependence of Radial Function

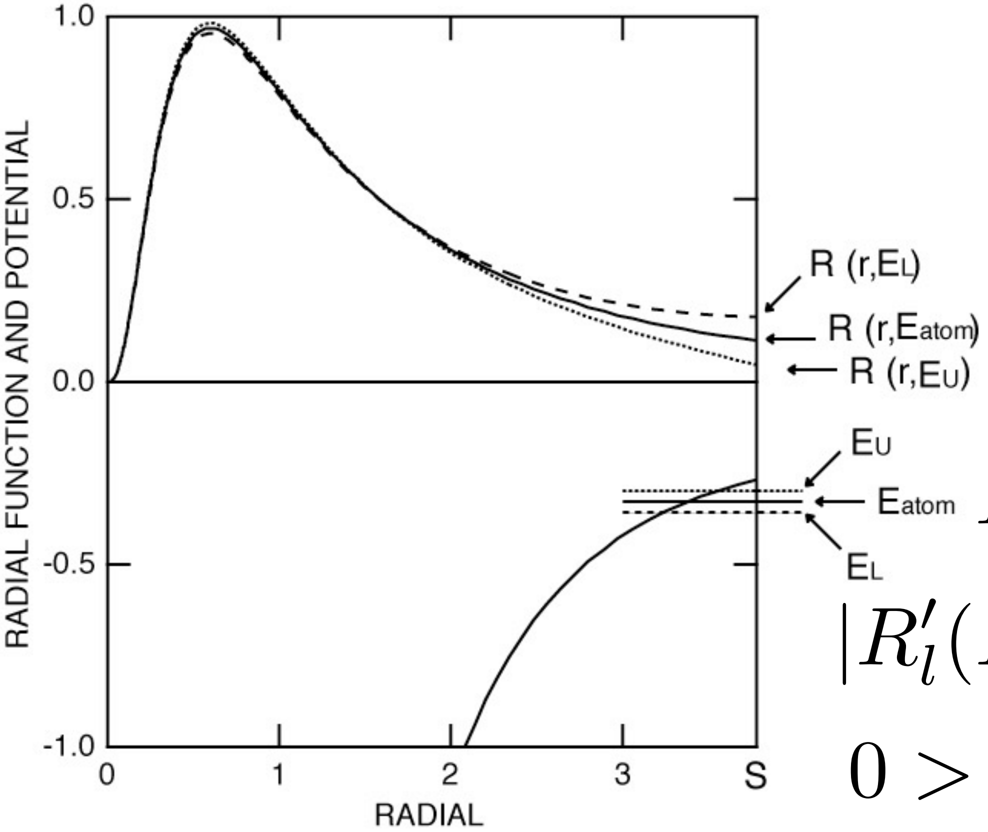
$$\frac{d^2 P_l(r;E)}{dr^2} = \left[\frac{l(l+1)}{r^2} + v(r) - E\right] P_l(r;E)$$



$$E_L < E_{atom} < E_U$$

Logarithmic Derivative

$$L_l(E) = \frac{R_l'(S;E)}{R_l(S;E)} = \frac{d}{dr}\ln R_l(r;E)\Big|_{r=S}$$



$$E_L < E_{atom} < E_U$$

$$R_l(E_L) > R_l(E_{atom}) > R_l(E_U)$$

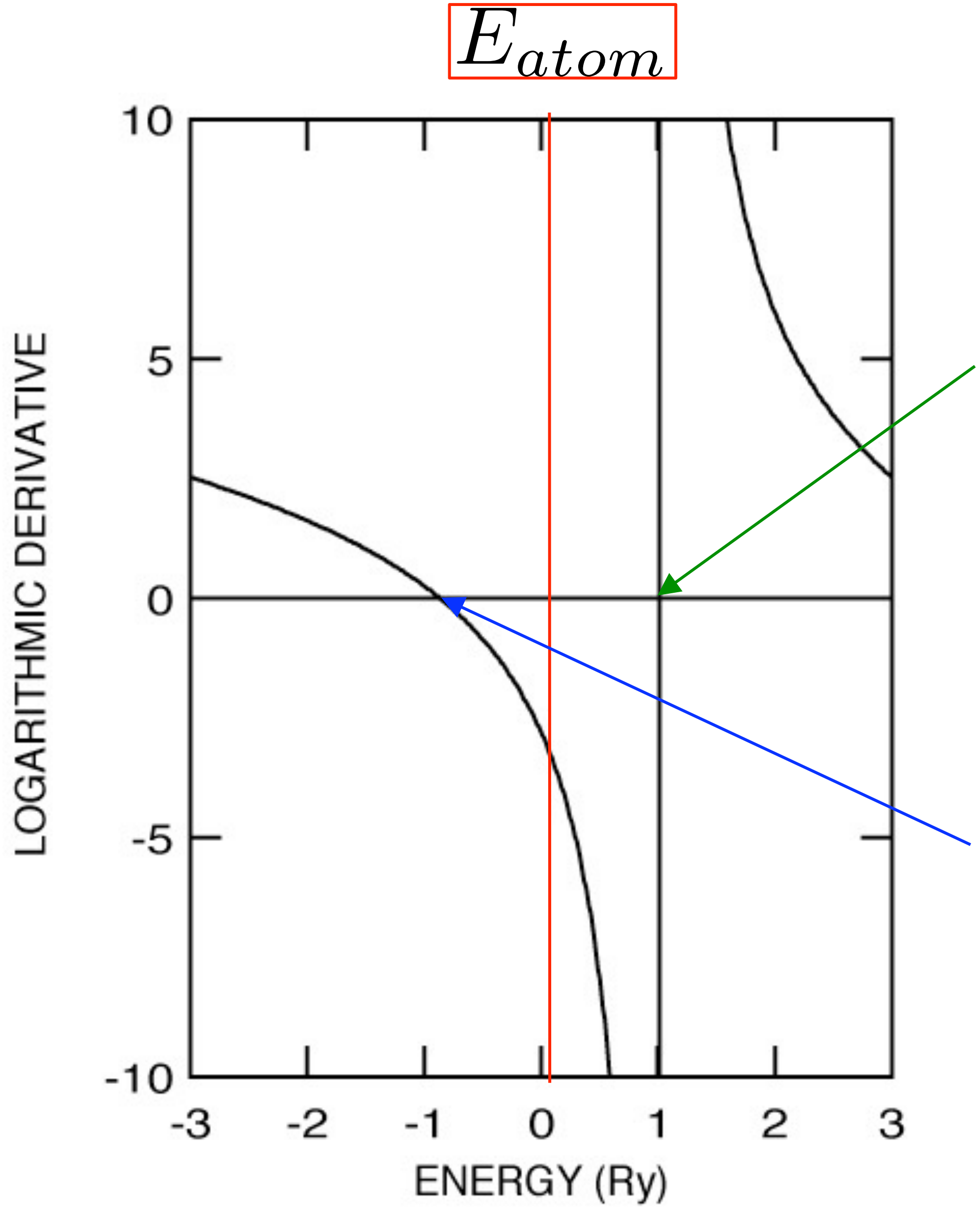
$$|R_l'(E_L)| < |R_l'(E_{atom})| < |R_l'(E_U)|$$

$$0 > L_l(E_L) > L_l(E_{atom}) > L_l(E_U)$$

Logarithmic Derivative

$L_l(E)$

bcc W-*d*



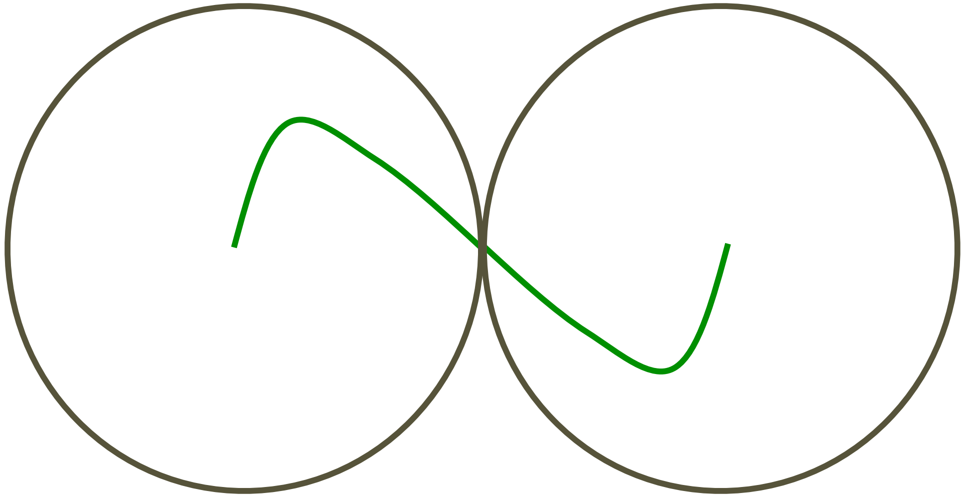
E_{atom}

$$\begin{cases} R_l(E_A) = 0 \\ R_l'(E_A) \neq 0 \end{cases}$$

$$\begin{cases} R_l(E_B) \neq 0 \\ R_l'(E_B) = 0 \end{cases}$$

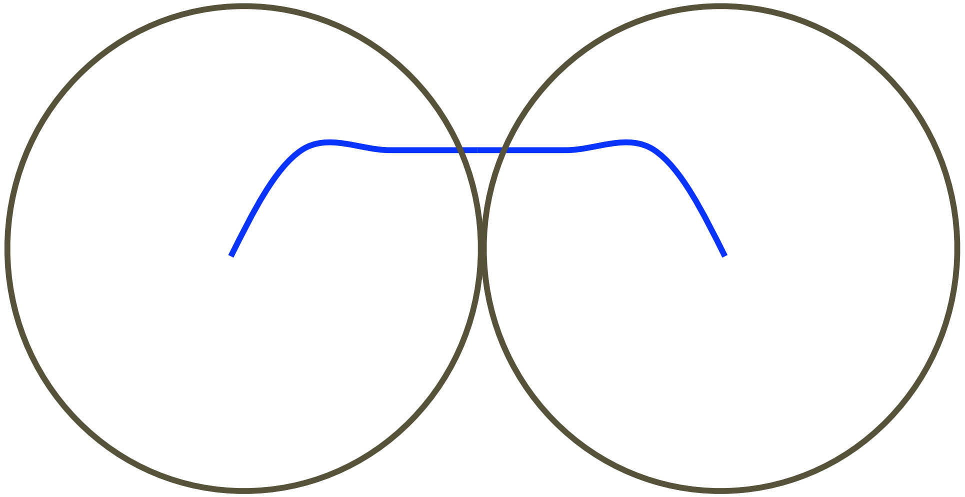
Logarithmic Derivative

$$\begin{cases} R_l(E_A) = 0 \\ R_l'(E_A) \neq 0 \end{cases}$$



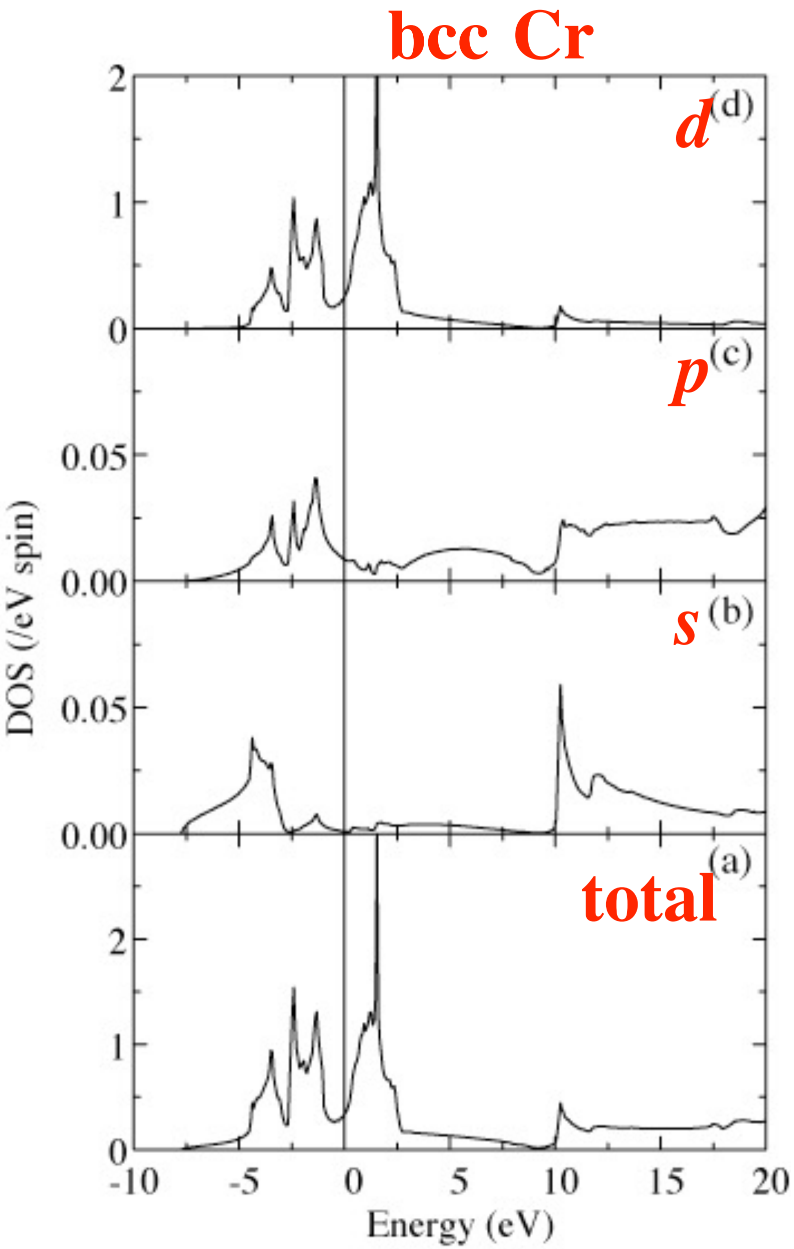
Anti-bonding state

$$\begin{cases} R_l(E_B) \neq 0 \\ R_l'(E_B) = 0 \end{cases}$$



Bonding state

Density of States



$$D(E) = \sum_{j,\mathbf{k}} \delta(E - \varepsilon_j^{\mathbf{k}})$$

$$= \sum_{j,\mathbf{k}} \langle \psi_j^{\mathbf{k}} | \psi_j^{\mathbf{k}} \rangle \delta(E - \varepsilon_j^{\mathbf{k}})$$

$$\sum_m |m\rangle\langle m| = 1$$

$$= \sum_m \left[\sum_{j,\mathbf{k}} \left| \langle \psi_j^{\mathbf{k}} | m \rangle \right|^2 \delta(E - \varepsilon_j^{\mathbf{k}}) \right]$$

$$= \sum_m D_m(E)$$

partial DOS

Wave Functions

- **LAPW Basis**

$$\tilde{\phi}^{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}$$

$$\phi^{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \sum_{\alpha l m} \left[A_{\alpha l m}^{\mathbf{k}+\mathbf{K}} R_l(r_\alpha) + B_{\alpha l m}^{\mathbf{k}+\mathbf{K}} \dot{R}_l(r_\alpha) \right] i^l Y_{lm}(\hat{\mathbf{r}}_\alpha)$$

- **Degrees of Variational Freedom**

K_{max} l_{max}

- **Choice of MT Sphere Radius**

Electron Density and Potential

$$\tilde{n}(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} n_{\mathbf{G}} \qquad n(\mathbf{r}) = \sum_{\alpha LM} n_{\alpha LM}(r_\alpha) i^L Y_{LM}(\hat{\mathbf{r}}_\alpha)$$

$$\tilde{v}(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} v_{\mathbf{G}} \qquad v(\mathbf{r}) = \sum_{\alpha LM} v_{\alpha LM}(r_\alpha) i^L Y_{LM}(\hat{\mathbf{r}}_\alpha)$$

- **Accuracy of Expansion**

$$G_{\max} \qquad L_{\max}$$

variational parameters?

- **Choice of MT Sphere Radius**

Perturbative Consideration

- **Second-Order Perturbation**

$$\Delta\varepsilon^{\mathbf{k}} = -\frac{|\langle \mathbf{k}+\mathbf{K}|\mathcal{H}|\mathbf{k}\rangle|^2}{|\mathbf{k}+\mathbf{K}|^2 - \varepsilon^{\mathbf{k}}}$$

- **Variational Parameters of the Wave Functions**

$$|\mathbf{k}+\mathbf{K}| \leq K_{\max}$$

$$l_{\max}$$

Muffin-Tin Sphere Radius

When a sufficient $l_{\max}$ is assumed,

- **In case of large MT sphere radius, because of smaller volume in the interstitial region fewer PW expansion is needed.**
- **In case of small MT sphere radius, because of larger volume in the interstitial region more PW expansion is needed.**
- **A variational dimensionless parameter**

$$RK_{\max}$$

Wave Functions and Electron Density

$$n(\mathbf{r}) = \sum_{\mathbf{k},n} |\psi_n^{\mathbf{k}}(\mathbf{r})|^2$$

$$G_{\max} \geq 2K_{\max}$$

$$L_{\max} \geq 2l_{\max}$$

- **Convergency of the electron density and potential expansion should be checked, especially when GGA is used.**

- **For small MT spheres used, higher $G_{\max}$ may be required to represent pseudized charge density.**

Muffin-Tin Sphere Radius

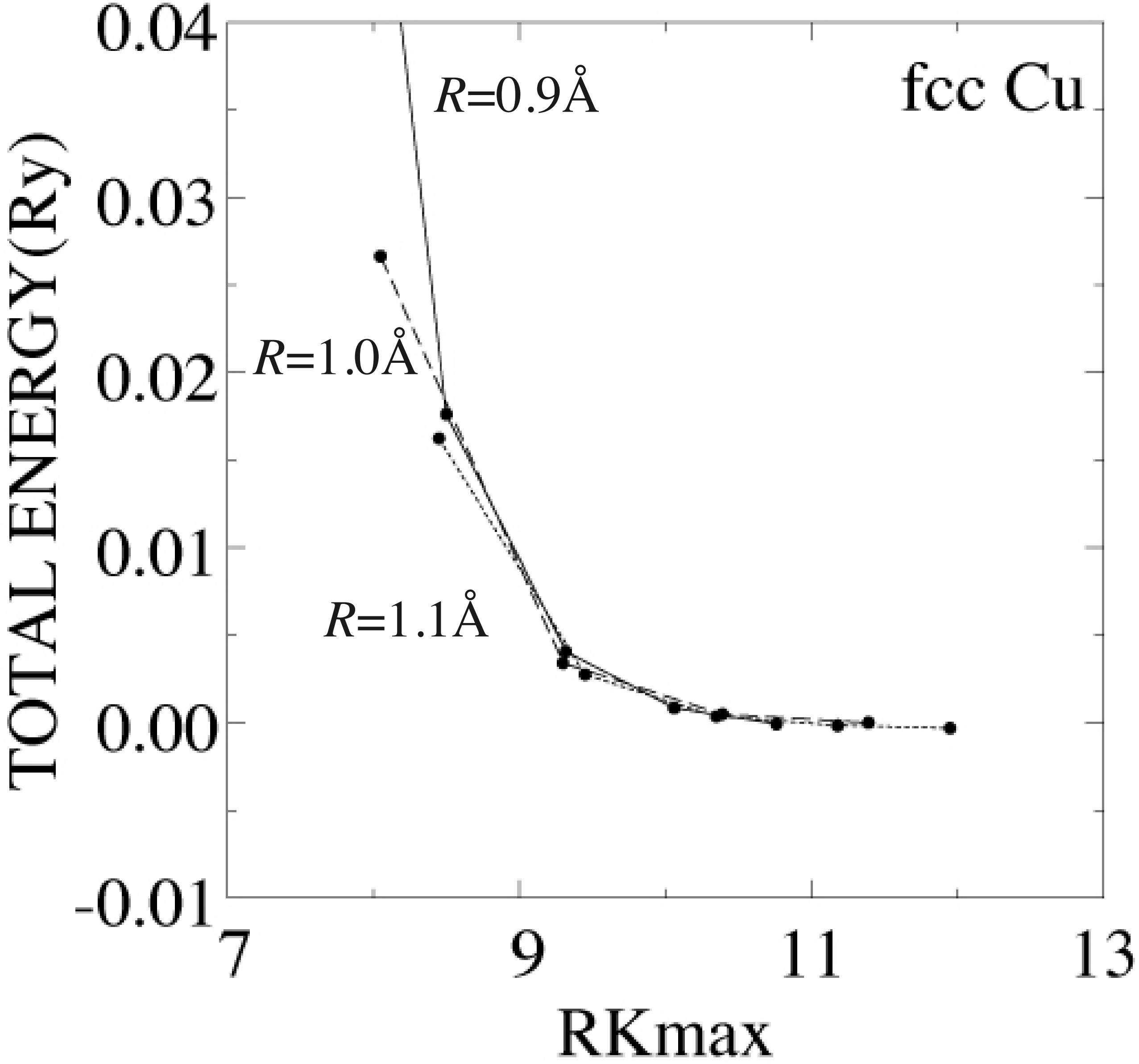
- **Non-overlapping spheres**

  A margin should be considered if the atomic positions are changed, for example in a structural optimization calculation.

- **Negligible penetration of the core functions outside**

Within both assumptions with sufficient $l_{\max}$ and $L_{\max}$, the accuracy does not depend on the choice of MT sphere radius but does on $RK_{\max}$.

Total Energy vs. Muffin-Tin Radius



Precision of FLAPW Method

- **Wave Functions** $RK_{\max}$
- **Electron Density and Potential**

$$G_{\max} \geq 2K_{\max} \qquad L_{\max} \geq 2l_{\max}$$

- **Choice of MT Sphere Radius**

- **Over-completeness of APW Basis Functions**

Since the PW basis is a complete set in all the space, an APW basis with the excessive number of PW results in indefinite solutions.

All-Electron vs. Pseudopotential

RESEARCH ARTICLE

DFT METHODS

Reproducibility in density functional theory calculations of solids

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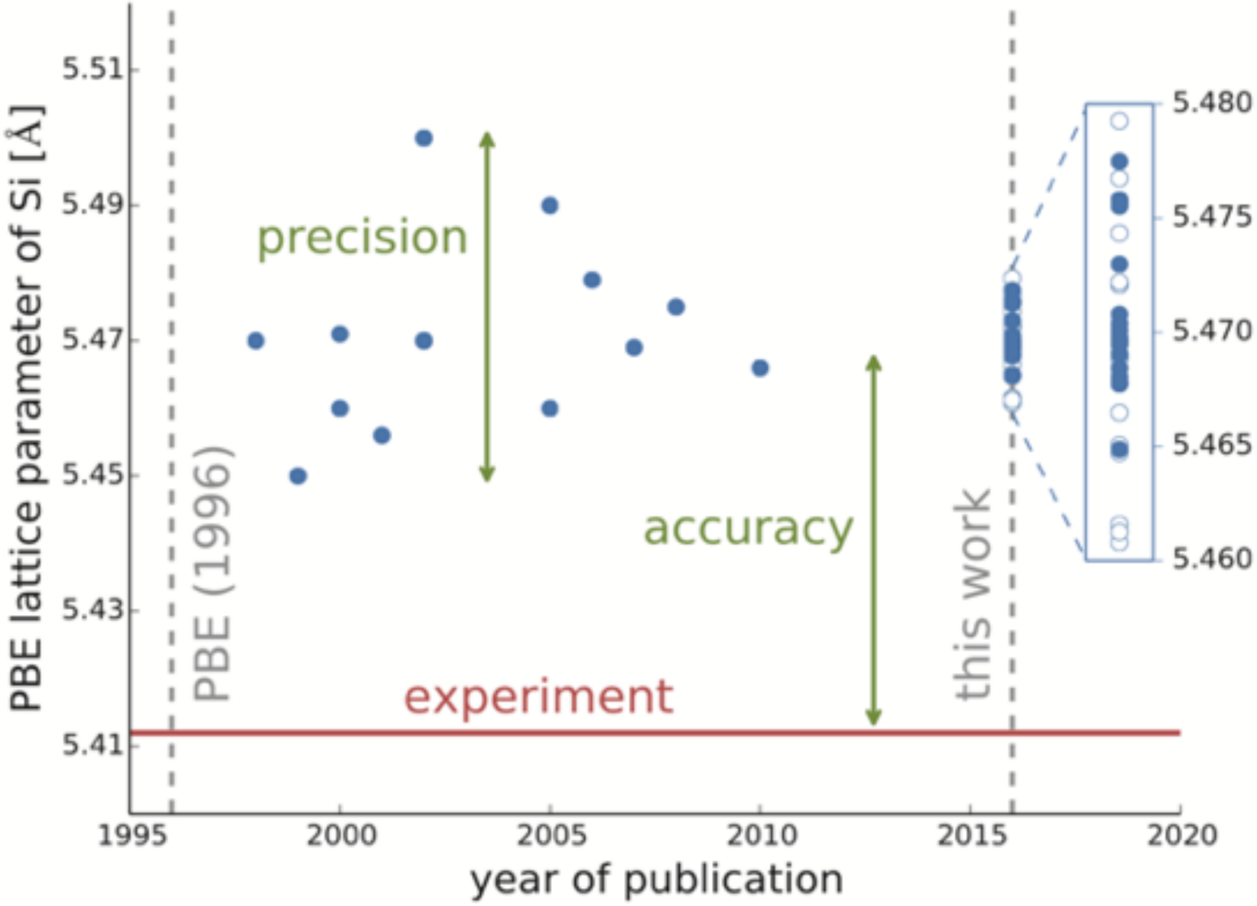

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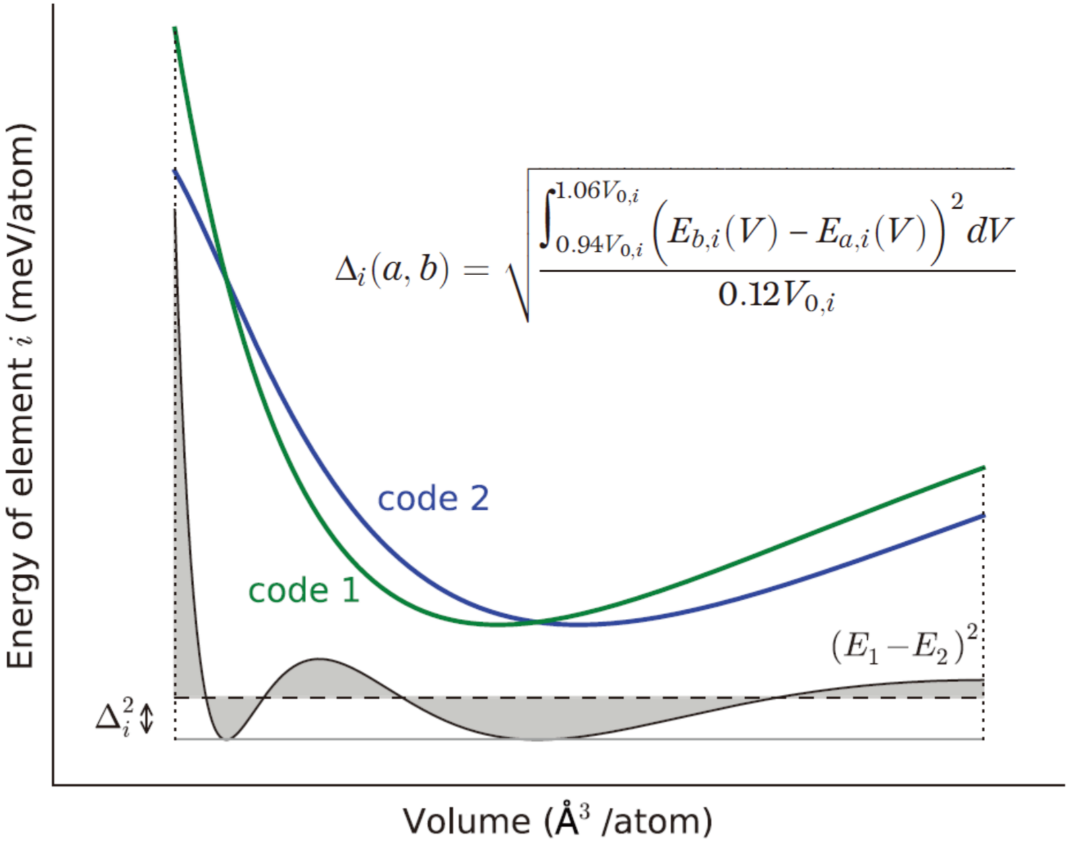
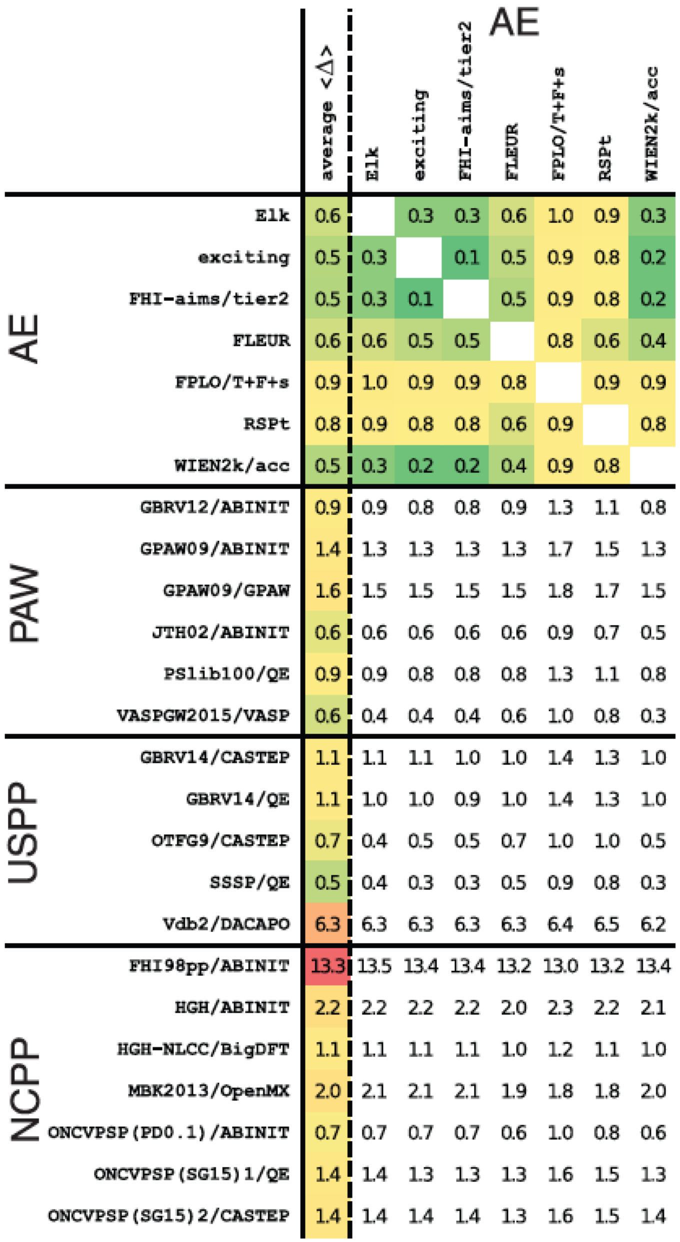
All-Electron vs. Pseudopotential

Δ-gauge



$$\Delta_i(a,b) = \sqrt{\frac{\int_{0.94V_{0,i}}^{1.06V_{0,i}} \Big(E_{b,i}(V) - E_{a,i}(V)\Big)^2 dV}{0.12V_{0,i}}}$$



		average <Δ>	AE						
			Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc
AE	Elk	0.6		0.3	0.3	0.6	1.0	0.9	0.3
	exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2
	FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2
	FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4
	FPLO/T+F+s	0.9	1.0	0.9	0.9	0.8		0.9	0.9
	RSPt	0.8	0.9	0.8	0.8	0.6	0.9		0.8
	WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8	
PAW	GBRV12/ABINIT	0.9	0.9	0.8	0.8	0.9	1.3	1.1	0.8
	GPAW09/ABINIT	1.4	1.3	1.3	1.3	1.3	1.7	1.5	1.3
	GPAW09/GPAW	1.6	1.5	1.5	1.5	1.5	1.8	1.7	1.5
	JTH02/ABINIT	0.6	0.6	0.6	0.6	0.6	0.9	0.7	0.5
	PSlib100/QE	0.9	0.9	0.8	0.8	0.8	1.3	1.1	0.8
	VASPGW2015/VASP	0.6	0.4	0.4	0.4	0.6	1.0	0.8	0.3
USPP	GBRV14/CASTEP	1.1	1.1	1.1	1.0	1.0	1.4	1.3	1.0
	GBRV14/QE	1.1	1.0	1.0	0.9	1.0	1.4	1.3	1.0
	OTFG9/CASTEP	0.7	0.4	0.5	0.5	0.7	1.0	1.0	0.5
	SSSP/QE	0.5	0.4	0.3	0.3	0.5	0.9	0.8	0.3
	Vdb2/DACAPO	6.3	6.3	6.3	6.3	6.3	6.4	6.5	6.2
NCPP	FHI98pp/ABINIT	13.3	13.5	13.4	13.4	13.2	13.0	13.2	13.4
	HGH/ABINIT	2.2	2.2	2.2	2.2	2.0	2.3	2.2	2.1
	HGH-NLCC/BigDFT	1.1	1.1	1.1	1.1	1.0	1.2	1.1	1.0
	MBK2013/OpenMX	2.0	2.1	2.1	2.1	1.9	1.8	1.8	2.0
	ONCVPSP(PD0.1)/ABINIT	0.7	0.7	0.7	0.7	0.6	1.0	0.8	0.6
	ONCVPSP(SG15)1/QE	1.4	1.4	1.3	1.3	1.3	1.6	1.5	1.3
	ONCVPSP(SG15)2/CASTEP	1.4	1.4	1.4	1.4	1.3	1.6	1.5	1.4

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Murnaghan’s Equation of State

$$p = \frac{B_0}{B'}\left[\left(\frac{\Omega}{\Omega_0}\right)^{-B'} - 1\right]$$

$$B_0 = -\left(\Omega\frac{dp}{d\Omega}\right)_0 \qquad B' = -\frac{1}{B_0}\left(\Omega\frac{dB}{d\Omega}\right)_0$$

$$E(\Omega) = \frac{B_0\Omega}{B'}\left[\frac{1}{B'-1}\left(\frac{\Omega}{\Omega_0}\right)^{-B'} + 1\right] + E'$$

1 a.u. in pressure = 1.47108×10^4 GPa

F. D. Murnaghan, Proc. Natl. Acad. Sci. USA 30, 244 (1944).