Basics of FLAPW Method

広島大学大学院先端物質科学研究科

小口 多美夫

Hiroshima University, ADSM

Tamio Oguchi

CMD Workshop

OUTLINE

- FLAPW Method
  - One-electron eq. and Bloch function
  - Augmentation
  - APW method
  - Linear method
  - Full potential method
- FLAPW Codes
  - FLAPW packages open to public
  - HiLAPW code
- Appendix: Single Muffin-tin Problem

Kohn-Sham Equations

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

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

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

★ **One-electron equations to describe independent Fermi particles in an effective field determined in a self-consistent way.**

Band Theory

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

Periodic system --> Band theory

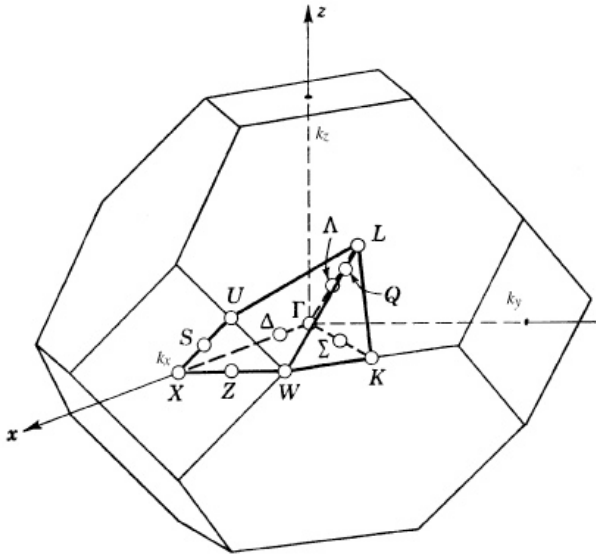
Bloch Theorem

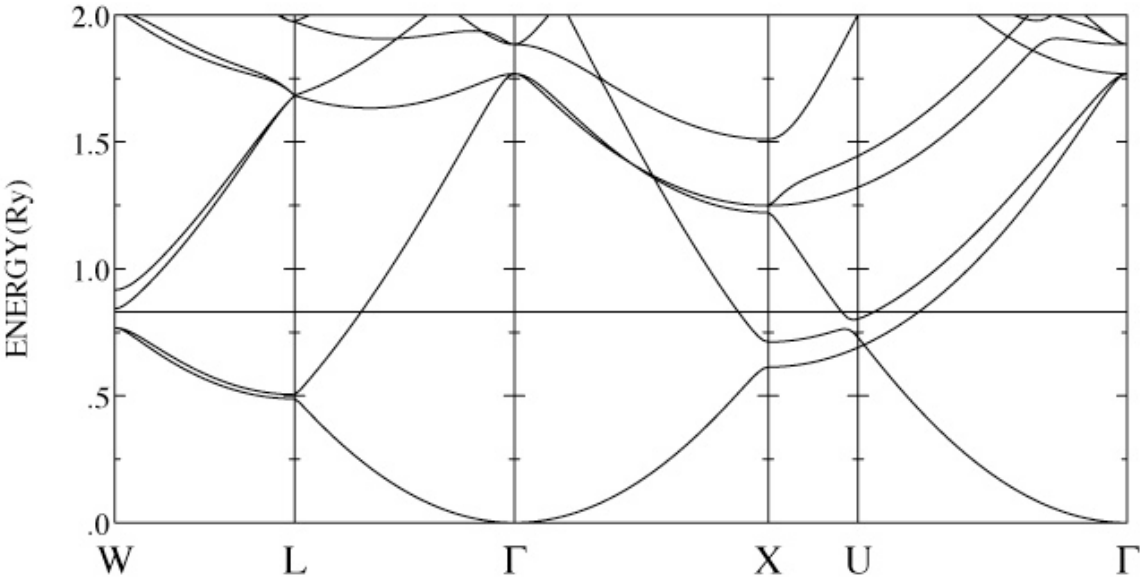
- **A quantum-mechanical state in a periodic system can be specified with a wave number k**

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

Dispersion relation: band strcuture

Brillouin Zone and Bands





BZ of fcc lattice

Band structure of fcc Al

independent quantum number

Textbook of Band Theory

バンド理論

物質科学の基礎として

内田老鶴圃　1999年

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**

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

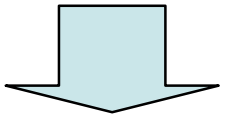
$$= \sum_{\mathbf{K}} a_{j,\mathbf{K}}^{\mathbf{k}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}$$

K: reciprocal lattice vector

Bloch Function

- **Normalized in a macroscopic volume Ω**
- **k points in BZ are dependent 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

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

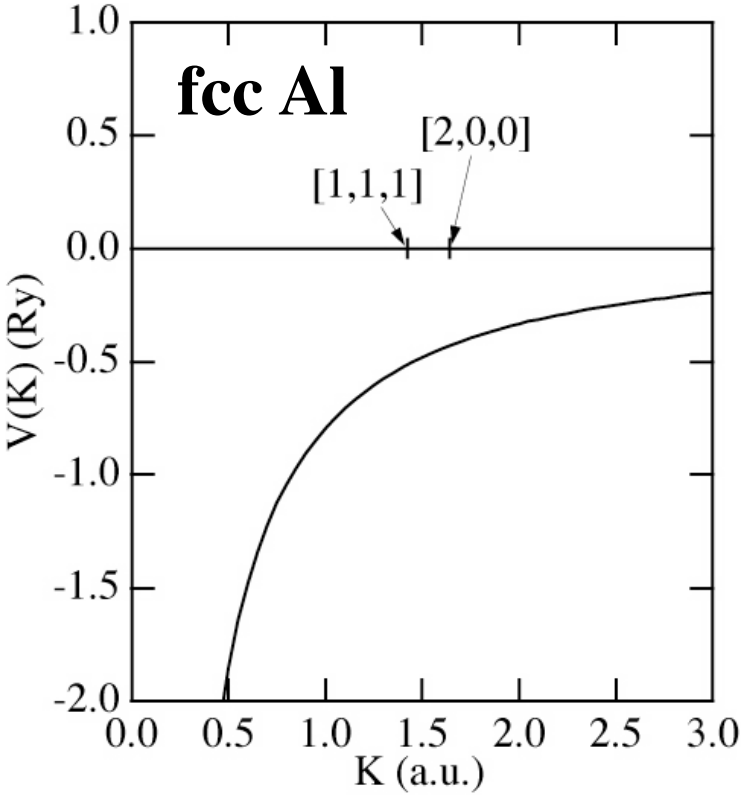
Matrix elements

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

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

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.

Core Functions

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

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

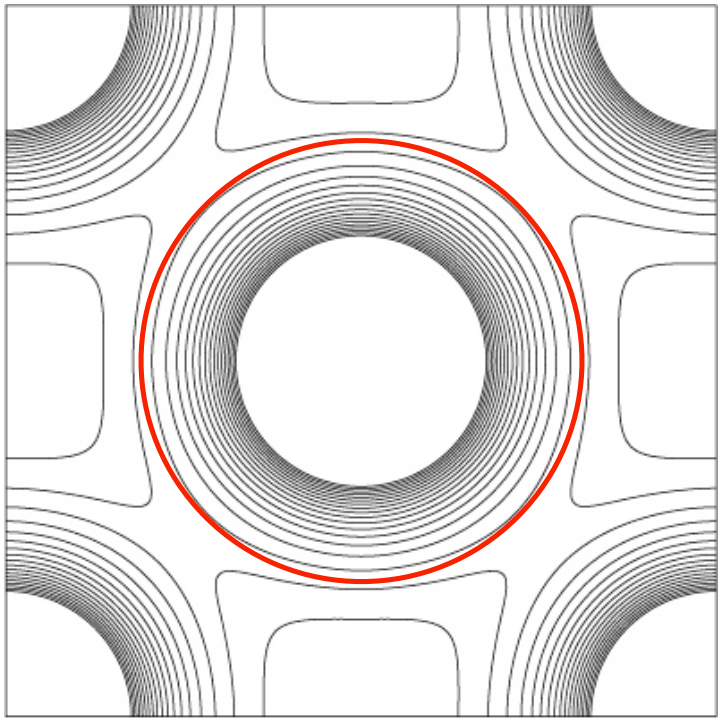
How to Solve the Problems

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 more localized functions**
   --> augmented or mixed basis

Muffin-tin Potential Approximation

Carystal 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

J.C. Slater, PR 51(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

J.C. Slater, PR 51(1937)846.

Secular Equation

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

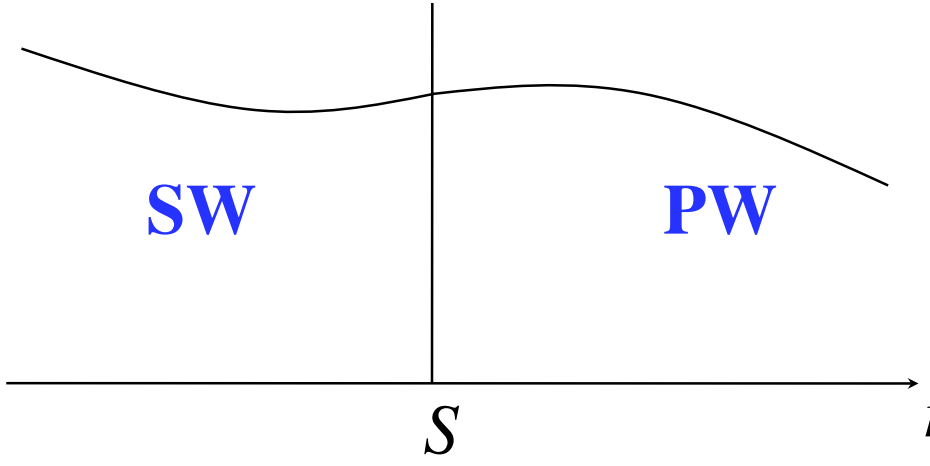
$$\langle \mathbf{k}+\mathbf{K}'|\mathcal{H}-E|\mathbf{k}+\mathbf{K}\rangle = \left\{\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{K}|^2 - E\right\}\delta_{\mathbf{K}',\mathbf{K}} + \Gamma^{\mathrm{APW}}_{\mathbf{K}',\mathbf{K}}(E)$$

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

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.



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

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

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

- **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 --> LMTO**

  KKR: Korringa-Kohn-Rostoker

  LMTO: Linear Muffin-Tin Orbital

LAPW Method

Augmentation basis

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

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

$$\begin{cases} A_{lm}^{\mathbf{k}+\mathbf{K}} \\ B_{lm}^{\mathbf{k}+\mathbf{K}} \end{cases}$$ **determined from the boundary conditions**

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

LAPW Method

$$A_{lm}^{\mathbf{k}+\mathbf{K}} = 4\pi S^2 a_l^{\mathbf{k}+\mathbf{K}} Y_{lm}^*(\mathbf{k}+\mathbf{K})$$

$$B_{lm}^{\mathbf{k}+\mathbf{K}} = 4\pi S^2 b_l^{\mathbf{k}+\mathbf{K}} Y_{lm}^*(\mathbf{k}+\mathbf{K})$$

$$a_l^{\mathbf{k}+\mathbf{K}} = |\mathbf{k}+\mathbf{K}| j'_{l\mathbf{K}} \dot{R}_l - j_{l\mathbf{K}} \dot{R}'_l$$

$$b_l^{\mathbf{k}+\mathbf{K}} = |\mathbf{k}+\mathbf{K}| j'_{l\mathbf{K}} R_l - j_{l\mathbf{K}} R'_l$$

$$j_{l\mathbf{K}} = j_l(|\mathbf{k}+\mathbf{K}|S) \qquad j'_{l\mathbf{K}} = \left.\frac{dj_l(x)}{dx}\right|_{x=|\mathbf{k}+\mathbf{K}|S}$$

$$R_l = R_l(S; E_l)$$

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

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

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

Matrix Elements in LAPW

in Rydberg atomic units

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

$$H_{\mathbf{K}',\mathbf{K}} = \langle \mathbf{k}+\mathbf{K}'|\mathcal{H}|\mathbf{k}+\mathbf{K}\rangle$$

$$= (\mathbf{k}+\mathbf{K}')\cdot(\mathbf{k}+\mathbf{K})U(\mathbf{K}'-\mathbf{K})$$

$$+\frac{4\pi S^4}{\Omega_0}\sum_l (2l+1)P_l\left((\mathbf{k}+\mathbf{K}')\cdot(\mathbf{k}+\mathbf{K})\right)$$

$$\times\left(E_l s_l^{\mathbf{K}',\mathbf{K}} + \gamma_l^{\mathbf{K}',\mathbf{K}}\right)$$

$$S_{\mathbf{K}',\mathbf{K}} = \langle \mathbf{k}+\mathbf{K}'|\mathbf{k}+\mathbf{K}\rangle$$

$$= U(\mathbf{K}'-\mathbf{K})$$

$$+\frac{4\pi S^4}{\Omega_0}\sum_l (2l+1)P_l\left((\mathbf{k}+\mathbf{K}')\cdot(\mathbf{k}+\mathbf{K})\right) s_l^{\mathbf{K}',\mathbf{K}}$$

Matrix Elements in LAPW

$$U(\mathbf{K}) = \delta_{\mathbf{K}} - \frac{4\pi S^2}{\Omega_0}\frac{j_1(KS)}{K}$$

$$s_l^{\mathbf{K}',\mathbf{K}} = a_l^{\mathbf{k}+\mathbf{K}'} a_l^{\mathbf{k}+\mathbf{K}} + b_l^{\mathbf{k}+\mathbf{K}'} b_l^{\mathbf{k}+\mathbf{K}} N_l$$

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

$$\gamma_l^{\mathbf{K}',\mathbf{K}} = \dot{R}_l R_l' \{|\mathbf{k}+\mathbf{K}| j'_{l\mathbf{K}} j_{l\mathbf{K}'} + |\mathbf{k}+\mathbf{K}'| j_{l\mathbf{K}} j'_{l\mathbf{K}'}\}$$

$$- \left\{ \dot{R}_l' R_l' j_{l\mathbf{K}} j_{l\mathbf{K}'} + \dot{R}_l R_l |\mathbf{k}+\mathbf{K}||\mathbf{k}+\mathbf{K}'| j'_{l\mathbf{K}} j'_{l\mathbf{K}'} \right\}$$

Coulmb Potential

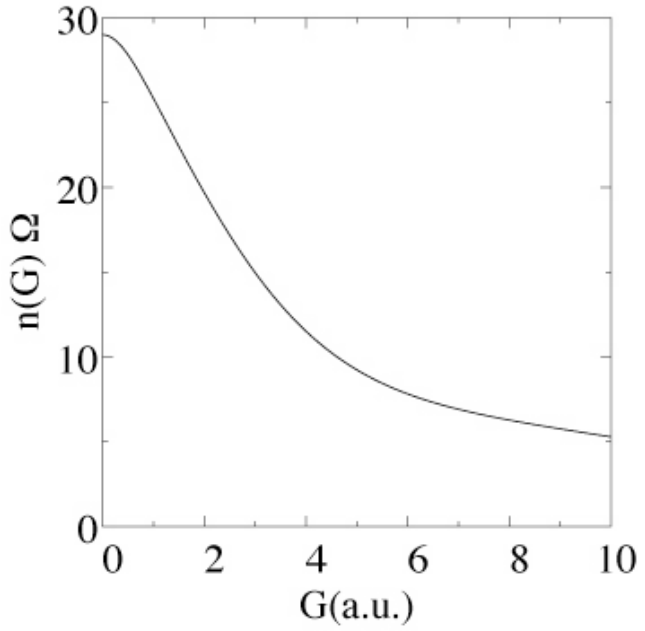
- **Coulomb potential for smooth density distribution**

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

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

- **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

- **Pseudized density inside the sphere**

$$\tilde{n}(\mathbf{r}) = \sum_{lm} Q_{lm} Y_{lm} \sum_{\eta} a_\eta r^{\nu_\eta}$$

$$\tilde{n}_{\mathbf{G}} = \frac{4\pi}{\Omega_0} \sum_{lm} \frac{(-i)^l (2l+2n+3)!!}{(2l+1)!! S^l}$$

$$\times \frac{j_{l+n+1}(GS)}{(GS)^{n+1}} q_{lm} Y_{lm}(\mathbf{G})$$

multipole moment

Full-potential Method

- **Potential inside the sphere**

$$v^{\mathrm{C}}(\mathbf{r}) = \int_S n(\mathbf{r}')G(\mathbf{r},\mathbf{r}')d\mathbf{r}' - \frac{S^2}{4\pi}\oint_S v^{\mathrm{C}}(\mathbf{S})\nabla G \cdot d\mathbf{S}$$

$$G(\mathbf{r},\mathbf{r}') = 4\pi \sum_{lm} \frac{Y^*_{lm}(\mathbf{r}')Y_{lm}(\mathbf{r})}{2l+1} \frac{r_<^l}{r_>^{l+1}} \left[1 - \left(\frac{r_>}{S}\right)^{2l+1}\right]$$

$$\nabla G \cdot \hat{n} = -\frac{4\pi}{S^2} \sum_{lm} \left(\frac{r}{S}\right)^l Y^*_{lm}(\mathbf{r}')Y_{lm}(\mathbf{r})$$

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**

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

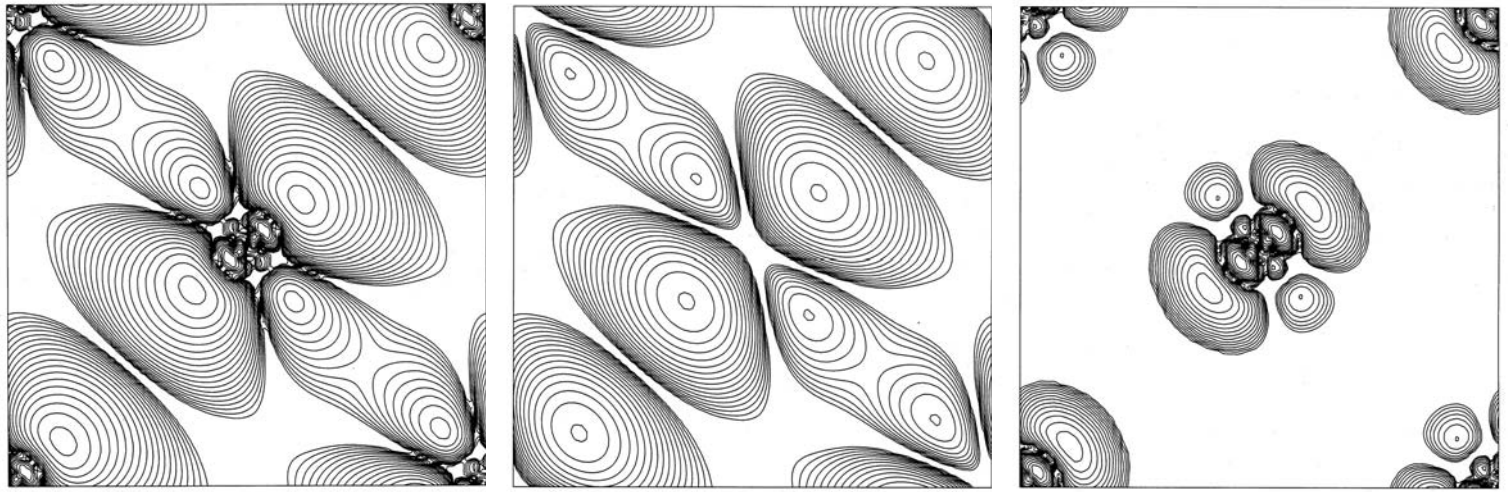
non-spherical part

FLAPW Method

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

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**

SUMMARY

FLAPW Method

- APW Method
- Linear Method
- Full-Potential Method

Highly-Precise All-electron Method

General-purpose first-principles method

for a variety of condensed matter systems

Single-MT Problem

Radial Equation in Rydberg units

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

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

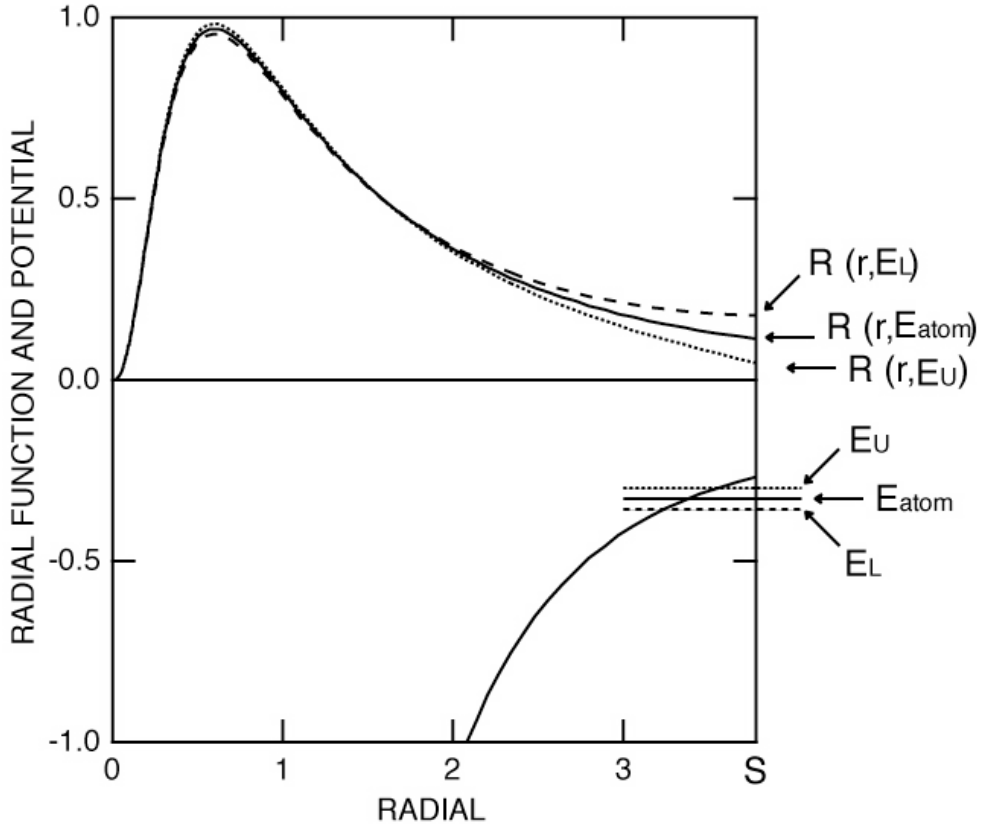
Radial function $P_l(r;E)=rR_l(r;E)$

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

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

Energy Dependence of Radial Function

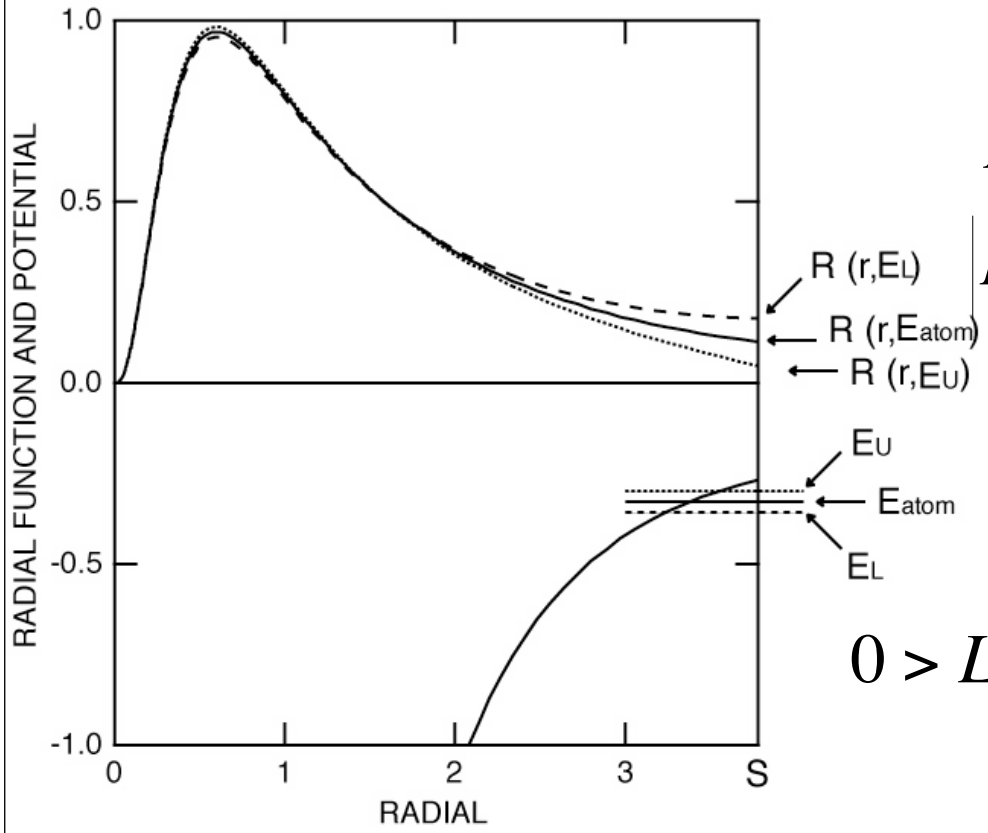
$$\frac{d^2 P_l(r;E)}{dr^2} = \left[\frac{l(l+1)}{r^2} + \upsilon(r) - E\right] P_l(r;E)$$



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

Logarithmic Derivative

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



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

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

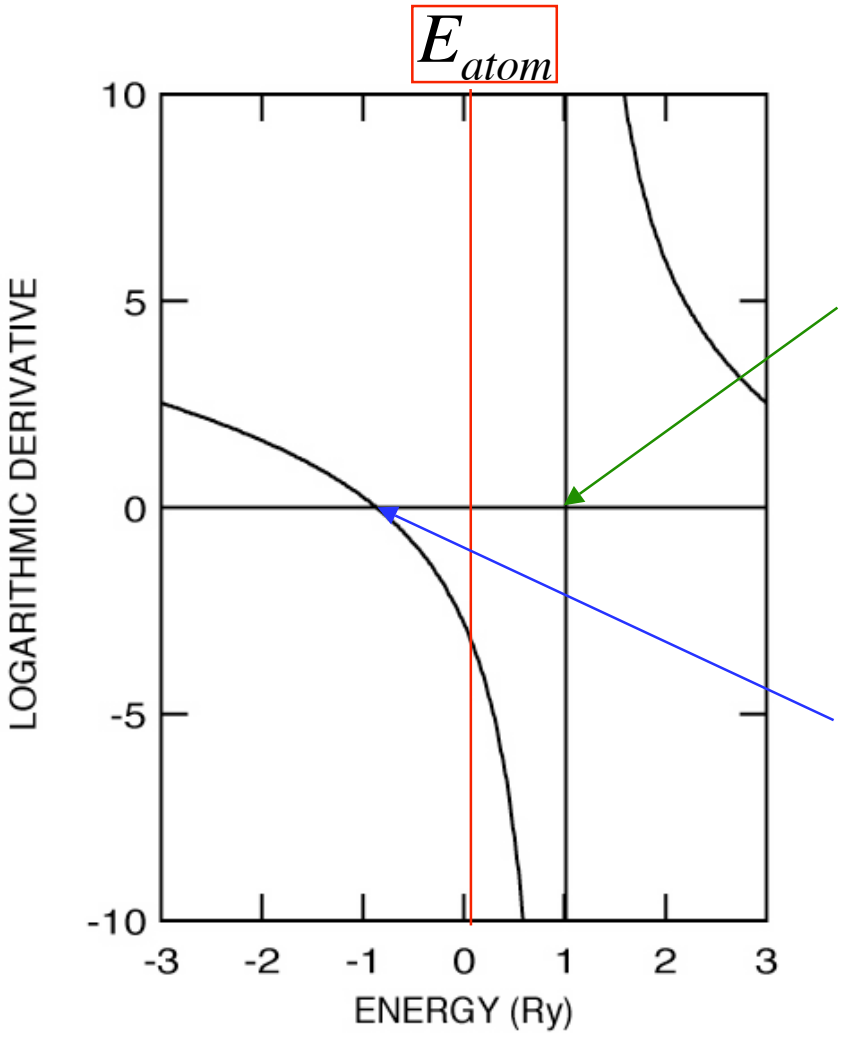
$$\left|R'_l(E_L)\right| < \left|R'_l(E_{atom})\right| < \left|R'_l(E_U)\right|$$

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

Logarithmic Derivative

$L_l(E)$

bcc W-*d*

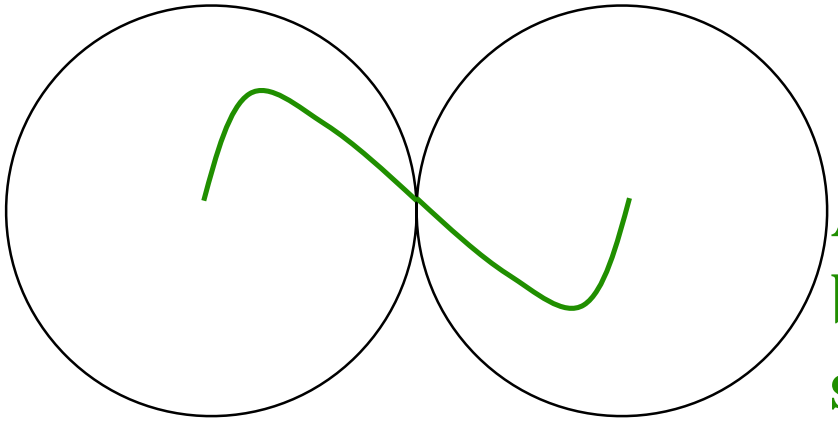


$$\begin{cases} R_l(E_A) = 0 \\ R_l'(E_A) \neq 0 \end{cases}$$

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

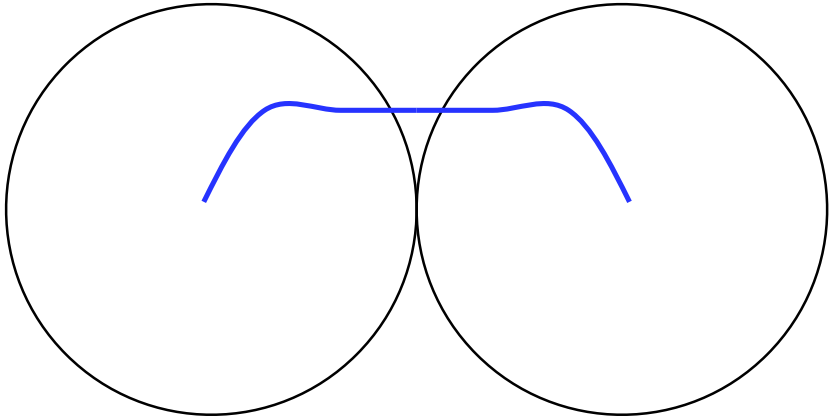
Logarithmic Derivative

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



Anti-bonding state

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



Bonding state

Practical Aspects in First-Principles Calculation

広島大学大学院先端物質科学研究科

小口 多美夫

Hiroshima University, ADSM

Tamio Oguchi

HIROSHIMA UNIVERSITY

HiLAPW

ADSM

CMD Workshop

IAMR

OUTLINE

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

First-Principles Calculation

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

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

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

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

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**

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

Self-Consistent Field

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

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

$v(\mathbf{r})$

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

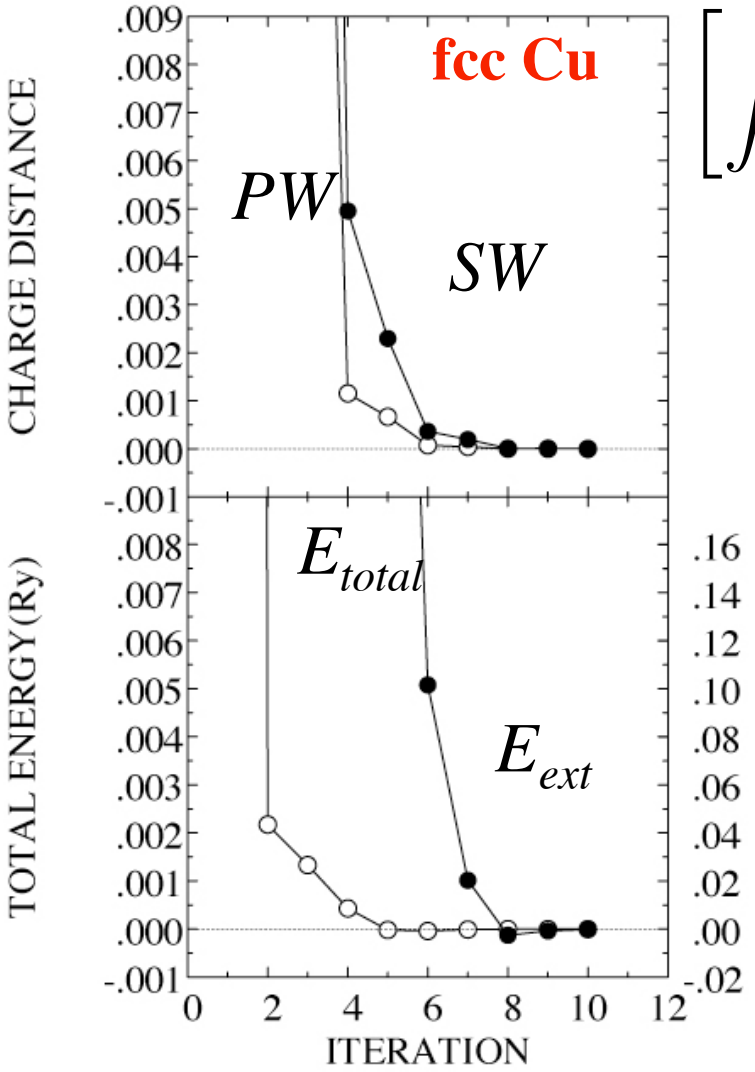
$n_{\text{out}}(\mathbf{r})$

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

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

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

Convergency to SCF



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

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

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

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

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

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

Crystal Structure and Atomic Position

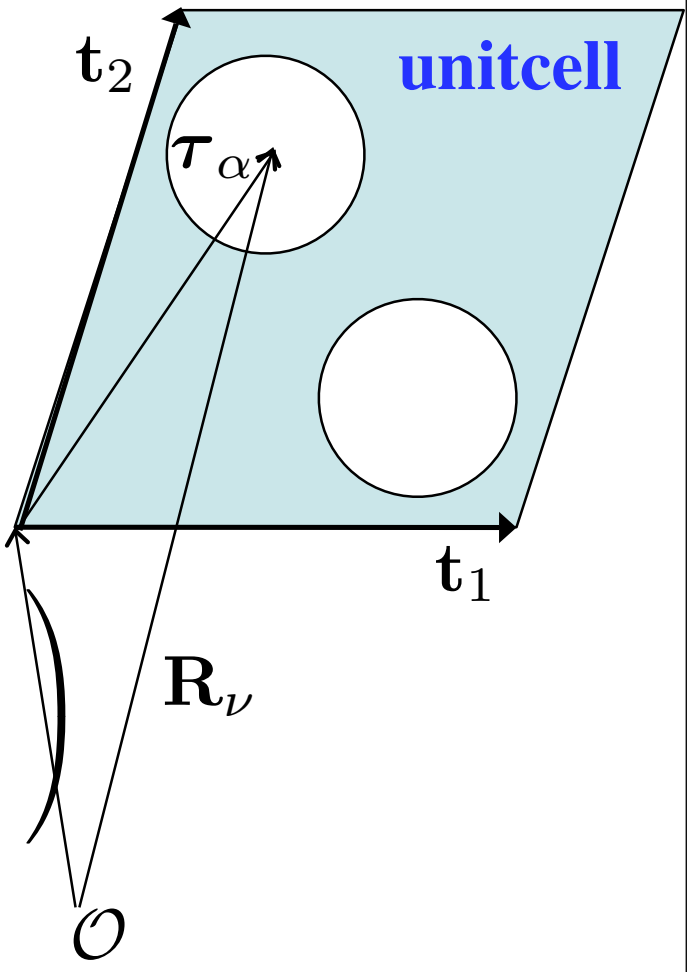
$$\mathbf{R}_\nu = \mathbf{R}_{lmn} + \boldsymbol{\tau}_\alpha \qquad \nu = (lmn\alpha)$$

- **Lattice Vector**

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

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

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**

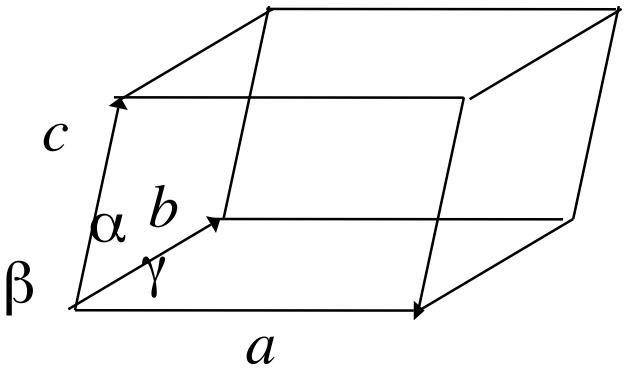
$$\begin{pmatrix} a_1^x & a_2^x & a_3^x \\ a_1^y & a_2^y & a_3^y \\ a_1^z & a_2^z & a_3^z \end{pmatrix} \Leftarrow (a, b, c, \alpha, \beta, \gamma)$$

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
monoclinic	a	b	c	90	90	γ	P,B
triclinic	a	b	c	α	β	γ	P

Lattice: System and Type

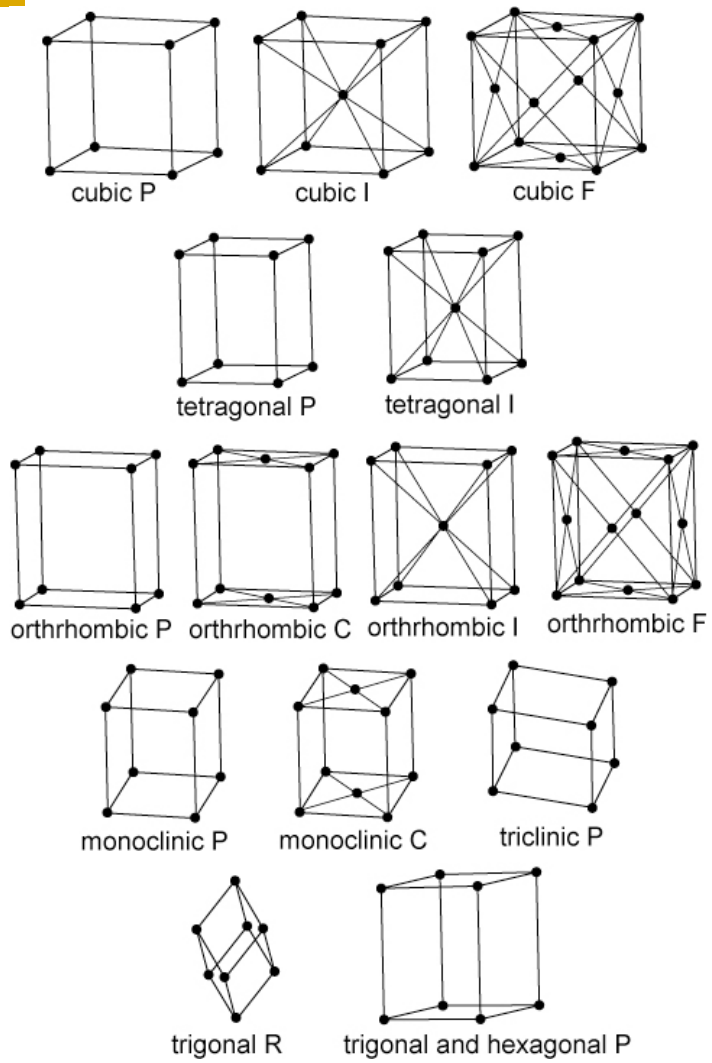
- **Lattice type**

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

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

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

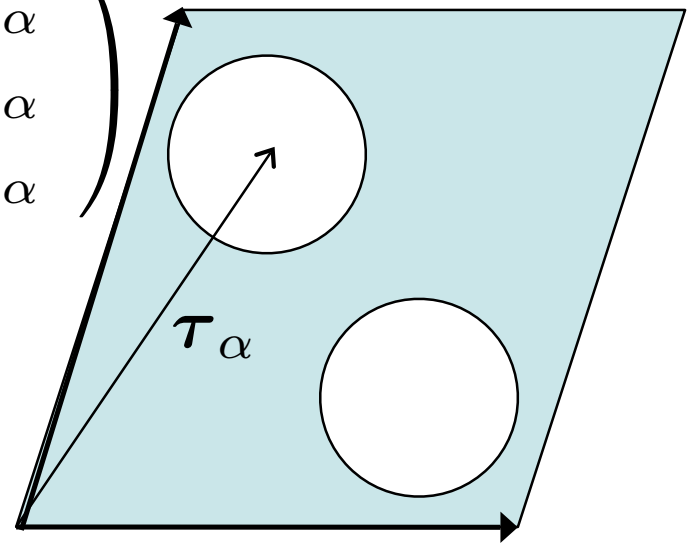
Lattice: System and Type



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

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

non-primitive translation vector

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

Diamond Structure

- **fcc** $a=b=c$, $\alpha=\beta=\gamma=90^{o}$
- **space group** **Fd-3m**

  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

Reciprocal Lattice

- **Definition**

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

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

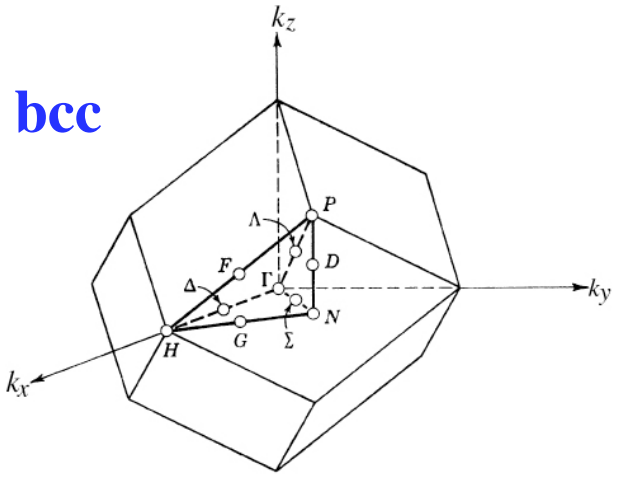
- **parallelepiped** $(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$

  easy to treat numerically

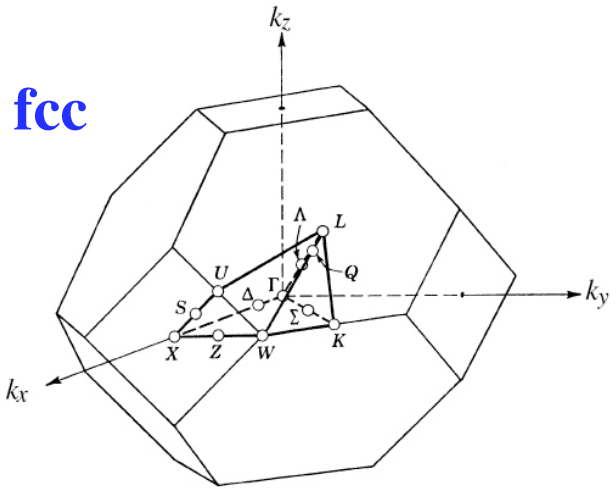
- **Voronoi Polyhedron**

  Wigner-Seitz cell

bcc



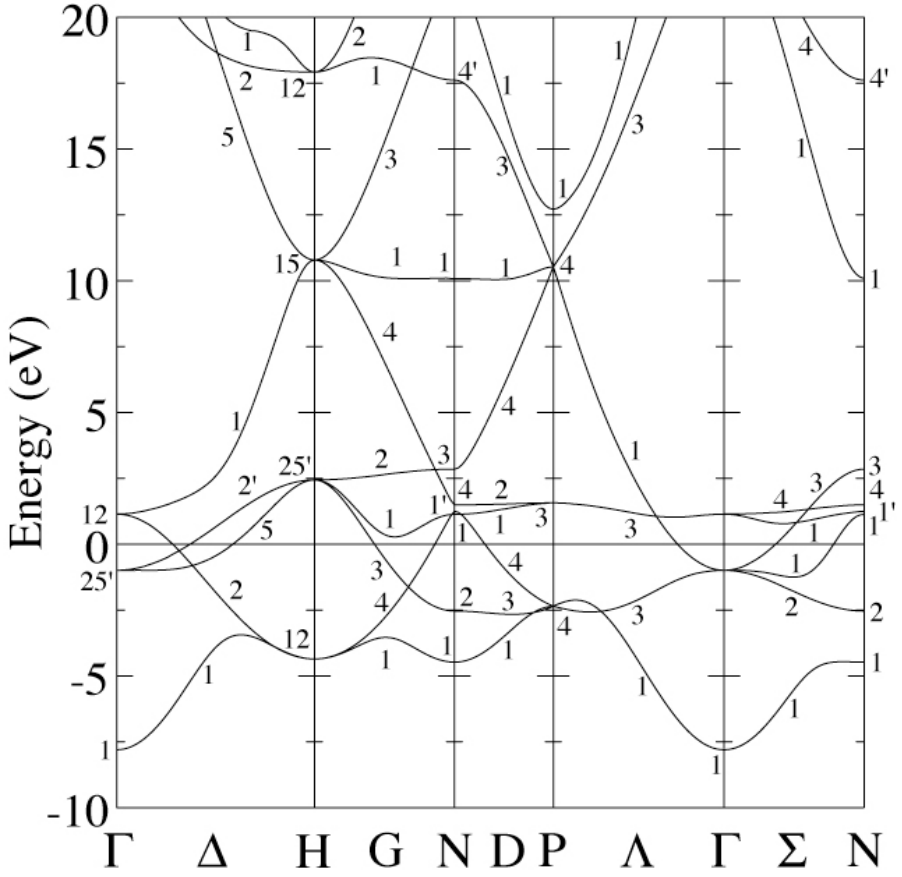
fcc



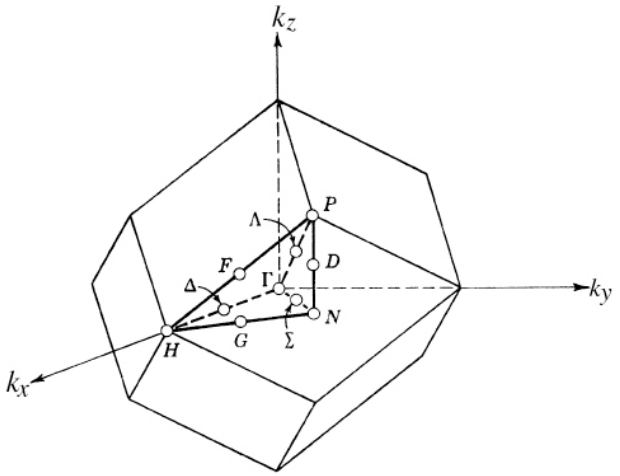
k Group

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

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



bcc Cr

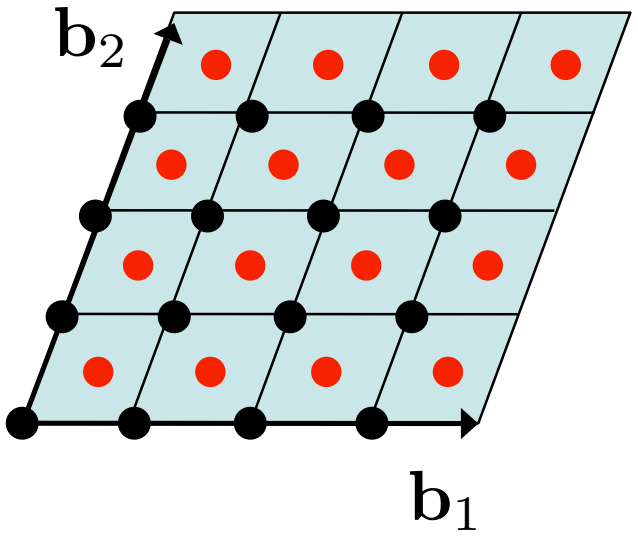


k Integration

k-point mesh

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

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



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

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**

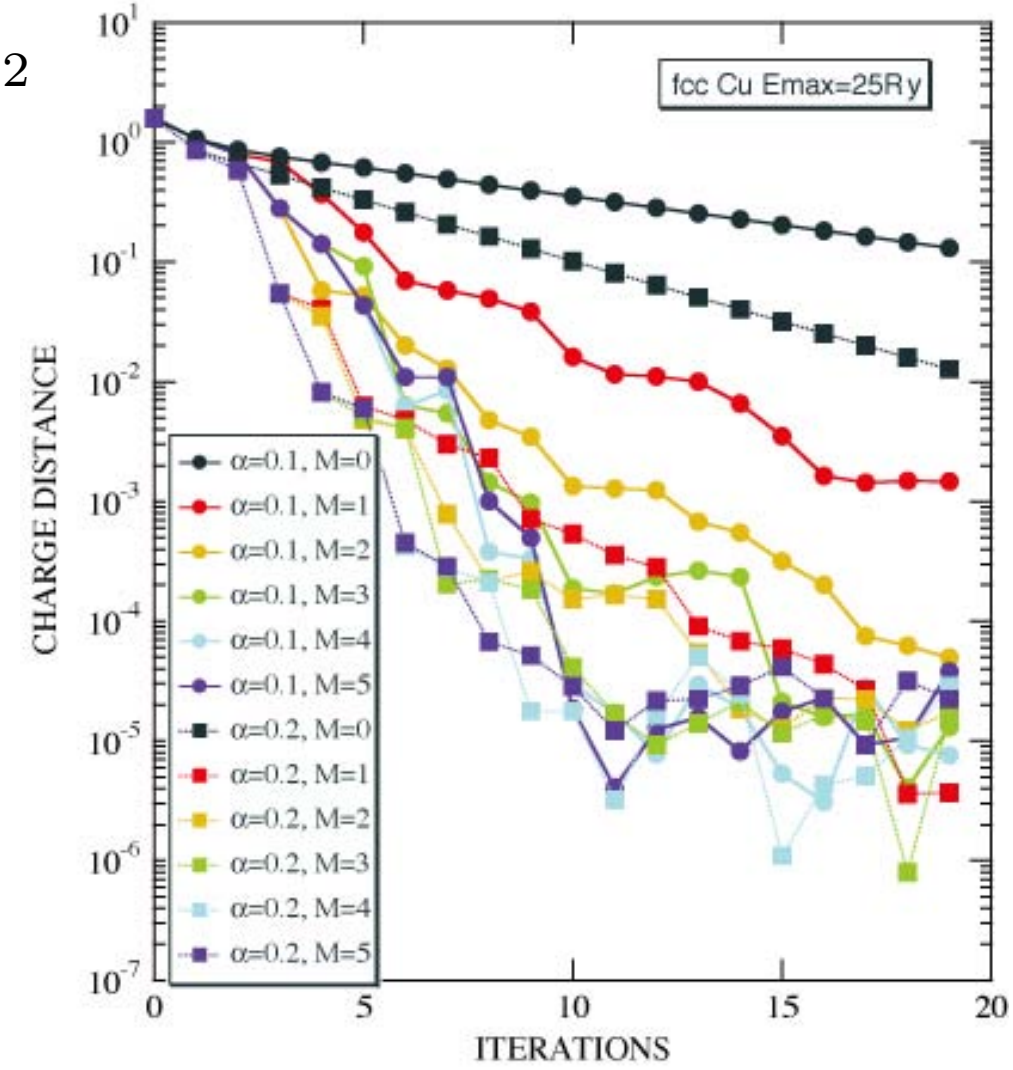
$$n_{\mathrm{in}}^{(i+1)} = (1-\alpha) \bar{n}_{\mathrm{in}}^{(i)} + \alpha \bar{n}_{\mathrm{out}}^{(i)}$$

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

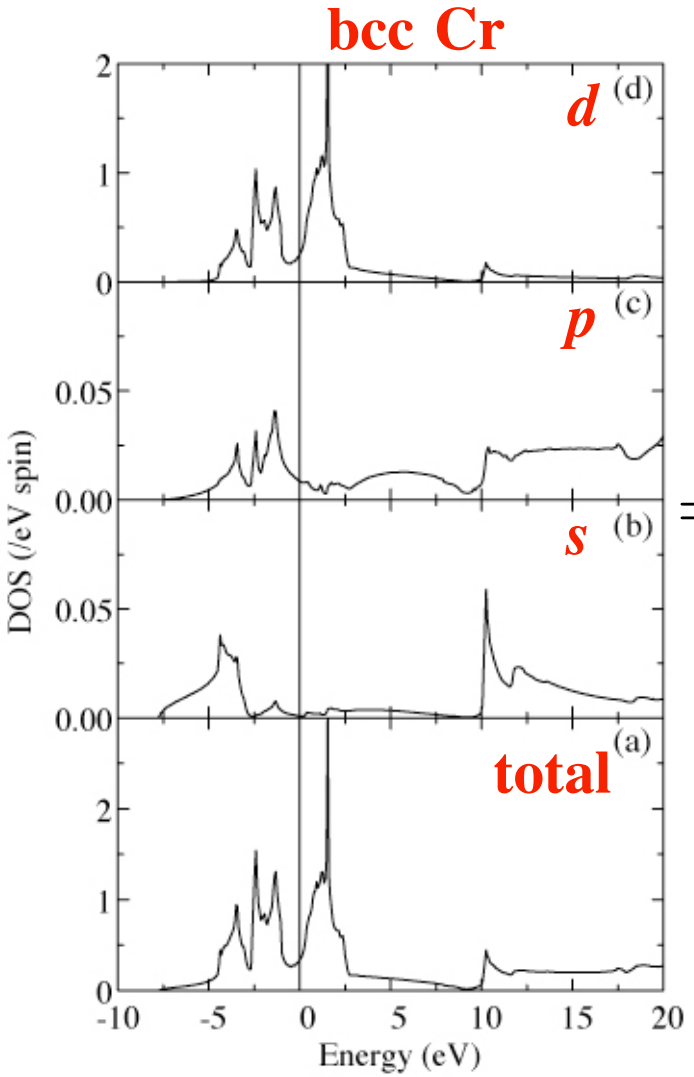
$$\min_{\beta} \int \left(\bar{n}_{\mathrm{in}}^{(i)} - \bar{n}_{\mathrm{out}}^{(i)} \right)^2 d\mathbf{r} \qquad \sum_{j=i-M}^{i} \beta^{(j)} = 1$$

Mixing of Electron Density

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



Density of States



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

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

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

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

$$= \sum_m D_m(E)$$ **partial DOS**

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

フローズンフォノン計算

運動方程式　$$M_\nu \ddot{u}_{\nu\alpha} = F_{\nu\alpha} = -\sum_{\nu'\beta} \frac{\partial^2 E}{\partial u_{\nu\alpha} \partial u_{\nu'\beta}} u_{\nu'\beta}$$

原子変位　$$u_{\nu\alpha} = \left(M_\nu\right)^{-1/2} C_{\nu\alpha} e^{i\left(\mathbf{q}\cdot\mathbf{R}_\nu - \omega(\mathbf{q})t\right)}$$

動的行列（Dynamical Matrix）

$$D_{\nu\alpha,\nu'\beta}(\mathbf{q}) = \left(M_\nu M_{\nu'}\right)^{-1/2} \sum_{\nu'} \frac{\partial^2 E}{\partial R_{\nu\alpha} \partial R_{\nu'\beta}} e^{-i\mathbf{q}\cdot\left(\mathbf{R}_\nu - \mathbf{R}_{\nu'}\right)}$$

$$\mathbf{D}(\mathbf{q})\mathbf{C} = \mathbf{C}\omega^2(\mathbf{q})$$

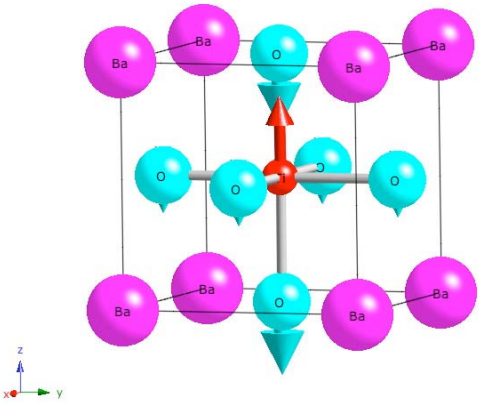
⇒ 格子振動モード

ソフトモード：立方晶$BaTiO_3$

(cm^{-1})	Ba	Ti	O1	O2	O2’
186*i*	-0.01	-0.62	1	0.51	0.51
0	1	1	1	1	1
165 180*	-0.66	1	0.78	0.97	0.97
277	0	0	0	1	-1
458 482*	-0.01	0.16	1	-0.69	-0.69

*IR @395K

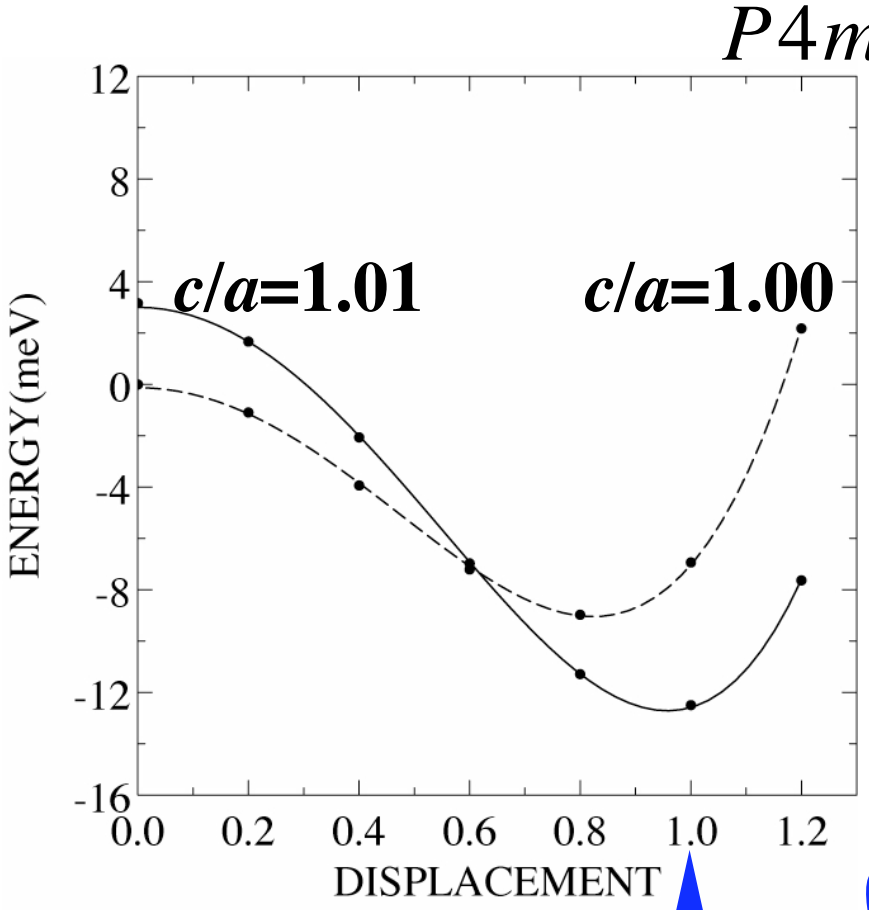
a = 4.00Å



Ti-3dとO-2pの共有結合性が重要

Ba^{2+}イオンはソフトモードに参加せず，イオン的状態に留まっている

$BaTiO_3$: 原子変位によるエネルギー変化



～100K

正方晶原子変位

u(Ti) = 0.054Å

u(O1) = –0.097Å

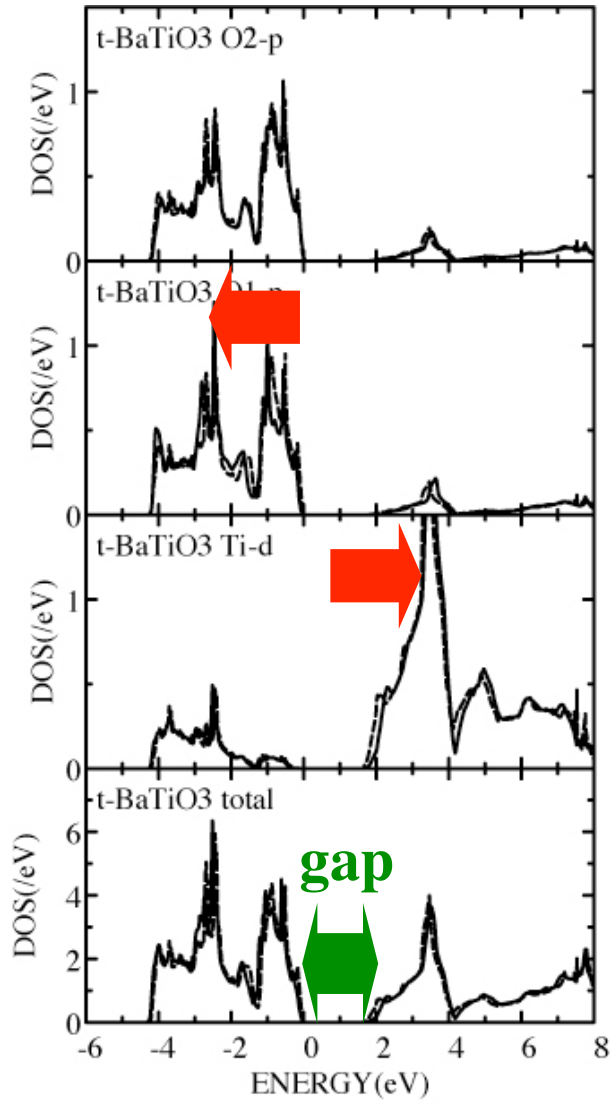
u(O2) = –0.061Å

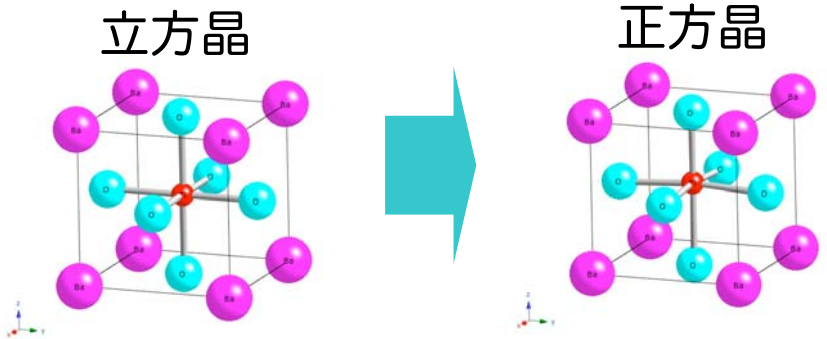
$BaTiO_3$: 変位による状態の変化

O2-p

O1-p

Ti-d





破線：変位なし（立方晶）

実線：変位あり（正方晶）

変位により軌道混成が増大

→　バンドのシフト

エネルギー利得

GETTING STARTED 1

- Login CMD Machine

  # ssh -X your_account@cmd2.phys.sci.osaka-u.ac.jp

- Copy the package into your home

  # cd

  # cp ~teac03/hilapw_1.12_tar.gz .

- Extract the package

  # tar zxvf hilapw_1.12_tar.gz

GETTING STARTED 2

- Set the PATH variable

  # vi .cshrc

  set path = (. $home/hilapw/bin $path)

- Activate the PATH

  # source ~/.cshrc

GETTING STARTED 3

- Get example data

  # cd hilapw1

  # mkdir Cu

  # cd Cu

  # getdata

  # tar xvf ~/hilapw/data/Cu.tar

BATCH JOB

- Script-file: JOB

```
#!/bin/csh
#$ -cwd
#$ -N HiLAPW
./JOB-SCF
```

- Commands

# qsub JOB	submit a batch job
# qstat	show the job status
# qdel job-ID	delete jobs from queues

OUTPUT GRAPHS

- Get the PS file

  total DOS

  # PSP < psp_tdos > tdos.ps

- View the PS file

  ghostscript

  # gs tdos.ps

  ghostview

  # gv tdos.ps

XCrySDen

XCrySDen is a **crystalline and molecular structure visualisation program**, which aims at display of isosurfaces and contours, which can be superimposed on crystalline structures and interactively rotated and manipulated. It can run on most *UNIX* platforms, without any special hardware requirements.

XCrySDen has been also ported to MAC OSX (requires X11) and Windows (requires CYGWIN).

The name of the program stands for ***Crystalline Structures and Densities*** and ***X*** because it runs under the X-Window environment.

http://www.xcrysden.org/

Draw Fermi Surface

- ferm.in

```
ferm.in
0.0 0.0 0.0                                          origin
1.26292   0.00000   0.00000 1.26292 63    b1 |b1| N1
0.63146   1.09372   0.00000 1.26292 63    b2 |b2| N2
0.00000   0.00000   0.94351 0.94351 47    b3 |b3| N3
```

- xferm: ferm.in
- xf2x: fermis.list --> fermis.bxsf
- insert Fermi energy in fermis.bxsf
- xcrysden