

Basics of FLAPW Method



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CMD Workshop

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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

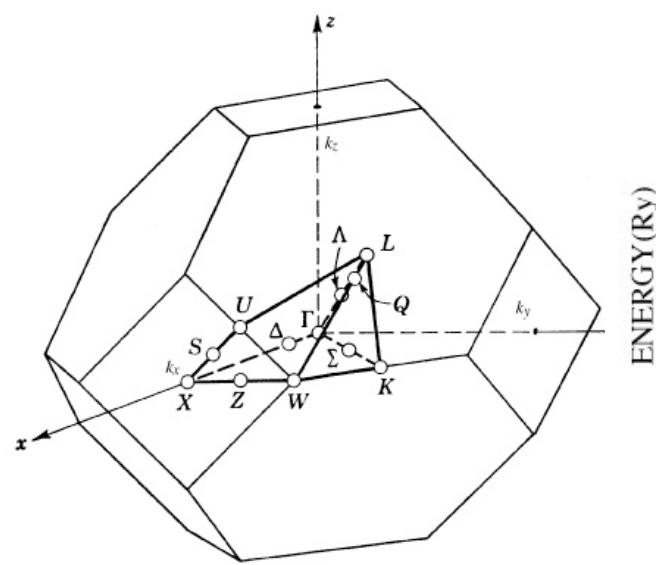
Bloch Theorem

- A quantum-mechanical state in a periodic system can be specified with a wave number \mathbf{k}

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

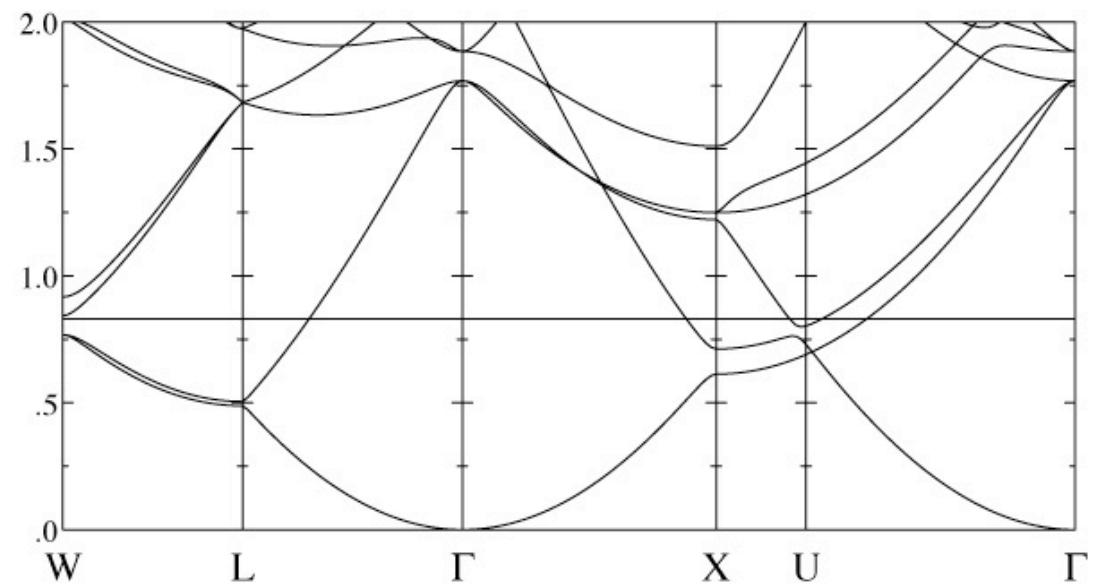
Dispersion relation: band structure

Brillouin Zone and Bands



BZ of fcc lattice

independent quantum number



Band structure of fcc Al

Textbook of Band Theory



バンド理論
物質科学の基礎として
内田老鶴園 1999年



Bloch Function

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

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

$$u_j^{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_j^{\mathbf{k}}(\mathbf{r}) : \textbf{periodic function}$$



represented in a
Fourier form

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

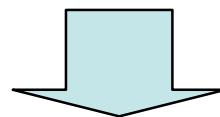
K: reciprocal lattice vector



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

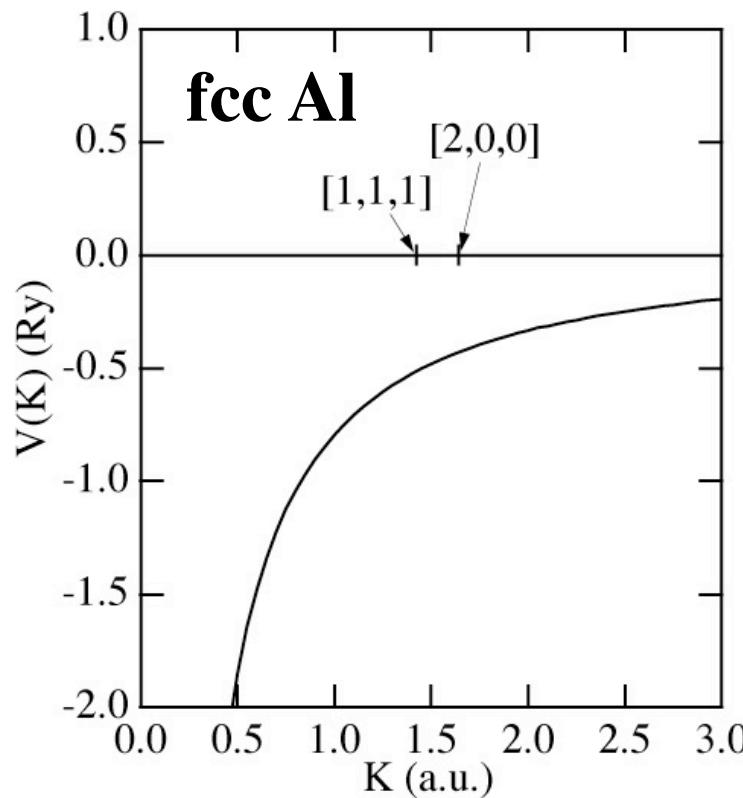
$$\langle \mathbf{k} + \mathbf{K}' | \mathcal{H} | \mathbf{k} + \mathbf{K} \rangle = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{K}|^2 \delta_{\mathbf{K}', \mathbf{K}} + V(\mathbf{K}' - \mathbf{K})$$

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



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

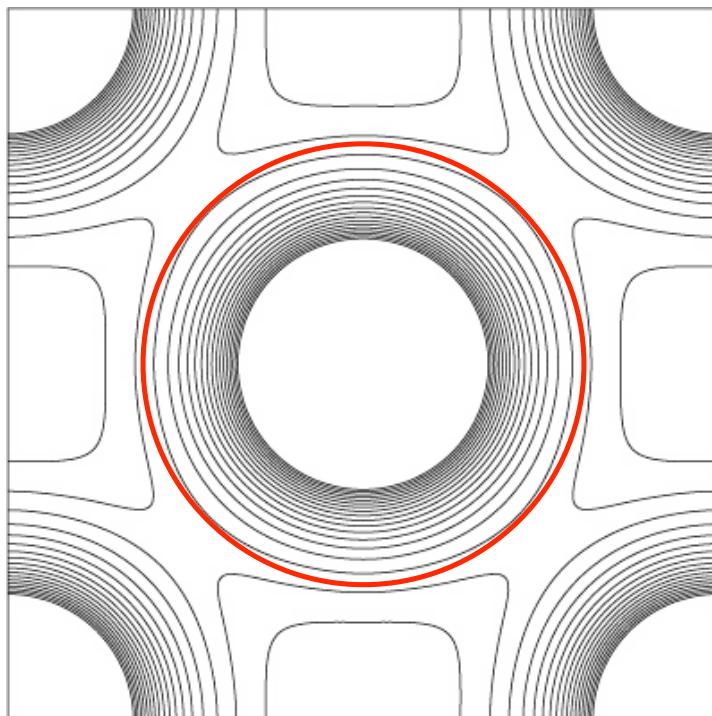
1. Contributions from core (nucleus and core electron potentials, and orthogonality to core electron states) are replaced by a soft (easily Fourier transformed) potential
→ **pseudopotential**

2. PW basis functions are augmented with more localized functions
→ **augmented or mixed basis**

Muffin-tin Potential Approximation



Crystal Potential



FCC Cu

- Spherical around atoms
- Constant in the interstitial



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

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

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

$$\begin{aligned} \langle \mathbf{k} + \mathbf{K}' | \mathcal{H} - E | \mathbf{k} + \mathbf{K} \rangle &= \left\{ \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{K}|^2 - E \right\} \delta_{\mathbf{K}', \mathbf{K}} \\ &\quad + \Gamma_{\mathbf{K}', \mathbf{K}}^{\text{APW}}(E) \end{aligned}$$

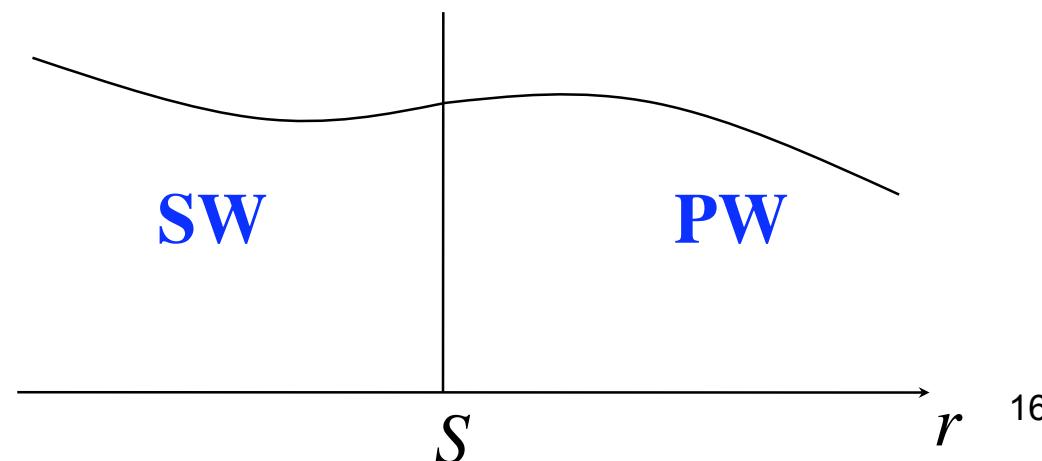
Matrix elements have non-linear energy dependence due to **logarithmic derivatives** of the radial functions.

Logarithmic Derivative



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

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 $\Gamma_{\mathbf{K}', \mathbf{K}}^{\text{APW}}(E)$ 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

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

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

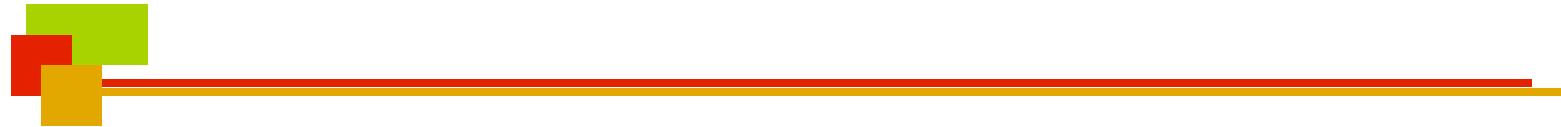
$$R_l(r; D) = R_l(r; E_0) + \omega(D) \dot{R}_l(r; E_0)$$



Linear Method

- APW → LAPW
- KKR → LMTO
 - KKR: Korringa-Kohn-Rostoker
 - LMTO: Linear Muffin-Tin Orbital

LAPW Method



Augmentation basis

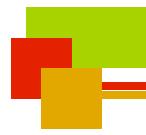
$$\phi^{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{lm} i^l \phi_{lm}^{\mathbf{k}+\mathbf{K}}(|\mathbf{r} - \mathbf{R}|) Y_{lm}(\mathbf{r} - \mathbf{R})$$

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

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

E_l energy parameter usually taken at the center of the occupied partial band²⁰

LAPW Method



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

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

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

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

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

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

Why the Linear Method Works Well?



Orthogonality to maximize the variational degree

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

Orthogonality to the core functions

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

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

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



$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}$$

in Rydberg atomic units

$$\begin{aligned} H_{\mathbf{K}',\mathbf{K}} &= \langle \mathbf{k} + \mathbf{K}' | \mathcal{H} | \mathbf{k} + \mathbf{K} \rangle \\ &= (\mathbf{k} + \mathbf{K}') \cdot (\mathbf{k} + \mathbf{K}) U(\mathbf{K}' - \mathbf{K}) \\ &\quad + \frac{4\pi S^4}{\Omega_0} \sum_l (2l+1) P_l ((\mathbf{k} + \mathbf{K}') \cdot (\mathbf{k} + \mathbf{K})) \\ &\quad \times \left(E_l s_l^{\mathbf{K}',\mathbf{K}} + \gamma_l^{\mathbf{K}',\mathbf{K}} \right) \end{aligned}$$

$$\begin{aligned} S_{\mathbf{K}',\mathbf{K}} &= \langle \mathbf{k} + \mathbf{K}' | \mathbf{k} + \mathbf{K} \rangle \\ &= U(\mathbf{K}' - \mathbf{K}) \\ &\quad + \frac{4\pi S^4}{\Omega_0} \sum_l (2l+1) P_l ((\mathbf{k} + \mathbf{K}') \cdot (\mathbf{k} + \mathbf{K})) s_l^{\mathbf{K}',\mathbf{K}} \end{aligned}$$

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



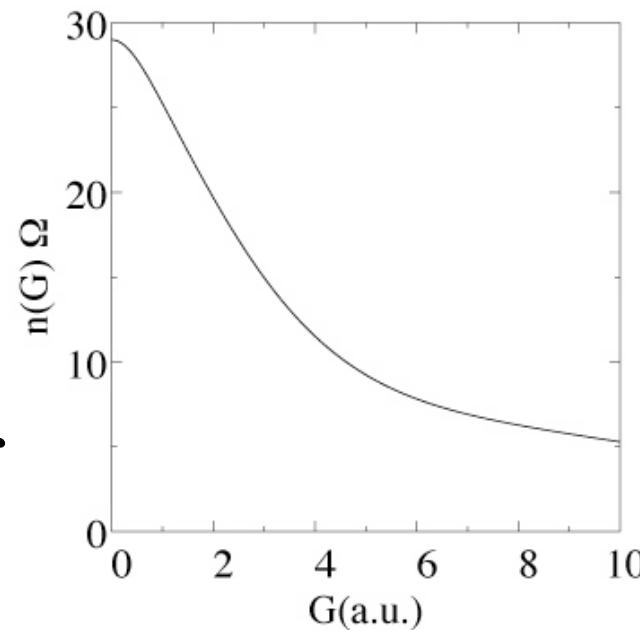
- Coulomb potential for smooth density distribution

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

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

- 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



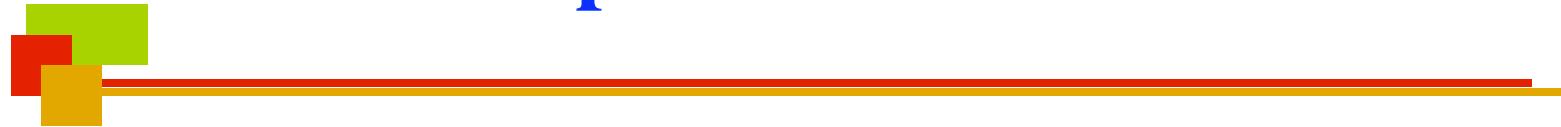
- Pseudized density inside the sphere

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

$$\begin{aligned}\tilde{n}_{\mathbf{G}} &= \frac{4\pi}{\Omega_0} \sum_{lm} \frac{(-i)^l (2l+2n+3)!!}{(2l+1)!! S^l} \\ &\quad \times \frac{j_{l+n+1}(GS)}{(GS)^{n+1}} q_{lm} Y_{lm}(\mathbf{G})\end{aligned}$$

multipole moment

Full-potential Method



- Potential inside the sphere

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

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

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

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

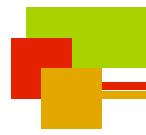
$$\Delta H_{\mathbf{K}',\mathbf{K}} = \langle \mathbf{k} + \mathbf{K}' | \Delta v | \mathbf{k} + \mathbf{K} \rangle$$

non-spherical part

FLAPW Method

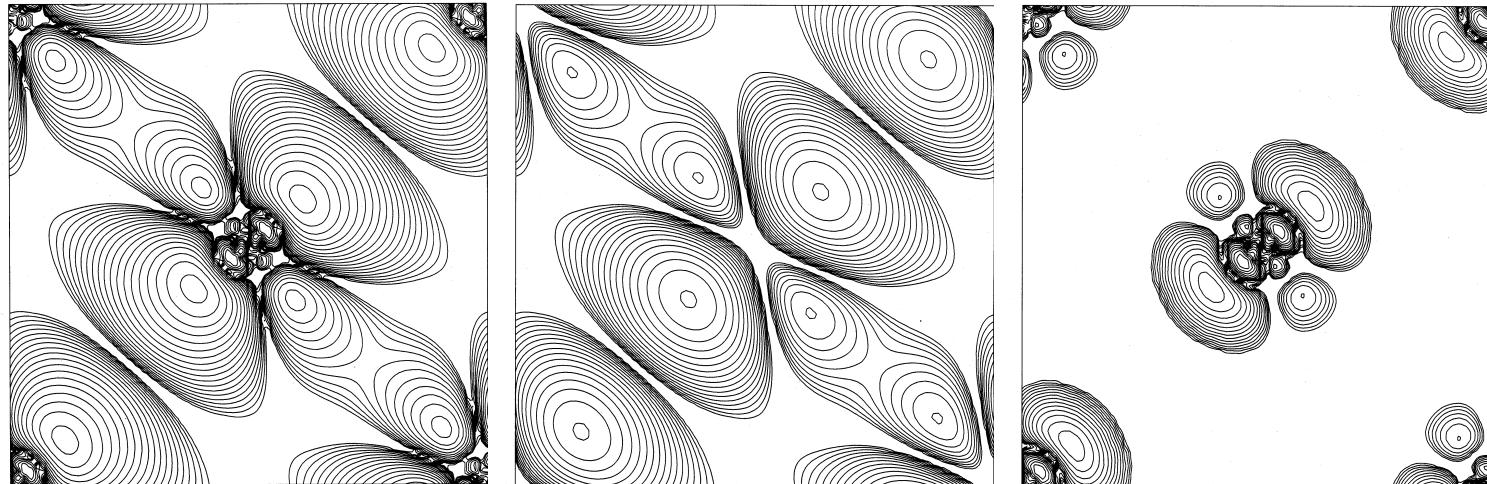


- **Two-dimensional slab models**
 - E. Wimmer, H. Krakauer, M. Weinert and A.J. Freeman, PRB 24 (1981) 864.
 - M. Weinert, E. Wimmer and A.J. Freeman, PRB 26 (1982) 4571.
- **Three-dimensional systems**
 - H.J.F. Jansen and A.J. Freeman, PRB 30 (1984) 561.



FLAPW Packages Open to Public

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



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

SUMMARY



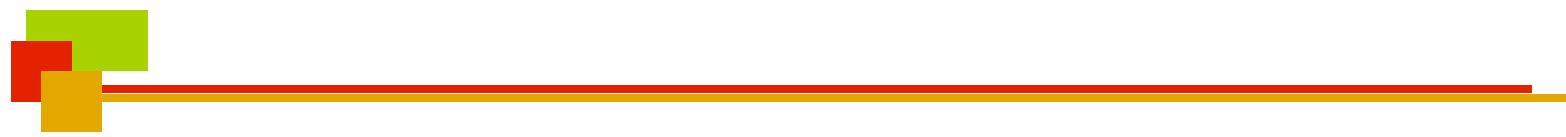
FLAPW Method

- 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

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

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

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

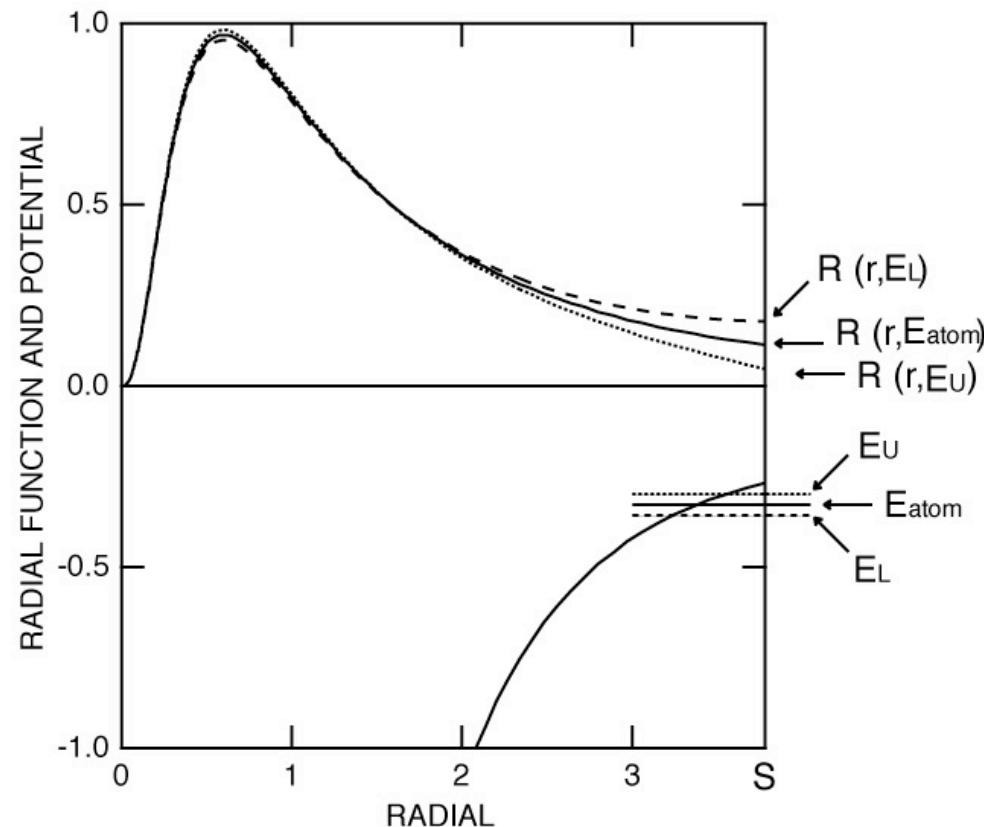
$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + v(r) - E \right] P_l(r; E) = 0$$

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

Energy Dependence of Radial Function



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

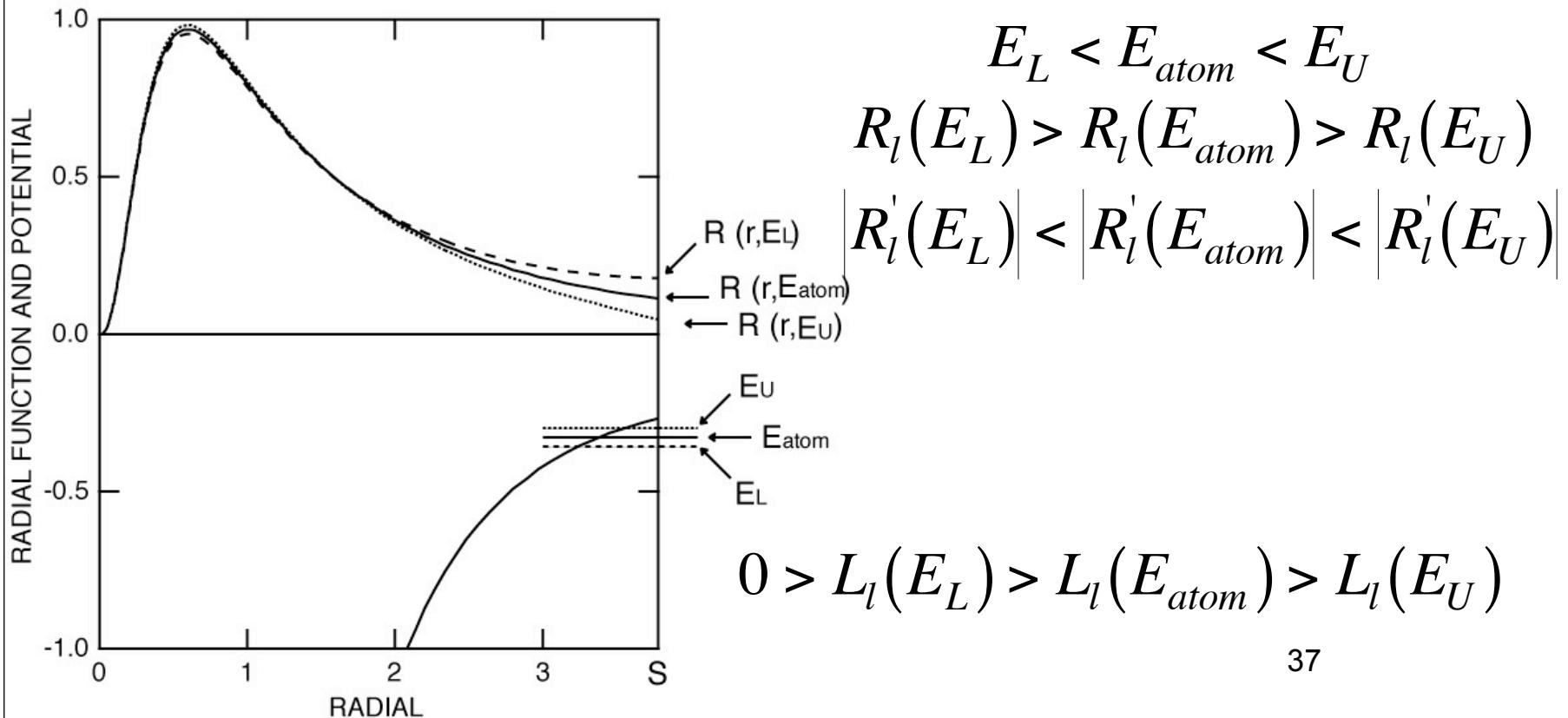


$$E_L < E_{atom} < E_U$$

Logarithmic Derivative



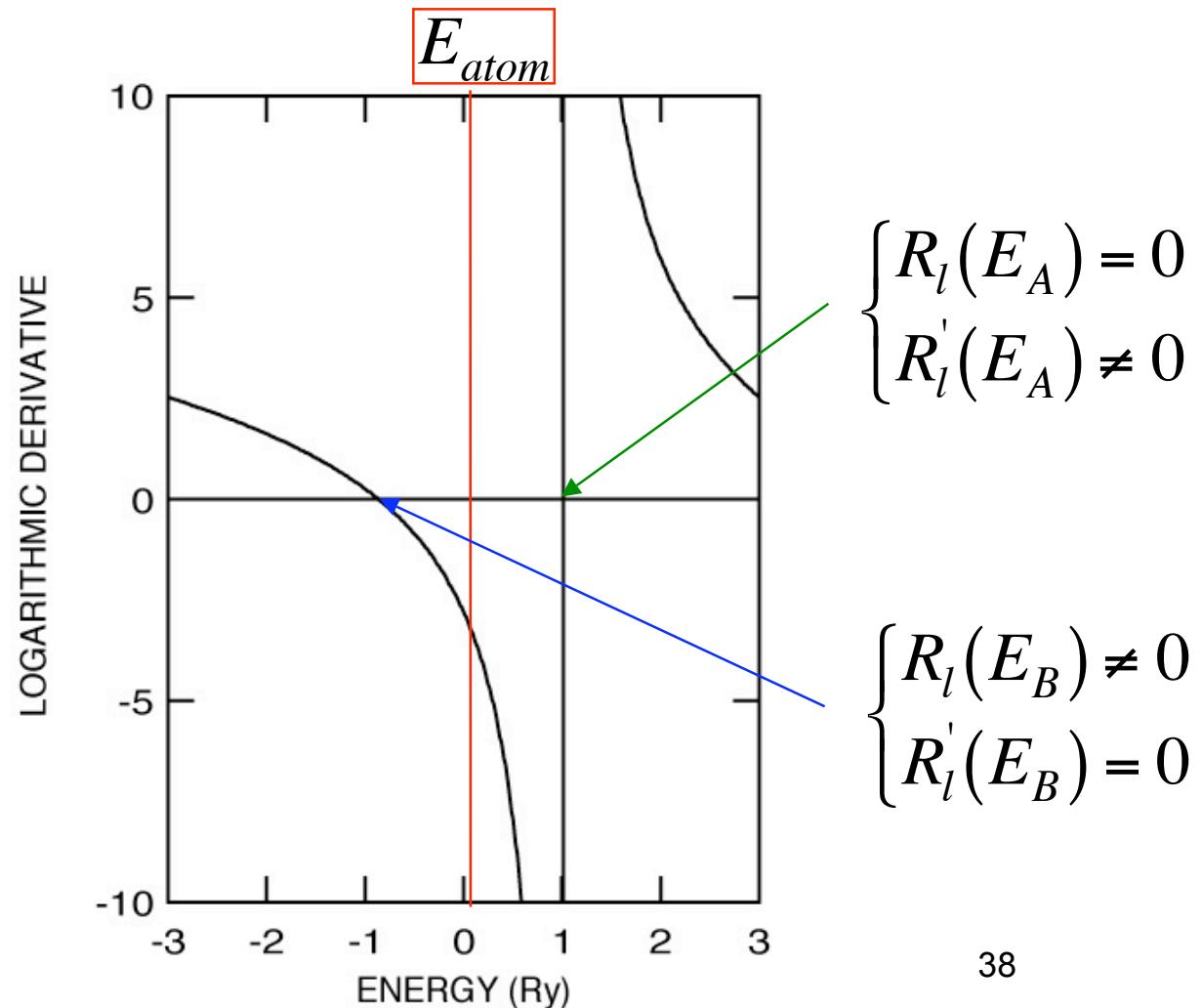
$$L_l(E) = \frac{R'_l(S; E)}{R_l(S; E)} = \left. \frac{d}{dr} \ln R_l(r; E) \right|_{r=S}$$



Logarithmic Derivative



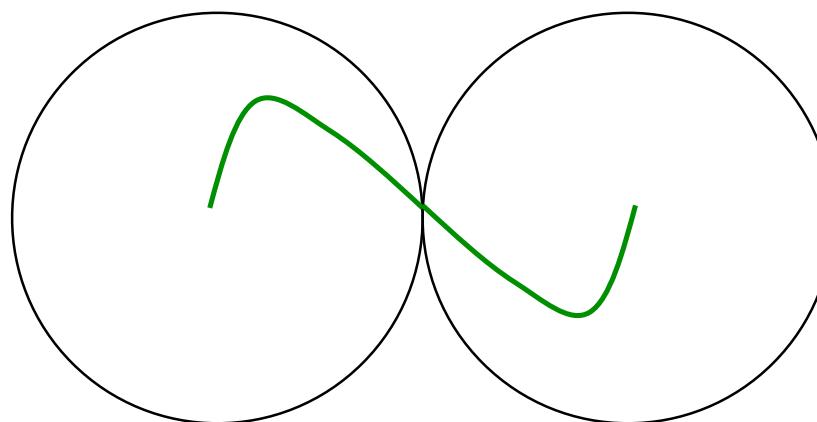
$L_l(E)$
bcc W-d



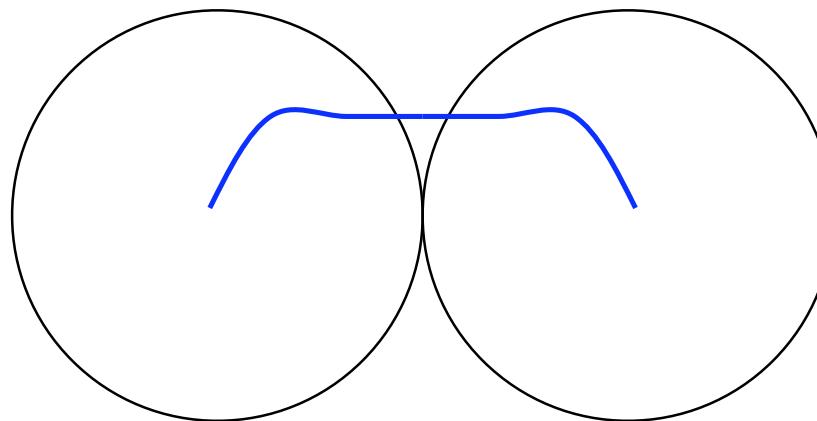
Logarithmic Derivative



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



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



Practical Aspects in First-Principles Calculation



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CMD Workshop





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

$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}$$

- Matrix elements

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



Basis Functions

- **Plane waves**
 - pseudopotential
 - simple, fast, extendable, transferability
- **Plane waves + Augmentation functions**
 - all-electron scheme
 - robust, precise, complicated
- **Local orbitals**
 - minimal
 - real space $\rightarrow \mathbf{O}(N)$

Self-Consistent Field



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

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

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

$$\mathbf{HC} = \mathbf{SCE}$$

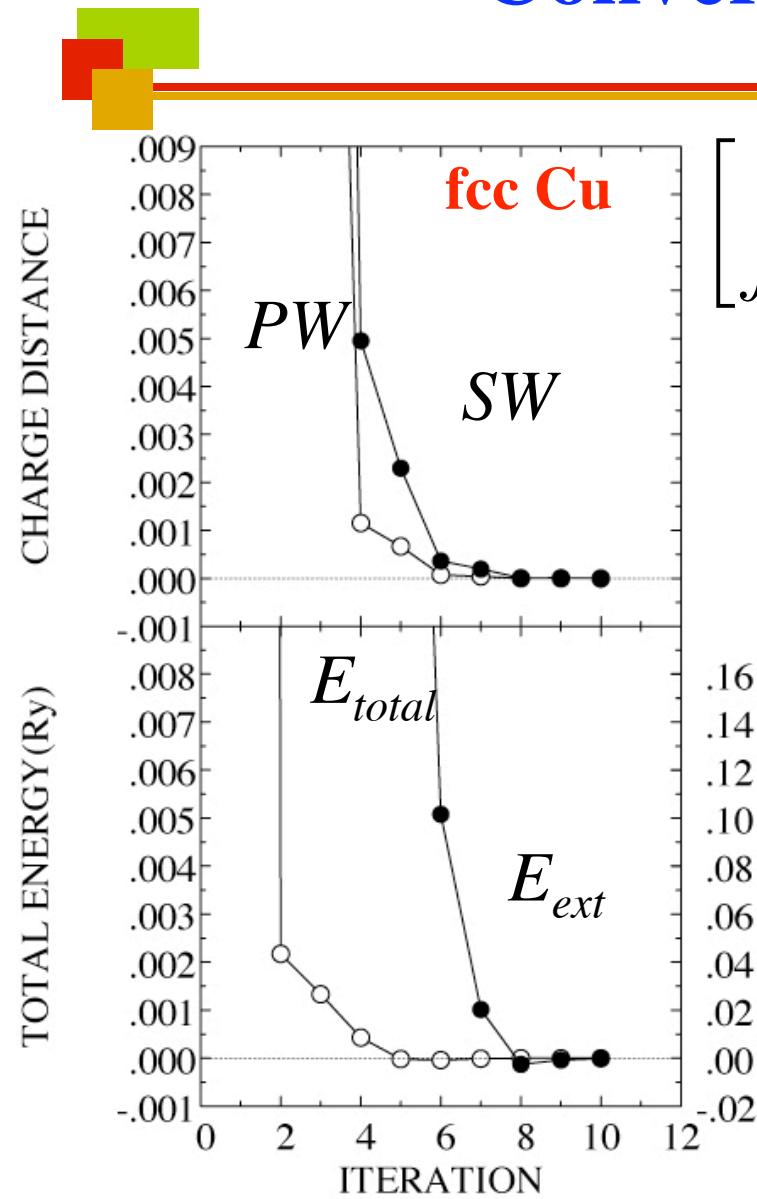
$$n_{\text{out}}(\mathbf{r})$$

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

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

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

Convergency to SCF



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

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

occ.

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

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

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

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

Crystal Structure and Atomic Position



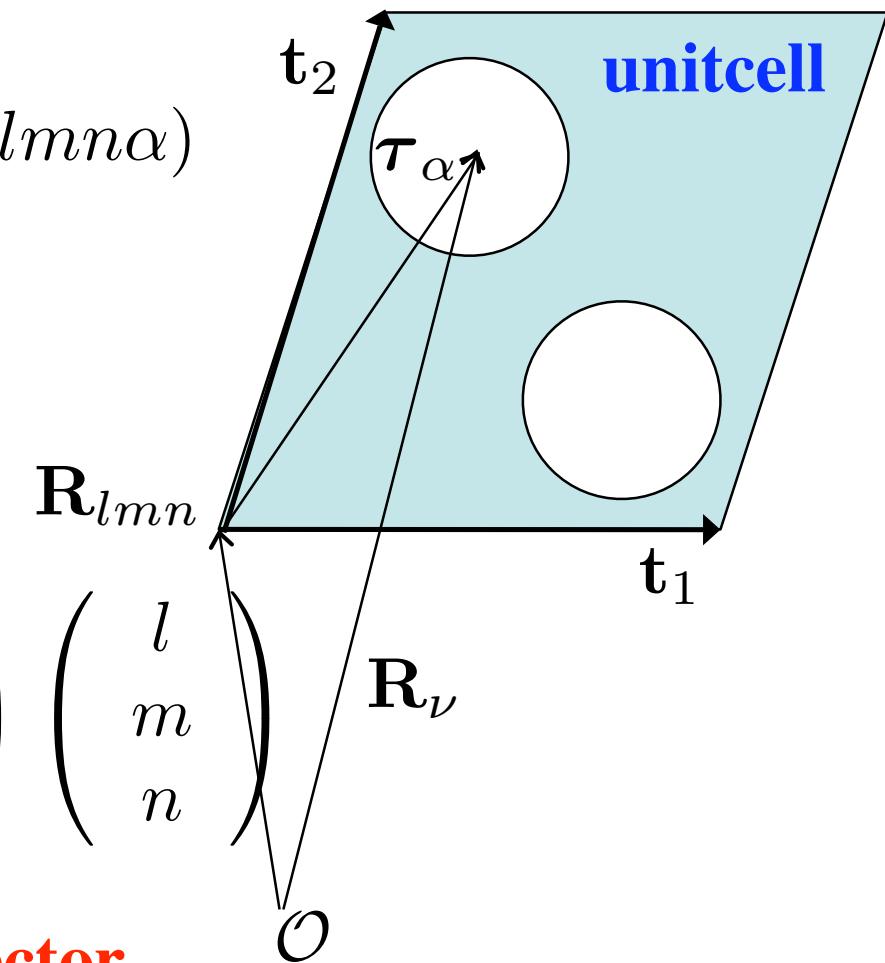
$$\mathbf{R}_\nu = \mathbf{R}_{lmn} + \boldsymbol{\tau}_\alpha \quad \nu = (lmn\alpha)$$

- Lattice Vector

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

$$\begin{pmatrix} R_{lmn}^x \\ R_{lmn}^y \\ R_{lmn}^z \end{pmatrix} = \underbrace{\begin{pmatrix} t_1^x & t_2^x & t_3^x \\ t_1^y & t_2^y & t_3^y \\ t_1^z & t_2^z & t_3^z \end{pmatrix}}_{\text{Primitive translation vector}} \begin{pmatrix} l \\ m \\ n \end{pmatrix}$$

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

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

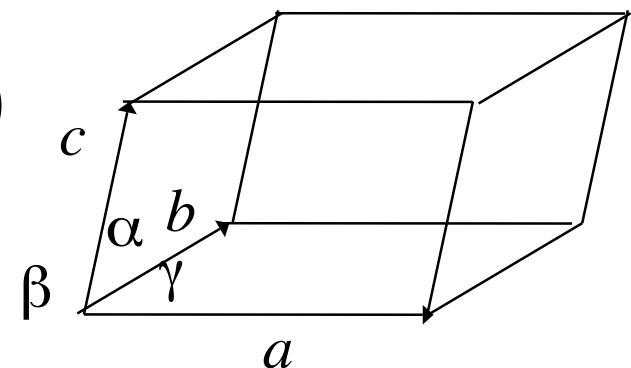
Lattice constants

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	10 P

Lattice: System and Type



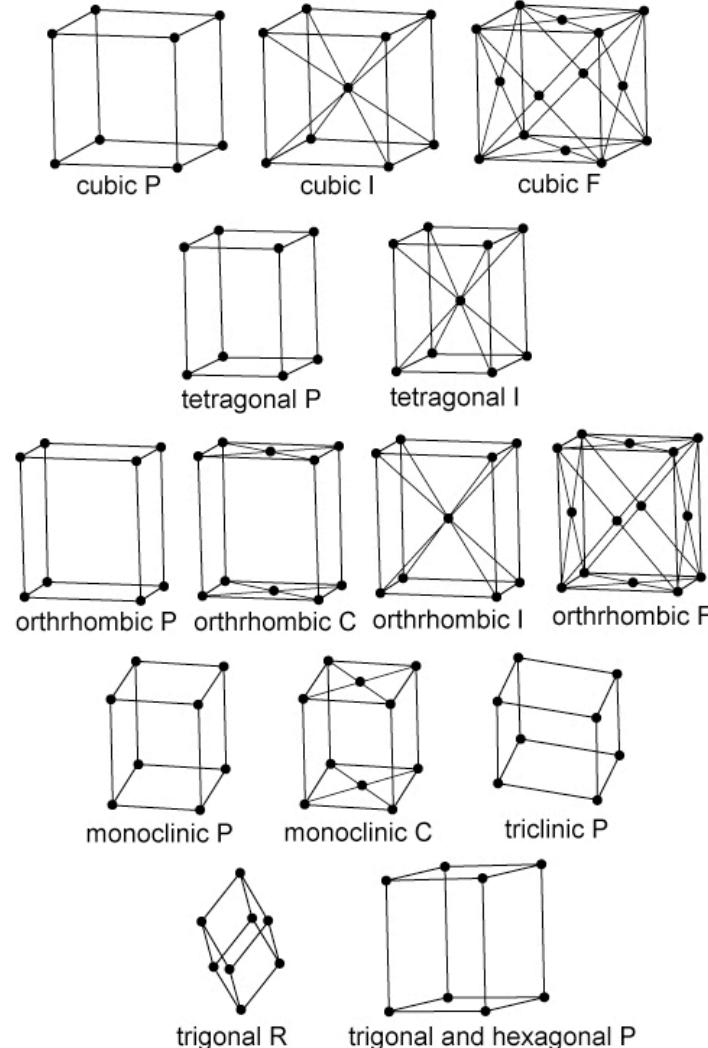
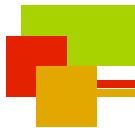
- Lattice type

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

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

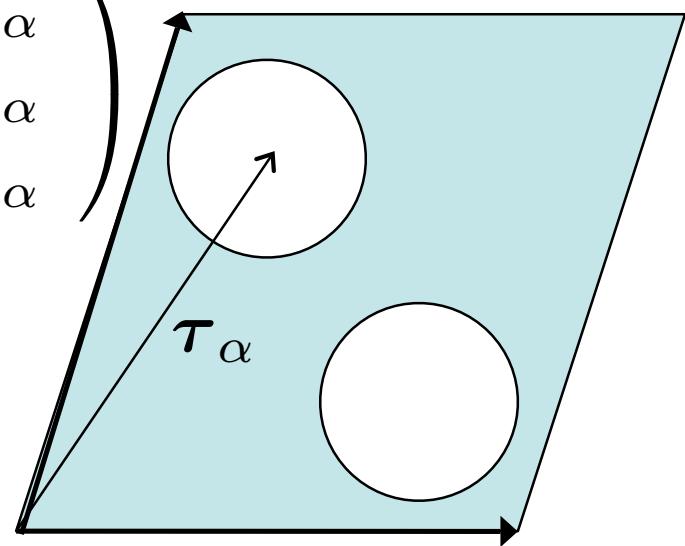
$$B = \begin{pmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \quad C = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}_{11}$$

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



A diagram showing a light blue parallelogram representing a unit cell. Inside the cell, there are three white circles representing atoms. A vector labeled τ_α points from the bottom-left atom to the top atom. Another vector also points from the bottom-left atom to the top atom. The top atom has a small arrow pointing towards it.

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

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

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



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



Space Group Symbol

1,2,3,4,6 : rotation axis

m : mirror plane

2₁ : twofold screw with $v=1/2$

4₂ : 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 it¹⁶



Reciprocal Lattice

- Definition

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

lattice vector

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

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

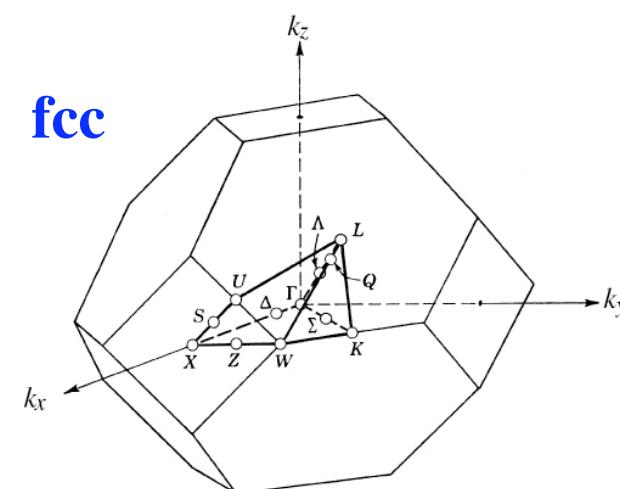
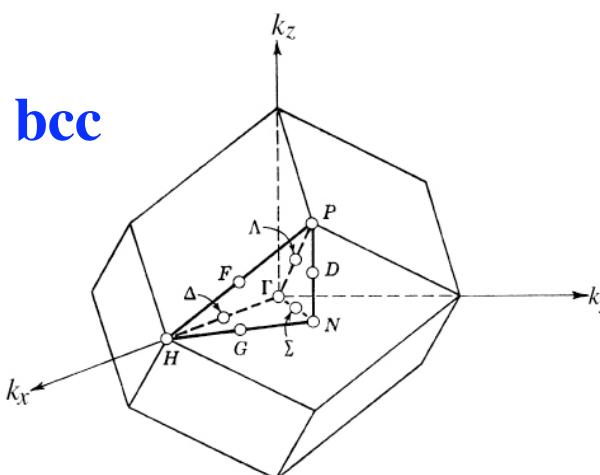
- Brillouin zone (BZ) = unitcell of reciprocal lattice
- States with \mathbf{k} inside BZ are independent
→ State sum = \mathbf{k} -integration inside BZ

Brillouin Zone



Unitcell of reciprocal lattice

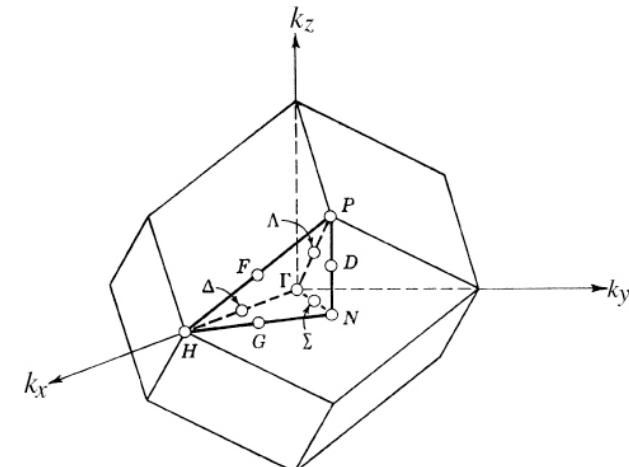
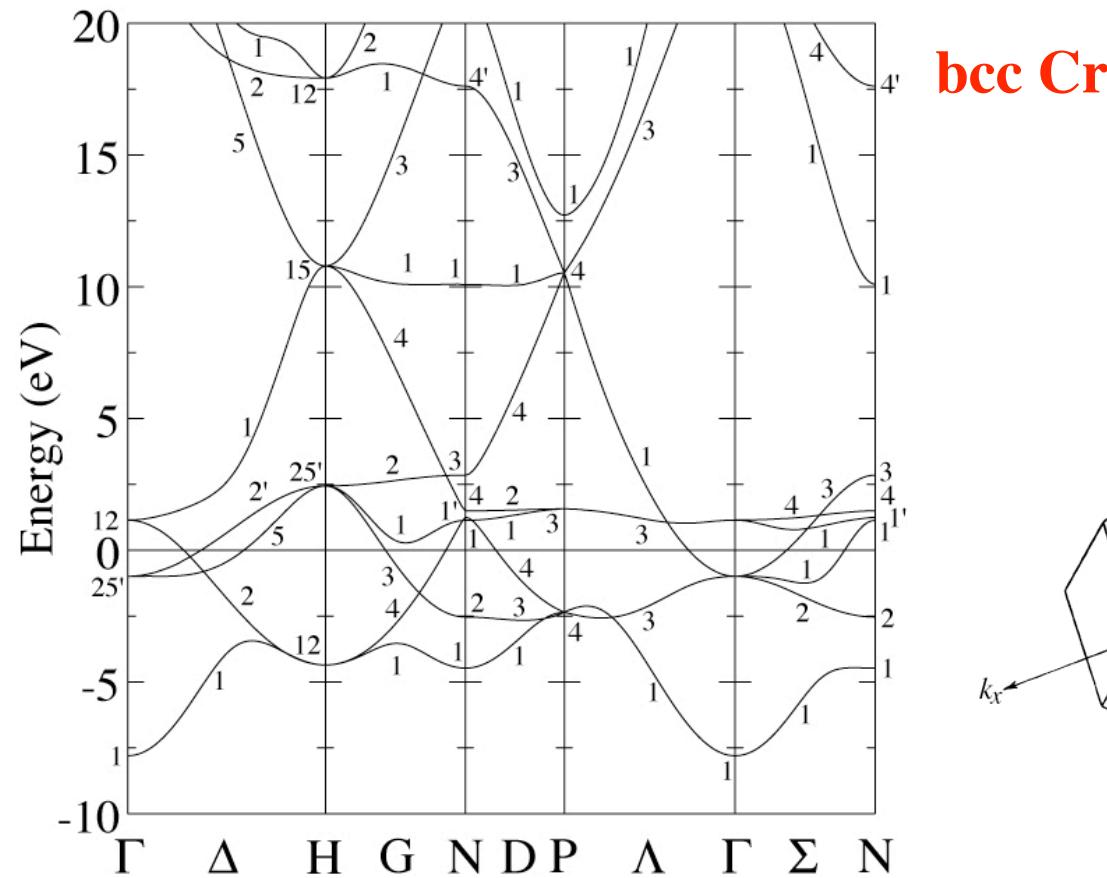
- parallelepiped ($\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$)
easy to treat numerically
- Voronoi Polyhedron
Wigner-Seitz cell



k Group

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

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



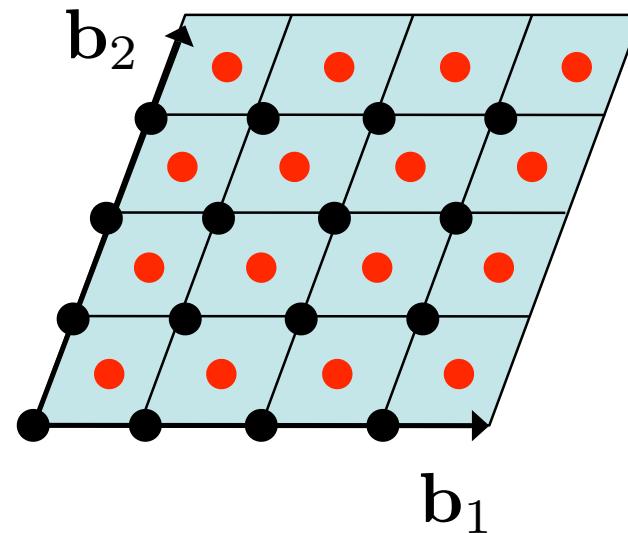
k Integration



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**

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

- **Extended Anderson Method**

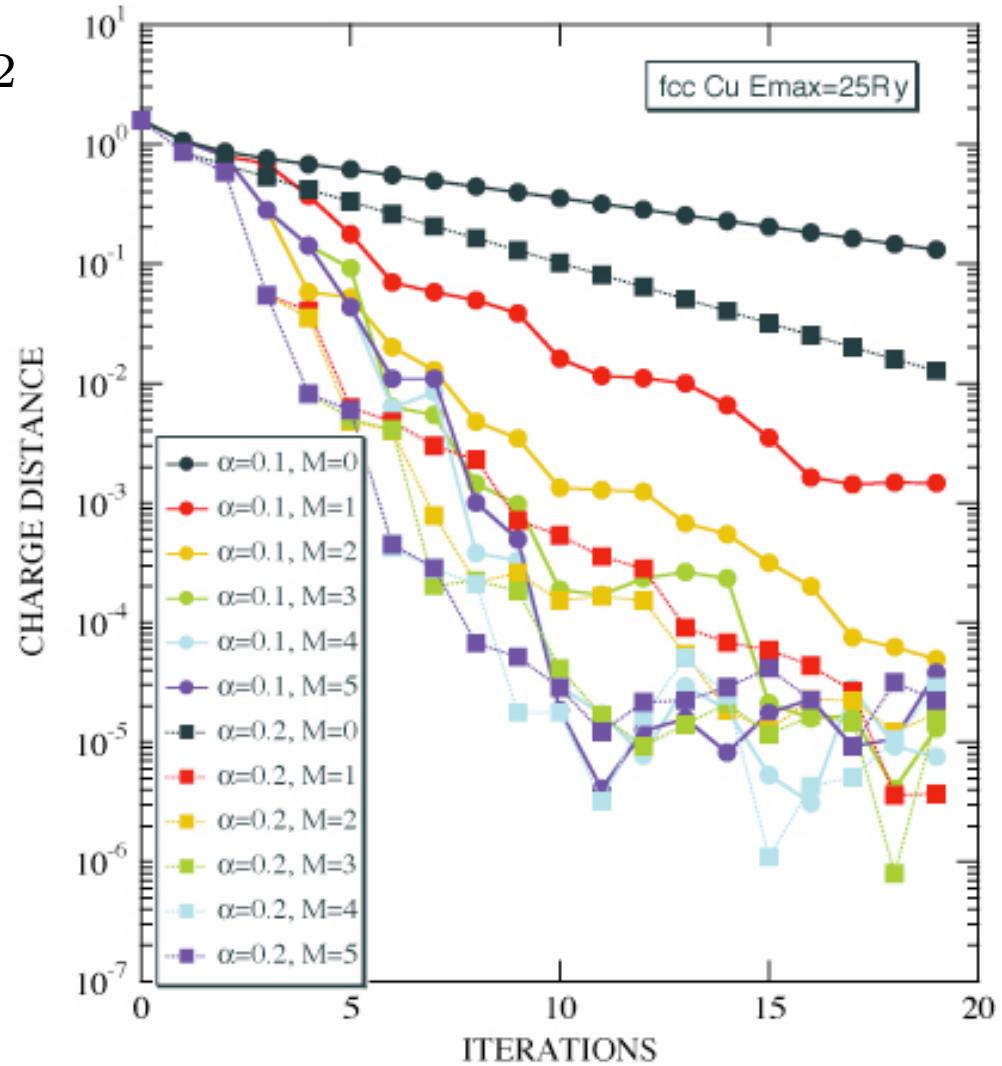
$$n_{\text{in}}^{(i+1)} = (1 - \alpha)\bar{n}_{\text{in}}^{(i)} + \alpha\bar{n}_{\text{out}}^{(i)}$$

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

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

Mixing of Electron Density

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



Density of States

