# First-principles calculation

# 第一原理計算

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# Plain wave approx.: Transfer matrix method

H. Mizuta, T. Tanoue, "The Physics and Applications of Resonant Tunnelling Diodes," Cambridge Univ Press (1995)

$$\Psi_i(x) = A_i \exp(ik_i x) + B_i \exp(-ik_i x) \qquad k_i = \sqrt{\frac{2m_i}{\hbar^2}(E - V_i)}$$

## Boundary conditions

$$\Psi_i(x_{i+1}) = \Psi_{i+1}(x_{i+1}) \qquad {m_i}^{-1}\Psi'_i(x_{i+1}) = {m_{i+1}}^{-1}\Psi'_{i+1}(x_{i+1})$$

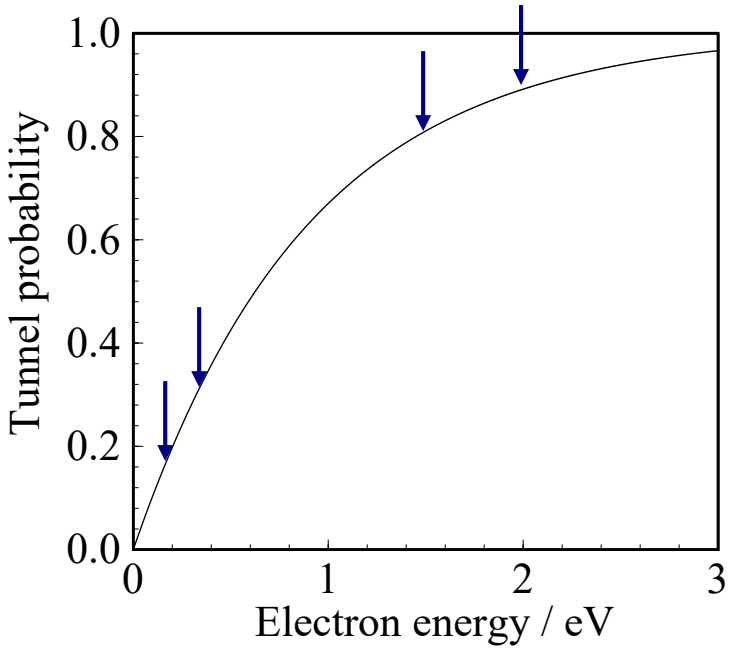
$$\begin{pmatrix} A_{i+1} \\ B_{i+1} \end{pmatrix} = \begin{pmatrix} \alpha^+_i P_i & \alpha^-_i / Q_i \\ \alpha^-_i Q_i & \alpha^+_i / P_i \end{pmatrix} \begin{pmatrix} A_i \\ B_i \end{pmatrix}$$

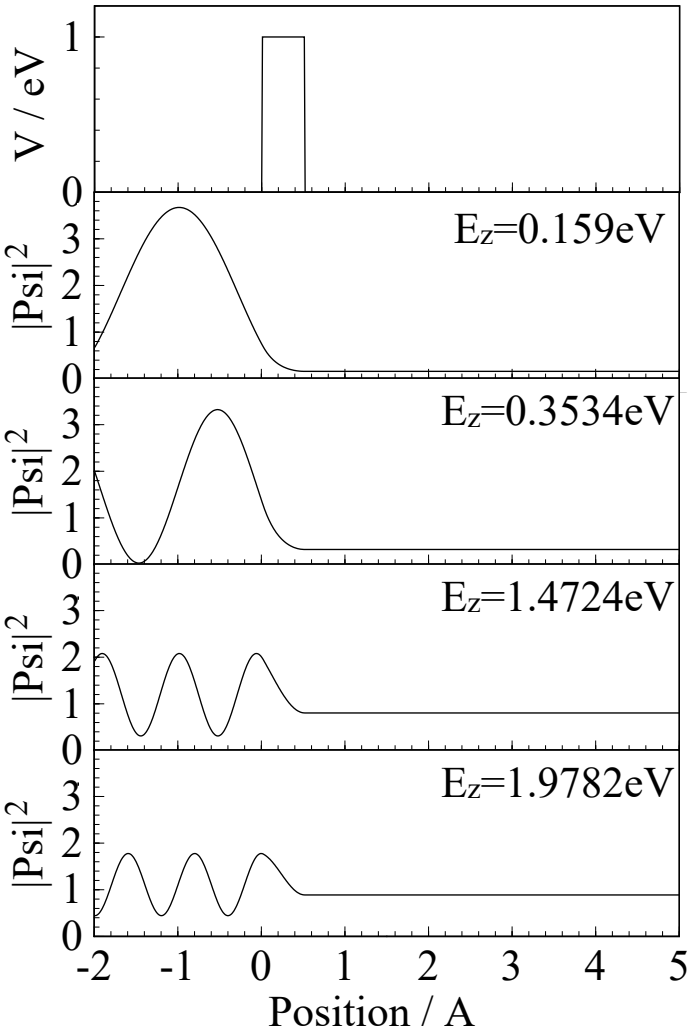
$$\alpha^{\pm}_i = \frac{1}{2}\left[1 \pm (m_{i+1}/m_i)(k_i/k_{i+1})\right]$$

$$P_i = \exp\left[i(k_i - k_{i+1})x_{i+1}\right]$$

$$Q_i = \exp\left[i(k_i + k_{i+1})x_{i+1}\right]$$

# Tunneling in a single barrier

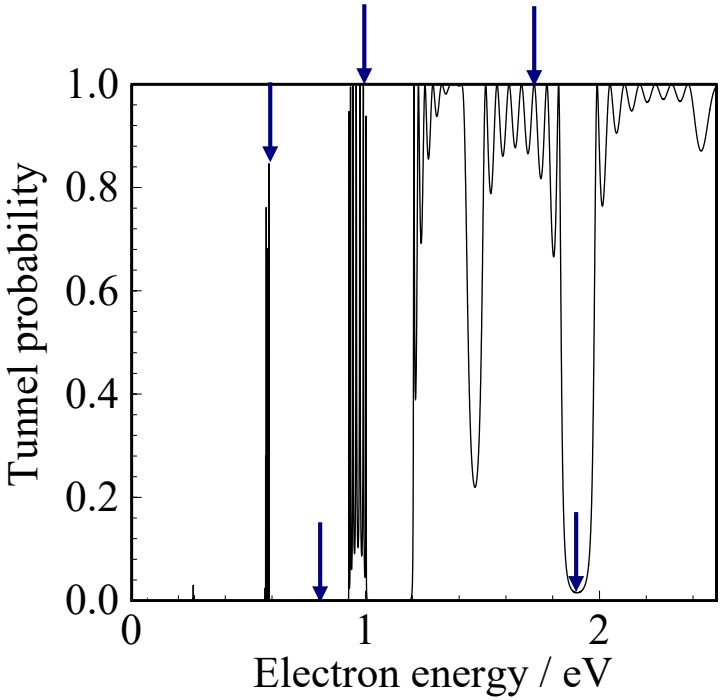


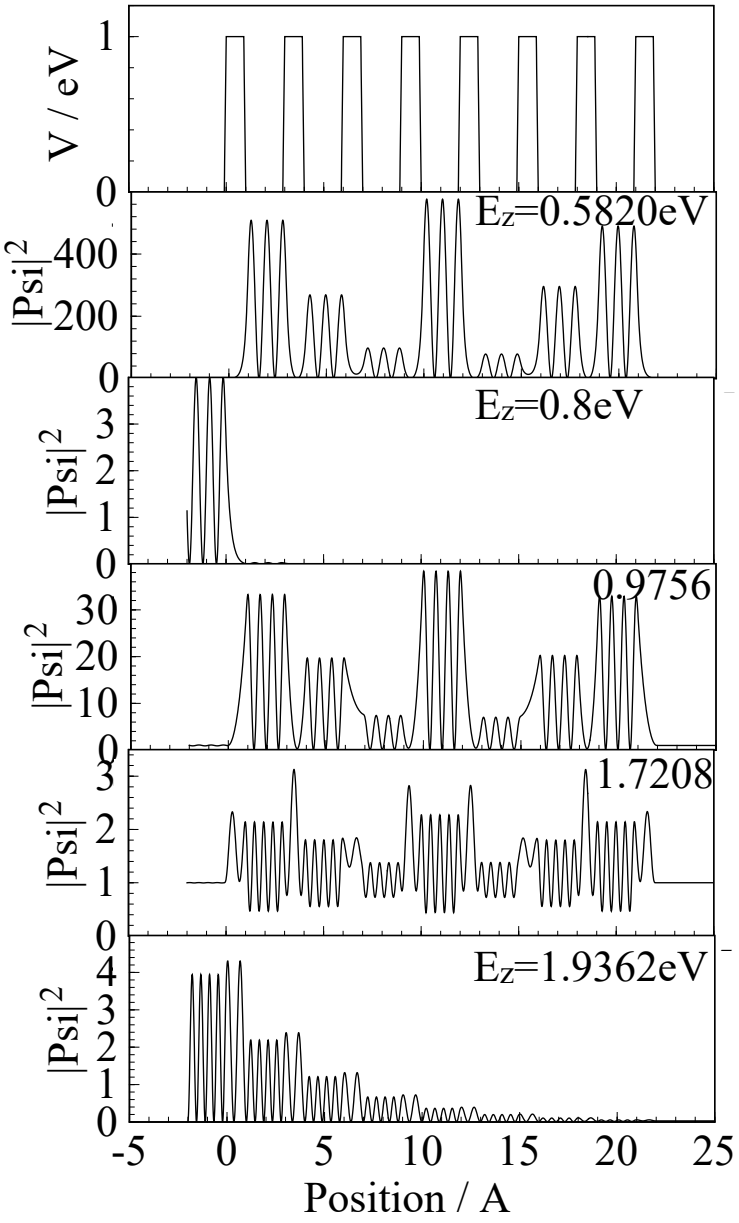




Wave function is scattered by the barrier (atom) and the transmittance must be < 1

=> For crystal with many atom, the total transmittance should be zero?

# Transmission through multiple quantum well (MQW): band



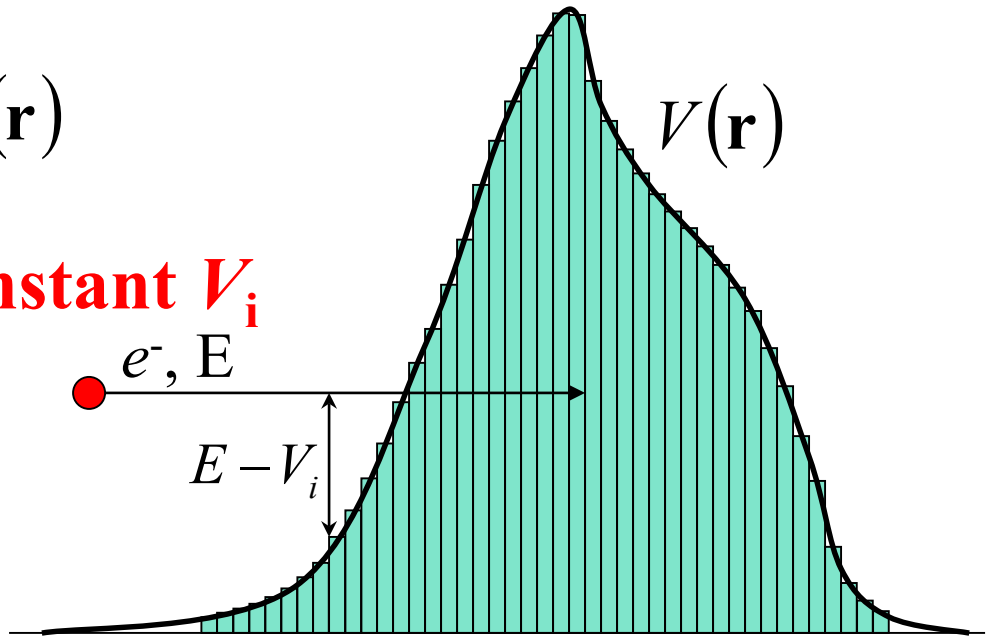
# Plain wave approx.: $e^-$ is a wave

**Schrödinger equation**

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

**By approximating $V(r)$ is constant $V_i$ in narrow region:**

$$\nabla^2\Psi(\mathbf{r}) = \frac{2m}{\hbar^2}[E - V_i]\Psi(\mathbf{r})$$




$$\Psi(\mathbf{r}) = A\exp(i\mathbf{k}_i \cdot \mathbf{r}) + B\exp(-i\mathbf{k}_i \cdot \mathbf{r})$$

$$k_i = \sqrt{\frac{2m}{\hbar^2}(E - V_i)}$$

**Exact $\Psi(r)$ is expressed as a connection of plain waves with different k in different regions**

# Plain wave basis

**Fourier transform**

Function with the period $a$ is expressed by summation of plain waves with wave vectors $k_l = \frac{2\pi}{a} l$

1D: $$f(x) = \sum_{l=-\infty}^{\infty} A_l \exp\left( i \frac{2\pi}{a} lx \right)$$

3D: $$f(\mathbf{r}) = \sum_{h,k,l=-\infty}^{\infty} A_{h,k,l} \exp\left( i\mathbf{G}_{hkl} \cdot \mathbf{r} \right)$$

Any function is exactly expressed if we can use infinite number of plain waves

- Due to limitation of time and memory, plain waves are limited

$$E_{cut} = \frac{\hbar^2}{2m_e} {k_{cut}}^2 = \frac{\hbar^2}{2m_e} \left| \boldsymbol{G}_{hkl,cut} \right|^2$$

Cut-off energy $E_{\mathrm{cut}}$ (or $k_{\mathrm{cut}}$, $|\boldsymbol{G}_{\boldsymbol{hkl},\mathrm{ut}}|$) limits the accuracy of the basis set

(For WIEN2k, $Rk_{\max} = \mathrm{Min}(R_{\mathrm{MT}}) * k_{\mathrm{cut}}$)

# Plain wave method

**Plain waves are employed as basis functions of LC**

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\sum C_{hkl}u_{hkl}(\mathbf{r}) \qquad u_{hkl}(\mathbf{r}) = \exp[i\mathbf{G_{hkl}}\cdot\mathbf{r}]$$

Plain waves with $\boldsymbol{G_{hkl}}$ forms a complete system for periodic functions:

If one can sum for all the *hkl* contribution, one can obtain the exact solution

=> **In actual we need to approximated by $|G_{\mathrm{hkl}}| < G_{\mathrm{max}}$ ($\hbar\omega < E_{\mathrm{cut}}$**

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \cdots & H_{1n}-ES_{1n} \\ H_{21}-ES_{21} & H_{22}-ES_{ss} & & H_{2n}-ES_{2n} \\ \vdots & & \ddots & \vdots \\ H_{n1}-ES_{n1} & H_{n2}-ES_{n2} & \cdots & H_{nn}-ES_{nn} \end{vmatrix} = 0$$

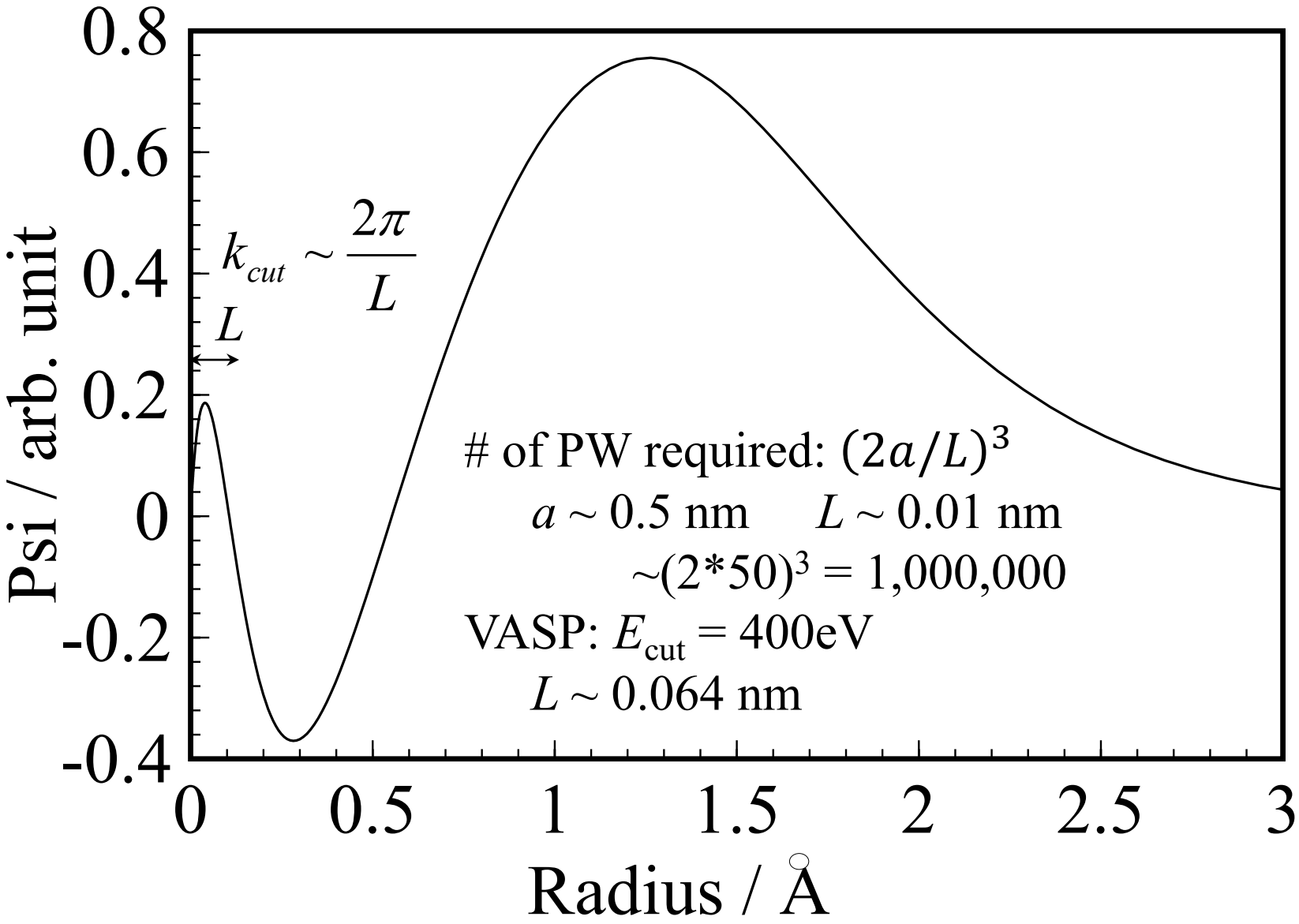
$$\langle u_{h'k'l'}|H|u_{hkl}\rangle = \int e^{-i(\mathbf{k}+\mathbf{G}_{h'k'l'})\cdot\mathbf{r}}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]e^{i(\mathbf{k}+\mathbf{G}_{kl})\cdot\mathbf{r}}d\mathbf{r}$$

$$= \delta_{hkl,h'k'l'}\frac{\hbar^2}{2m}k^2 + \underline{V^*(\mathbf{G}_{hkl}-\mathbf{G}_{h'k'l'})}$$

**Most of calculation time would be paid for Fourier transformation of potential**

**=> GPU can accelerate calculation speed efficiently**

# 3s radial function for Na atom (DV-Xα)



# How to reduce # of plain waves

- Orthogonalized Plane Wave Method: OPW
  Use combinations of plain waves that are orthogonal to core wave functions
- Pseudo Potential Method: PP
  Effective core potential (pseudo potential) that include the effects of nuclei charge and core electrons
  **CASTEP, VASP, PWscf**
- Augmented plain wave
  (L/APW: Linearlized/Augumented Plane Wave Method)
  Atomic wave functions are used in a limited sphere around nuclei (Muffin-Tin(MT) spheres), and plain waves are used outside
  **WIEN2k**
- Linear Combination of Atomic Orbitals: LCAO
  Atomic wave functions are used instead of plain wavesう
  **CRYSTAL, Gaussian, Atomistic Toolkit (VNL), DV-Xα**

# First-principles calculations and DFT

# 第一原理計算と密度汎関数理論

# General references for band calculations

## 初心者、材料学者向け

バンド構造を用いた材料開発（実践編）
　神谷利夫、応用物理学会結晶工学分科会
　　結晶工学スクールテキスト第14版（2018年）

材料電子論入門 第一原理計算の材料科学への応用
　田中功、松永克志、大場史康、世古敦人 共著、内田老鶴圃 (2017).

## 量子計算の実際

密度汎関数理論入門 理論とその応用
　佐々木泰造、末原茂共訳、吉岡書店 (2014).

## 量子計算の物理的基礎

固体電子構造論 密度汎関数理論から電子相関まで
　藤原毅夫著、内田老鶴圃 (2015)

物質の電子状態
　R.M. マーチン著、寺倉清之、寺倉郁子、善甫康成訳、 Springer Japan (2010).

密度汎関数法の基礎
　常田貴夫著、講談社 (2012).

# References for specific method / programs

- 第一原理シミュレータ入門 －**PHASE** ＆ CIAO－
  山本 武範、濱田 智之、山崎 隆浩、岡本 政邦
  アドバンスソフト発行、2004年初版
- 固体の中の電子 **WIEN2k** 入門追加版
  和光システム研究所、2006
- (Xα – APW) スレーター分子軌道計算
  菅野暁、足立裕彦、塚田捷、東京大学出版会 1982
- (LAPW) Planewaves, pseudopotentials, and the LAPW Method
  Ed. David J. Singh, Lars Nordstrom, Springer, 2006
- (**CRYSTAL**) Hartree-Fock ab inito treatment of crystalline solids
  C. Pisani, R. Dovesi, C. Roetti, Springer, 1988
- The LMTO Method
  H.L. Skriver, Springer, 1984
- (Tight-Binding) 固体の電子構造と物性
  W.A. ハリソン、現代工学社、1980

# Definition of first-principles calculations

**Broad definition:**

Provide answers with required accuracy based on fundamental physics equation without empirical parameters

**for Quantum calculations:**

**Provide high-accuracy total energy based on quantum physics equations only from atomic species and coordinates**

# What are known from total energy?

**FP calculation: Provide high accuracy total energy *E***

**=> In principle, all properties can be calculated**

- **Stable structure:** Find lattice parameters & atom coordinates with minimum *E*
- **Electronic structure (band structure):** $e_i(\boldsymbol{k}) = E(n_{\boldsymbol{k},i}) - E(n_{\boldsymbol{k},i} - 1)$
- **Elastic tensors**

$U = U_0 + \frac{1}{2}\sum_{i,j,k,l} C_{ijkl} e_{ij} e_{kl}$ Calculate $U(e_{ij})$ from $e_{ij}$

$\sigma_{ij} = \sum_{k,l} C_{ijkl} e_{kl}$ Calculate stress $\sigma_{ij}$ from $e_{ij}$

- **Dielectric tensors**

$U = U_0 + \frac{1}{2}\sum_{i,j} \varepsilon_{ij} E_i E_j$ Calculate $U(E_i)$ from $E_i$

$D_i = \varepsilon_0 + P_i = \sum_j \varepsilon_{ij} E_j$ Polarization $P_i$ are calculated from **Berry phase**

**Choice of energy function *U*:**

0 K, constant *V*: Internal energy *E* (total energy given by DFT)

0 K, constant *P*: Enthalpy $H = U + PV$

>0 K, constant *V*: Helmholz energy

$F = U + F_{\text{electron}} + F_{\text{phonon}}$

from electron DOS from phonon DOS

# What are known by first-principles?

1. **Visualize wave functions, charge density etc**
   - Carrier transport path, defects, electron localization etc
2. **High accuracy total energy**
   - Stabile structure
   - Atomic structures that are difficult determined by experiments (amorphous, soid-solutions, hydrogen etc)
   - **Formation energy etc**
   - Defect formation energy, Equilibrium Fermi level
3. **Quantitative calculations of electronic structure**

   Band structure
   Optical spectrum
   Carrier transport
   Chemical bond
   Magnetism
4. **Electron – lattice coupling properties**

   Elastic tensor, dielectric tensor (Bery phase), piezoelectric tensor etc
   Phonon dispersion, IR / Raman spectra

# Fundamental and variation of quantum theory

**Difference between classical and quantum theory:**

Planck constant $h = 6.626\times10^{-34}$ Js can be neglected or not

**Conjugate physical quantities $q, p_q$ must satisfy $[q, p_q] = qp_q - p_q q = ih/2\pi$**

=> Naturally lead to the Heisenberg's uncertainty relationship

**Formulation: Any of the following can be used, but some are better to solve some problem**

1. Heisenberg's matrix mechanics: Matrix equation
   Eigen values (Eigen energies) and eigen states(algebraic vectors) are obtained
2. **Wave mechanics (Schrödinger eq): Differential equation**
   **Incorporate quantum commutation relation to classical Hamiltonian**
   **Eigen values and eigen states (vectors in function space) are obtained**
3. Second quantization (Quantum field theory): Noncommutative algebraic equation
   Quantize fields so as to satisfy the quantum commutation relation
   Eigen values and eigen states (state vectors $\prod_q \hat{a}_q^\dagger |0\rangle$:
   Apply generation operator $\hat{a}_q^\dagger$ to vacuum $|0\rangle$)
4. **Density functional theory: Hohenberg-Kohn theorem**
   **Mathematics theorem: Physical properties are functionals of ρ($r$)**
   **One-electron eq similar to Schrödinger eq is used (Kohn-Sham equation)**

# No program that can calculate everythin

**Similar accuracy should be expected if 'first-principles' codes are used**

**=> We can combine / connect several programs that have required functions**

**Example:**

1. **Stable structure, electron structure: VASP (fast)**
2. **Core levels, XAS: Wien2k (can calculate core levels)**
3. **COOP/COHP : LOBSTER**
4. **Phonon dispersion : Phonopy**
5. **Raman scattering intensity : raman-sc**
6. **Carrier transport : BoltzTraP**

# (One-electron) Hartree-Fock equation

**Pauli exclusion principle:** Anti-symmetry of wave function against an exchange of two electrons

$$\left\{-\frac{1}{2}\nabla_l{}^2 - \sum_m \frac{Z_m}{r_{lm}} + \sum_m \int \frac{\varphi_m^*(\mathbf{r}_m)\varphi_m(\mathbf{r}_m)}{r_{lm}} d\mathbf{r}_m + V_{Xl}(\mathbf{r}_l)\right\}\varphi_l(\mathbf{r}_l) = \varepsilon_l \varphi_l(\mathbf{r}_l)$$

$$V_{Xl}(\mathbf{r}_l) = -\frac{\sum_m \int \frac{\varphi_l^*(\mathbf{r}_l)\varphi_m^*(\mathbf{r}_m)\varphi_m(\mathbf{r}_m)\varphi_l(\mathbf{r}_l)}{r_{lm}} d\mathbf{r}_m}{\varphi_l^*(\mathbf{r}_l)\varphi_l(\mathbf{r}_l)}$$

**One-electron Schrödinger equation considering the Pauli exclusion principle:**

**(one-electron) Hartree-Fock equation**

**The calculation of the four-center integrals of the exchange potential $V_{Xl}$ is very heavy**

**in particular for crystals**

# Slater's Xα method: towards LDA

Exchange potential of Hartree-Fock eqation

$$V_{Xl}(\mathbf{r}_l) = -\frac{\sum_m \int \frac{\phi_l^*(\mathbf{r}_l)\phi_m^*(\mathbf{r}_m)\phi_m(\mathbf{r}_m)\phi_l(\mathbf{r}_l)}{r_{lm}} d\mathbf{r}_m}{\phi_l^*(\mathbf{r}_l)\phi_l(\mathbf{r}_l)}$$

Approximate by plain waves

$$V_{Xl}(\mathbf{r}_l) = -3\alpha\left\{\frac{3}{4\pi}\rho_\uparrow(\mathbf{r}_l)\right\}^{1/3}$$

**Slater's Xα potential + Discreate Variational Integral = DV-Xα method**

**To be recognized as a variation of LDA (local density functional approximation)**
**Kohn-Sham exchange potential: $\alpha = 2/3$**

# Density Function Theory: DFT

## Hohenberg-Kohn theorem

1. For interacting electron gas in external potential $V_{ext}(\boldsymbol{r})$, $V_{ext}(\boldsymbol{r})$ is determined uniquely if all electron density $\rho(\boldsymbol{r})$ is given.
2. Total energy is given as a functional of $\rho(\boldsymbol{r})$ $E[\rho(\boldsymbol{r})]$, and the $\rho(\boldsymbol{r})$ that gives the minimum $E[\rho(\boldsymbol{r})]$ determines the ground state

- Easy incorporate electron correlation effects
  => good for many particle problems
- Fundamentally, both 'exchange interaction' and 'electron correlation interaction' are exactly incorporated as functionals of total electron density
- But, we need approximation through the functionals
- Usually one-electron equation is employed to solve actual problems

# One-electron eq: Kohn-Sham equation

Total energy

$$E = T_0[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|} d\mathbf{r}d\mathbf{r}' + E_{XC}[\rho]$$

Kinetic energy without interaction

Electron – nuclei interaction

Electron – electron interaction

Exchange interaction
Correlation interaction

**Variational principle**

$$\rho(\mathbf{r}) = \sum_i \phi_i^*(\mathbf{r})\phi_i(\mathbf{r})$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(\rho(\mathbf{r})) + V_{e-e}(\rho(\mathbf{r})) + V_{XC}(\rho(\mathbf{r}))\right)\phi(\mathbf{r}) = \varepsilon\phi(\mathbf{r})$$

**Identical to Schrödinger equation for a single electron syste**

**$V_{xc}$: Unknown. Assumption of DFT**

**What are the physical meaing of $\phi(r)$ and ε?**

# Schrödinger equation and DFT

**Hartree-Fock (HF) eq (One-electron Schrödinger eq)**

$$\left\{-\frac{1}{2}\nabla_l^{\,2}+V_{ext}(\mathbf{r}_l)+V_{e-e}(\mathbf{r}_l)+V_{Xl}(\mathbf{r}_l)\right\}\phi_l(\mathbf{r}_l)=\varepsilon_l\phi_l(\mathbf{r}_l)$$

**Kohn-Sham eq (DFT: Density Functional Theory)**

$$\left\{-\frac{1}{2}\nabla^2+V_{ext}(\rho(\mathbf{r}))+V_{e-e}(\rho(\mathbf{r}))+V_{XC}(\rho(\mathbf{r}))\right\}\phi(\mathbf{r})=\varepsilon\phi(\mathbf{r})$$

- **Similar equations**
  - **Schrödinger eq:**
    1. **Quantize classical Hamiltonian化**
    2. **The variables are coordinates of all electrons $r_l$**
    3. (HF) Energy eigen values correspond to ionization potential
  - **DFT:**
    1. Hohenberg-Kohn theorem（Ground state is determined by $\rho(r)$）
    2. **Depending only on the coordinate of the space $r$**
    3. Energy eigen values correspond to chemical potential

# Solutions of one-electron eq for H atom

## Hartree-Fock (HF) eq

$$\left\{-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \int \frac{\rho(\mathbf{r}_m)}{|\boldsymbol{r}_m - \mathbf{r}|} d\mathbf{r}_m - \int \frac{\rho(\mathbf{r}_m)}{|\boldsymbol{r}_m - \mathbf{r}|} d\mathbf{r}_m\right\}\varphi(\mathbf{r}) = \varepsilon\varphi(\mathbf{r})$$

**Self-interaction (SI) is cancelled for HF**

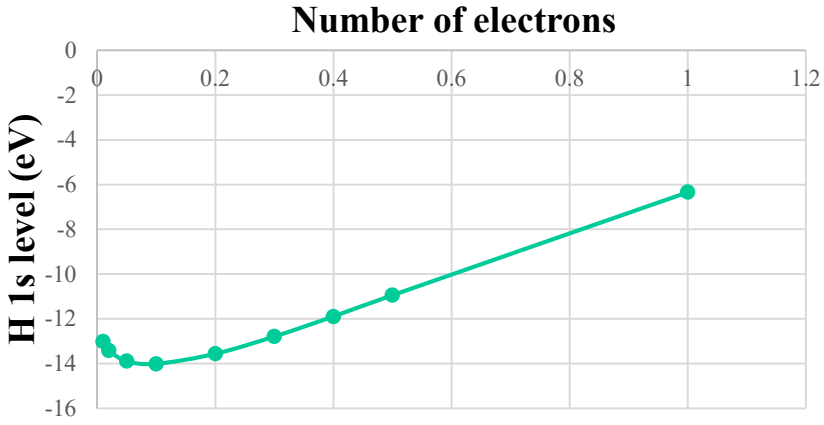
## Slater's X$\alpha$ (DFT)

$$\left\{-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \int \frac{\rho(\mathbf{r}_m)}{|\boldsymbol{r}_m - \mathbf{r}|} d\mathbf{r}_m - 3\alpha\left\{\frac{3}{4\pi}\rho(\mathbf{r})\right\}^{1/3}\right\}\varphi(\mathbf{r}) = \varepsilon\varphi(\mathbf{r})$$

**SI is not cancelled perfectly for DFT**

**Calculated by VASP with PAW LDA**
**NELECT varied**

**Exact: E(1s) = -13.6 eV**




| Ne | 1s | E(tot) |
|---|---|---|
| 0.01 | -13.0213 | 10.61942 |
| 0.02 | -13.4201 | 10.48618 |
| 0.05 | -13.892 | 10.0727 |
| 0.1 | -14.0148 | 9.3697 |
| 0.2 | -13.5659 | 7.98014 |
| 0.3 | -12.7931 | 6.655476 |
| 0.4 | -11.8945 | 5.416286 |
| 0.5 | -10.9442 | 4.270649 |
| 1 | -6.33495 | -0.02861 |
| HF | | |
| Analytical | -13.6 | -13.6 |

# Physical meaning of 'eigenvalue' $\varepsilon_i$

- **Hartree-Fock: Koopmans theorem**

  Energy difference by extracting an $e^-$ from a orbital

  $$\varepsilon_i = E(n_i) - E(n_i - 1)$$

  Corresponding to ionization potential

  Fundamentally corresponding to the binding energy measured by photoemission spectroscopy,
  but actually the calculated levels are overestimated (too deep)

- **DFT: Janak theorem**

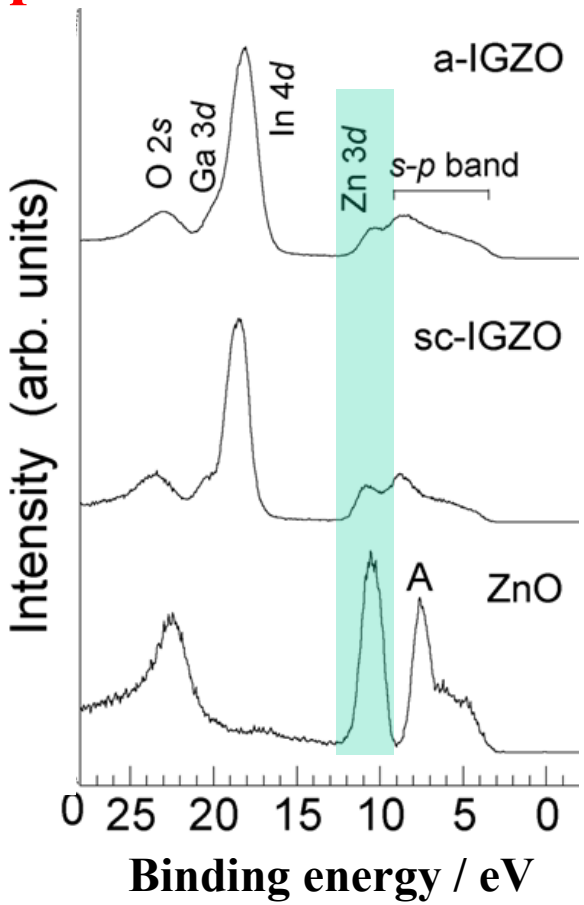
  $$\varepsilon_i = \frac{\partial E}{\partial n_i}$$

  Corresponding to chemical potential

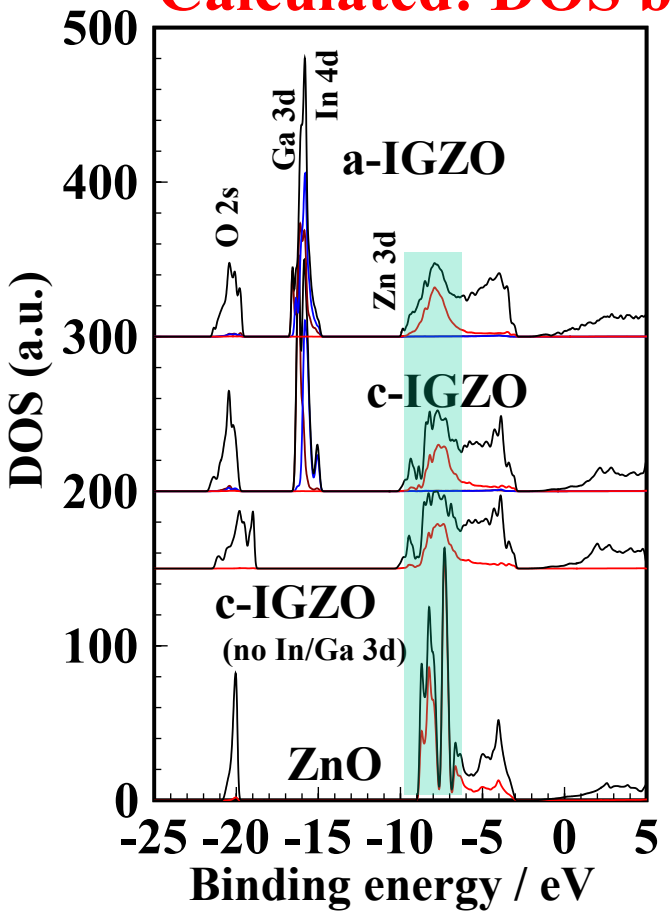
  Underestimated compared to PES binding energy

# XPS and DOS of Zn-based oxides

## Experimental: XPS




## Calculated: DOS by PBE




**Zn 3*d* measured from $E_F$**

XPS : -11 eV

DFT(PBE96) : -8 eV

**Underestimation problem of DFT**

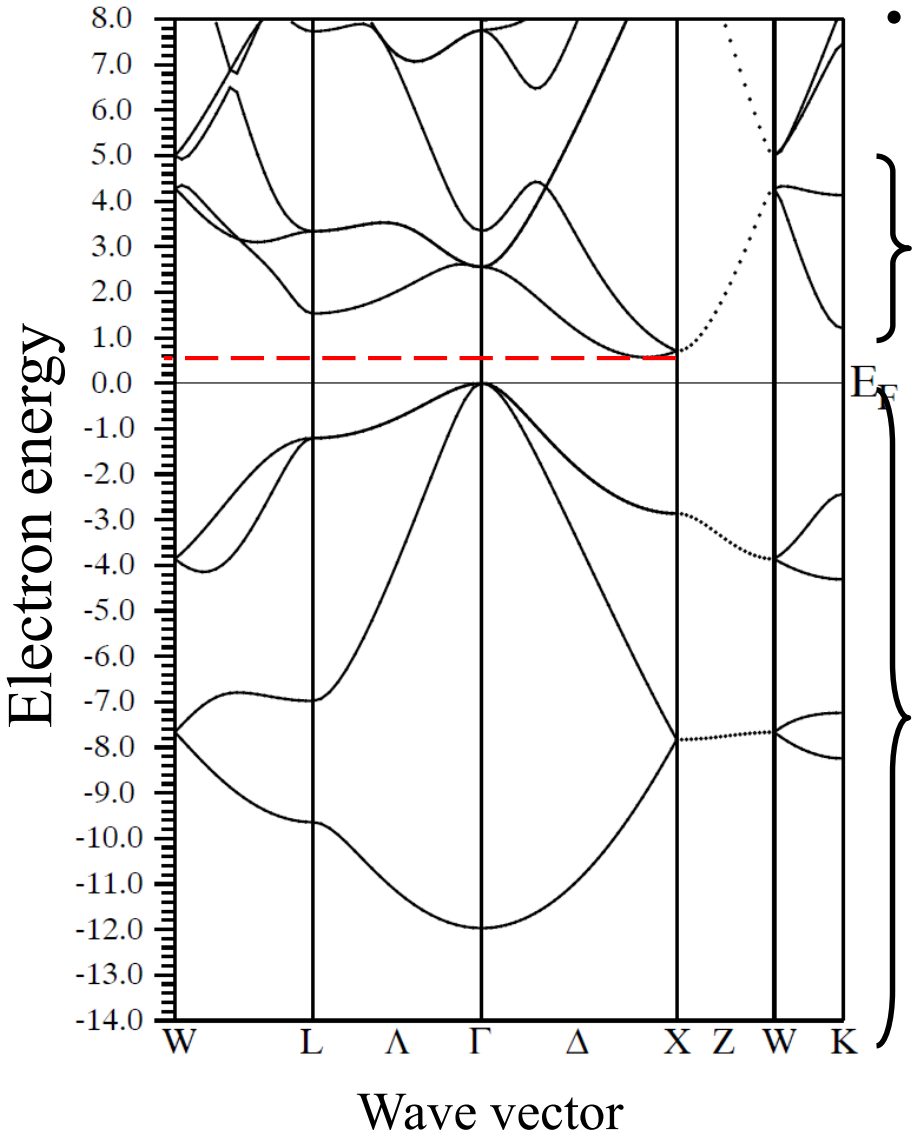
* Bandgap
* Deep levels
* Vacuum level

# How to understand band structure

# バンド構造の読み方

# How to read band structure

**Si** (WIEN2k, PBE96)




- **Vertical axis indicate the energy of $e^-$**
  That is, electron is more stable for deeper energy
- If not explained explicitly
  **The energy origin is the Fermi energy**
- **$e^-$ can take energy levels on the curves**

Unoccupied states (Conduction band)
Virtual states,
but empirically confirmed to reflect the actual CB

Occupied states
Valence band
Real states

# How to read band structure

1. Horizontal axis indicates
   Bloch's **wave vector *k***
   ***k*** can roughly be regarded as
   **the propagation direction of *e*⁻ momentum**

**What is wave number *k* …**

**Newton mech:** $E = \frac{m}{2}v^2 + V = \frac{P^2}{2m} + V$

$\mathbf{P} \rightarrow \hbar\boldsymbol{k}$

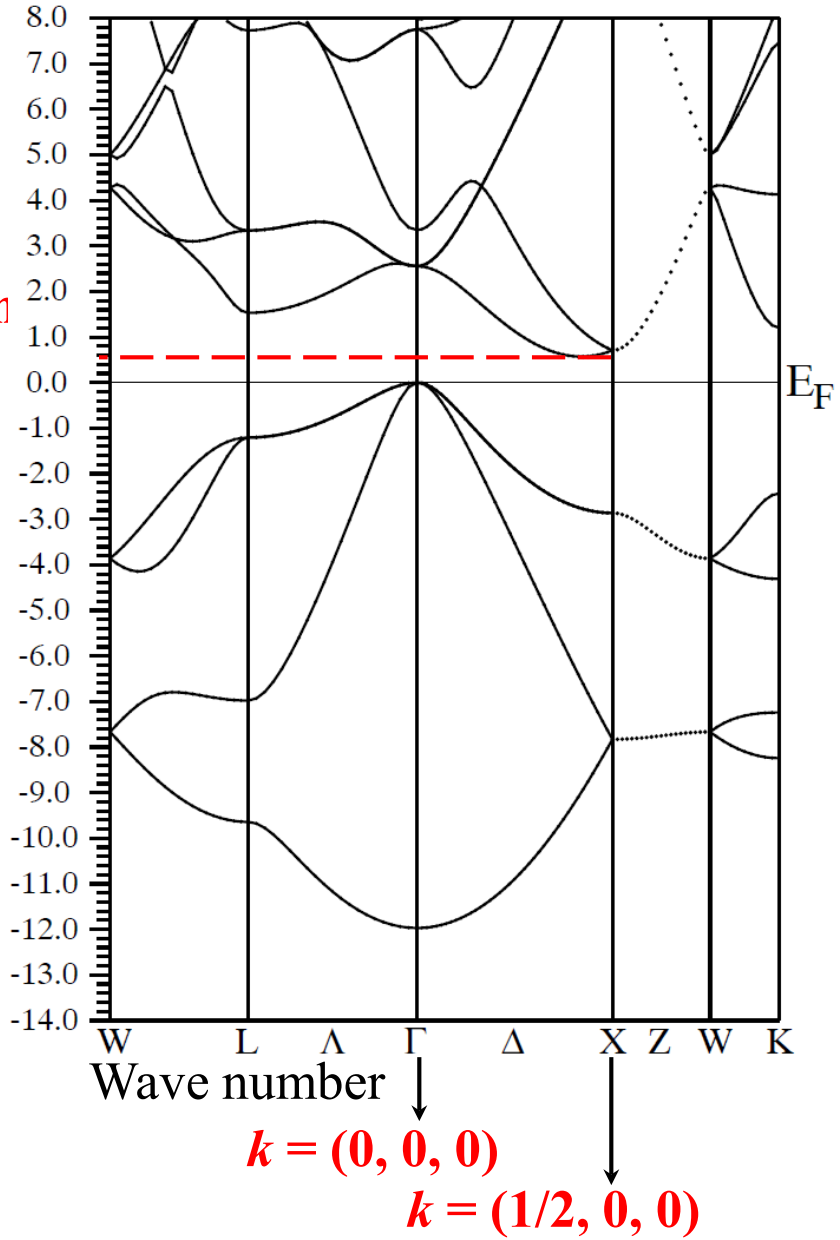
**Quant mech:** $E = \frac{\hbar^2}{2}k^2 + V$

**バンド理論 (Blochの定理)**

$$\phi_{kl} = \sum_j \exp\left(i\mathbf{k}\cdot\mathbf{r}_j\right)\cdot u_j(\mathbf{r}-\mathbf{r}_j)$$

***k***: Bloch's wave number
***ħk***: Crystal momentum

***Note*: The direction of velocity is *–k* for negative *m***

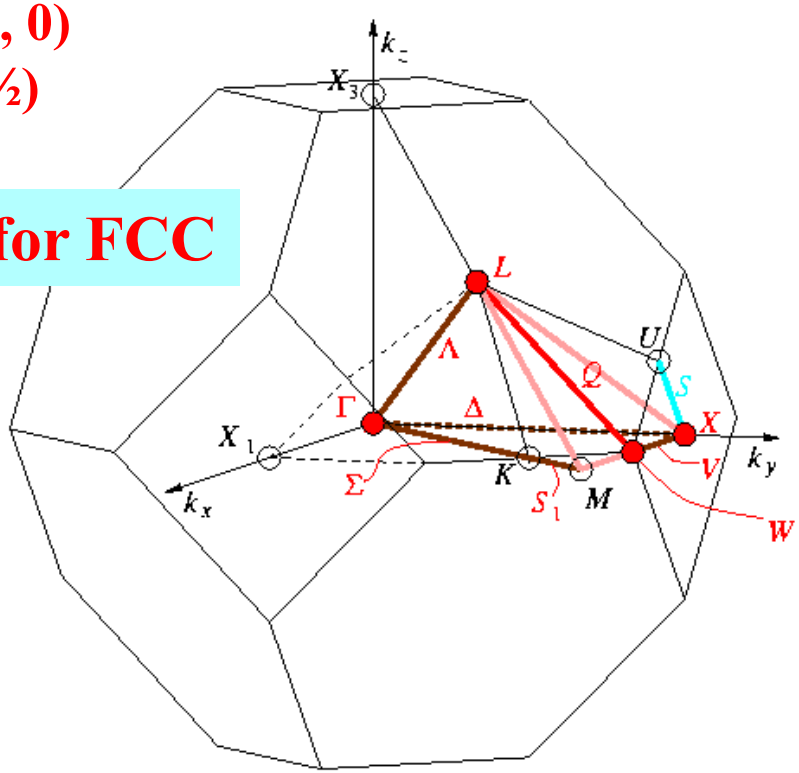


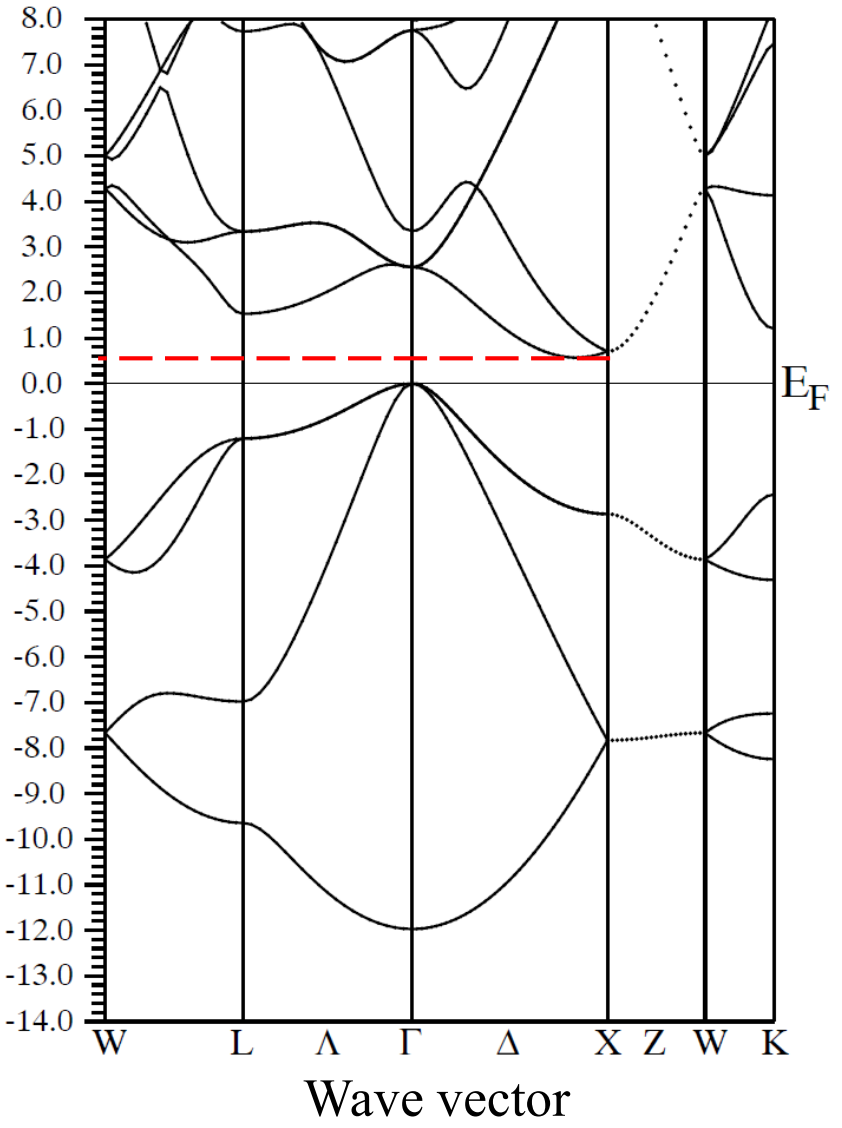
# How to read band structure

Only high-symmetry ***k*** points are drawn
W, L, Γ, X, K etc indicate
the **high-symmetry *k* points and lines**
Check e.g. by databases

for simple lattice
**Γ: *k* = (0, 0, 0) (unit may be in e.g. 1/*a*)**
**X: (1/2, 0, 0)**
**Z: (0, 0, ½)**

**1st BZ for FCC**



# How to know the definitions of the symbols – Crystallographic database –

## http://www.cryst.ehu.es/cryst/

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**Space-group symmetry**

| | |
|---|---|
| GENPOS | Generators and General Positions of Space Groups |
| WYCKPOS | Wyckoff Positions of Space Groups |
| HKLCOND | Reflection conditions of Space Groups |
| MAXSUB | Maximal Subgroups of Space Groups |
| SERIES | Series of Maximal Isomorphic Subgroups of Space Groups |
| WYCKSETS | Equivalent Sets of Wyckoff Positions |
| NORMALIZER | Normalizers of Space Groups |
| KVEC | The k-vector types and Brillouin zones of Space Groups |
| SYMMETRY | Geometric interpretation of matrix column representations of |

Quick access to some tables: Space Groups, Plane Groups, Layer Groups

Bilbao Crystallographic Server in forthcoming schools and workshop

News:

- New Artic … Acta Crys … 05/2019: Gal … al. "Automati … calculation o … symmetry-ac … tensors in m … and non-mag … materials: a … tool of the Bi … Crystallograp … Server." *Acta* … (2019) **A75**, … 447.
- New Artic … Nature 03… Vergniory *et* …

The k-vector types and Brillouin zones of the space groups

**Brillouin-zone databases of space groups**

The Brillouin-zone database offers **k**-vector tables and figures which form the background of a classification of the irreducible representations of all 230 space groups.

The space groups are specified by their sequential number as given in the *International Tables for Crystallography*, Vol. A. You can give this number, if you know it, or you can choose it from the table with the space group numbers and symbols if you click on *choose it*.

To get the **k**-vector types described in three different basis (primitive, conventional and ITA) click on the bottom *Comparative listing of k-vector types*.

To get the **k**-vector types using a minimal reciprocal wyckoff position click on the bottom *Optimized listing of k-vector types using ITA description*.

If you are using this progam in the preparation of a paper, please cite it in the following form:

M. I. Aroyo, D. Orobengoa, G. de la Flor, E.S. Tasci, J. M. Perez-Mato and H. Wondratschek.

Please, enter the sequential number of the space group as given in *International Tables for Crystallography*, Vol. A, or choose it: 223

Comparative listing of k-vector types

Optimized listing of k-vector types using ITA description

k-vector identification

Bilbao Crystallographic Server → k-vector types and Brillouin zones

The k-vector types of space group *Pm-3n* (223)

(Table for arithmetic crystal class m -3 mP)

Pm-3m-$O_h^1$ (221) to Pn-3m- $O_h^4$(224)

Reciprocal-space group (Pm-3m)*, No.221

Brillouin zone

| k-vector description | | ITA description | | | |
|---|---|---|---|---|---|
| CDML[1] | | Wyckoff Position | | | Coordinates |
| Label | Coefficients | | | | |
| GM | 0,0,0 | 1 | a | m-3m | 0,0,0 |
| R | 1/2,1/2,1/2 | 1 | b | m-3m | 1/2,1/2,1/2 |
| M | 1/2,1/2,0 | 3 | c | 4/mm.m | 1/2,1/2,0 |
| X | 0,1/2,0 | 3 | | | |
| DT | 0,u,0 | 6 | | | |
| T | 1/2,1/2,u | 6 | | | |
| LD | u,u,u | 8 | | | |
| Z | u,1/2,0 | 12 | | | |
| SM | u,u,0 | 12 | | | |
| S | u,1/2,u | 12 | | | |
| A | u,v,0 | 24 | | | |
| B | u,1/2,v | 24 | | | |
| C | u,u,v[GMMR] ex | 24 | | | |
| J | u.v.u[GMXR] ex | 24 | | | |

The k-vector types of space group *Pm-3n* (223)

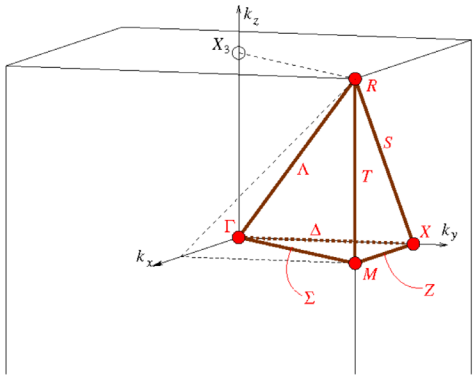
**Brillouin zone**

( Diagram for arithmetic crystal class m -3 mP )

Pm -3 m-$O_h^1$ (221) to Pn -3 m-$O_h^4$ (224)

Reciprocal-space group ( Pm -3 m )*, No. 221

The table with the k vectors.

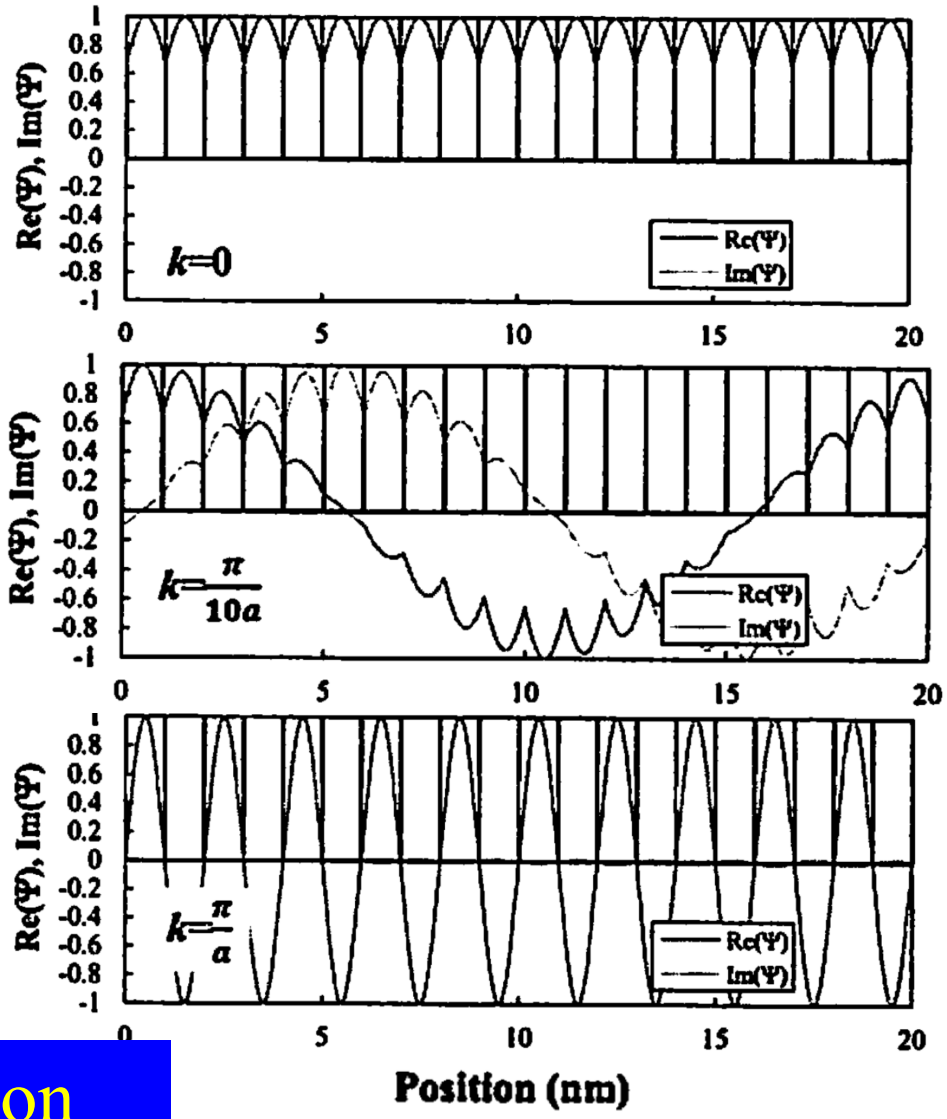


# Meaning of Bloch's $k$ vector *(by Prof. Sugiyama)*

Γ ($k$=0) : Bonding

Arbitrary $k \neq 0$ :
Considering many unit cells

BZ boundary : }
Anti-bonding




Shape of crystal wave function is very different depending on $k$

# Band structure: metal

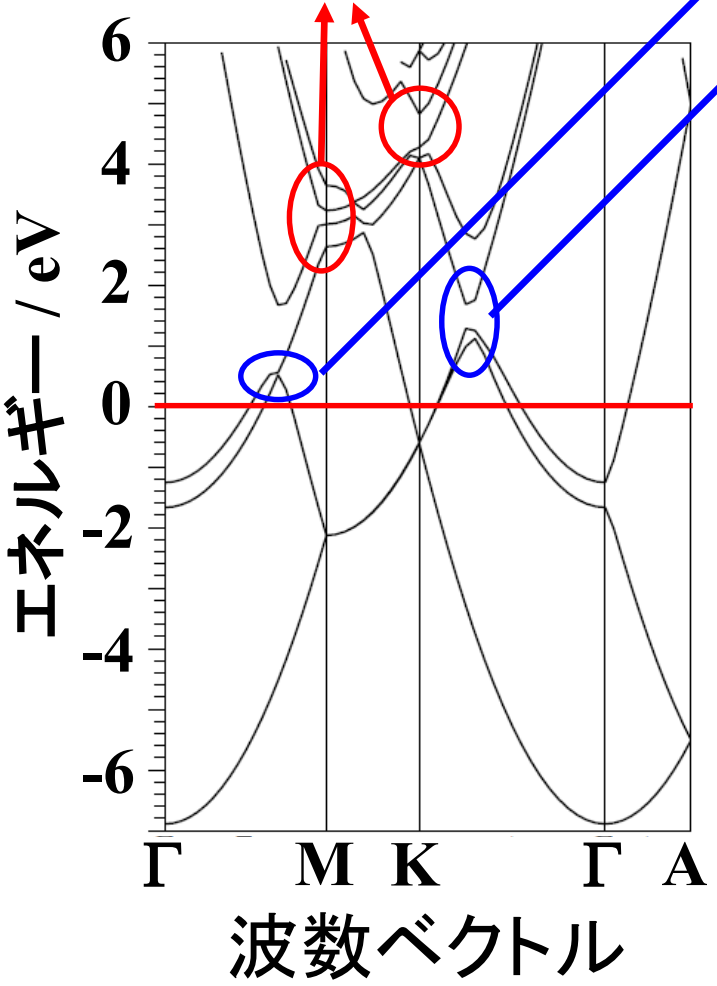
## Mg

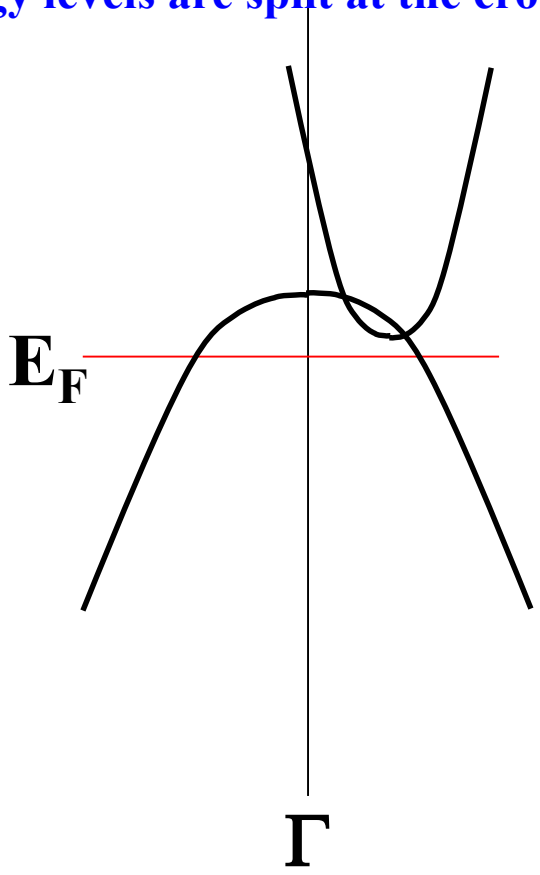
$E_g$ by free electron model:

Bragg diffraction

Two bands are crossing
=> Different symmetry

If two wave functions with the same symmetry,
the energy levels are split at the crossing point

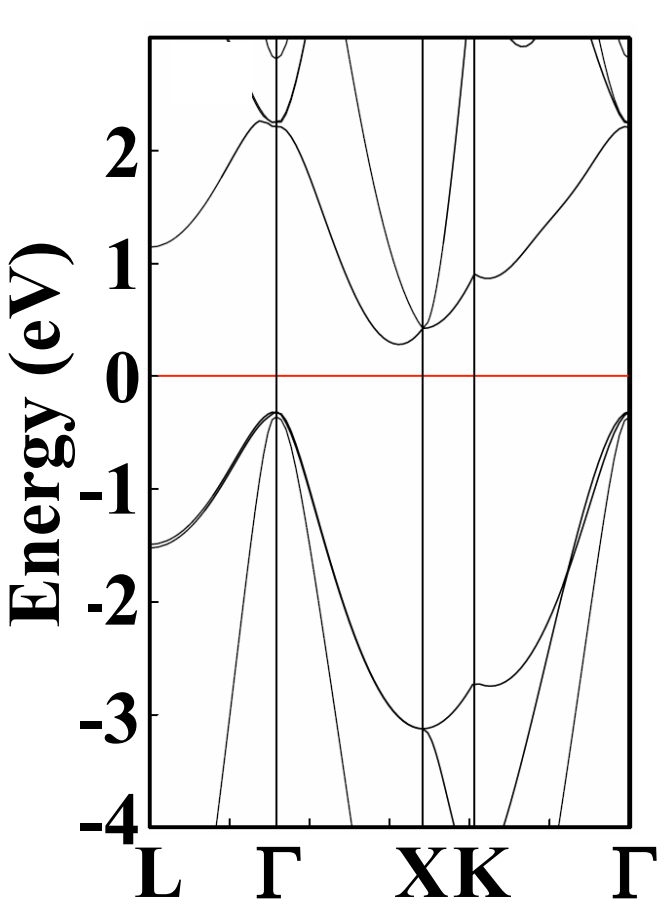


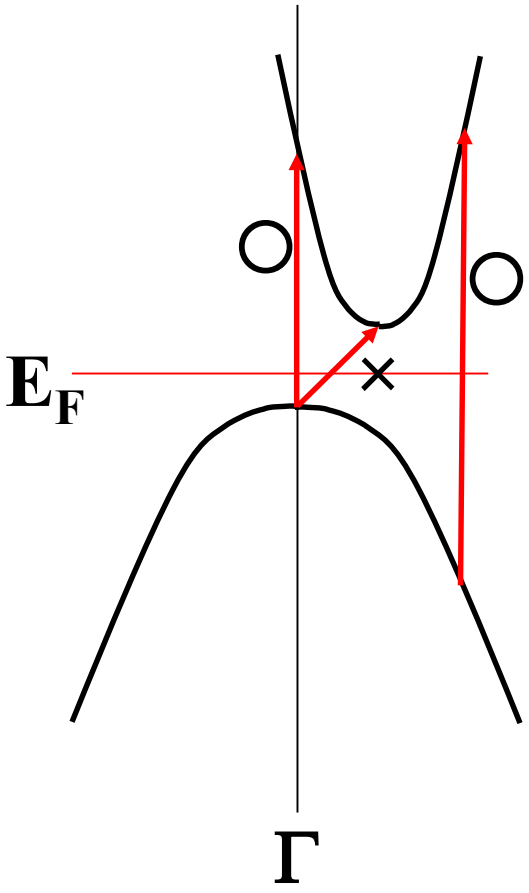



# Band structure: Semiconductor

**Si Indirect-transition type:**

**Optical absorption coefficient is very small near the fundamental bandgap**



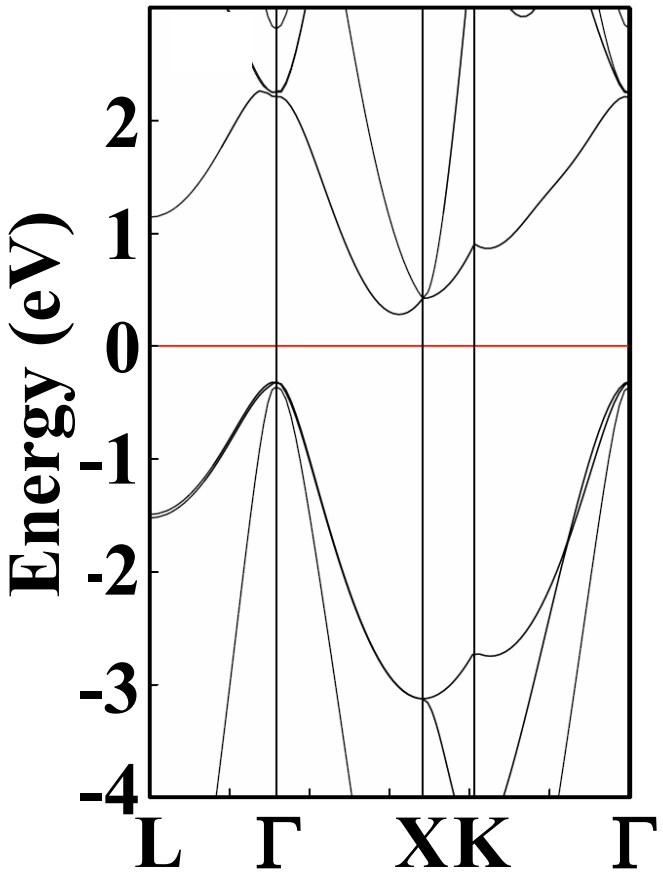
# Band structure: Semiconductor

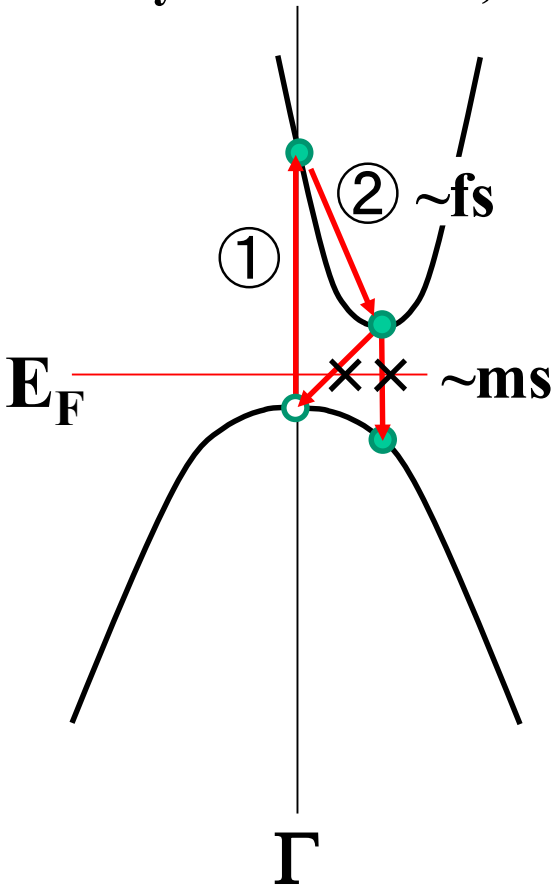
**Si Indirect-transition type:**

**Weak optical absorption, not good for solar cell**

**Slow recombination, good for solar cell**

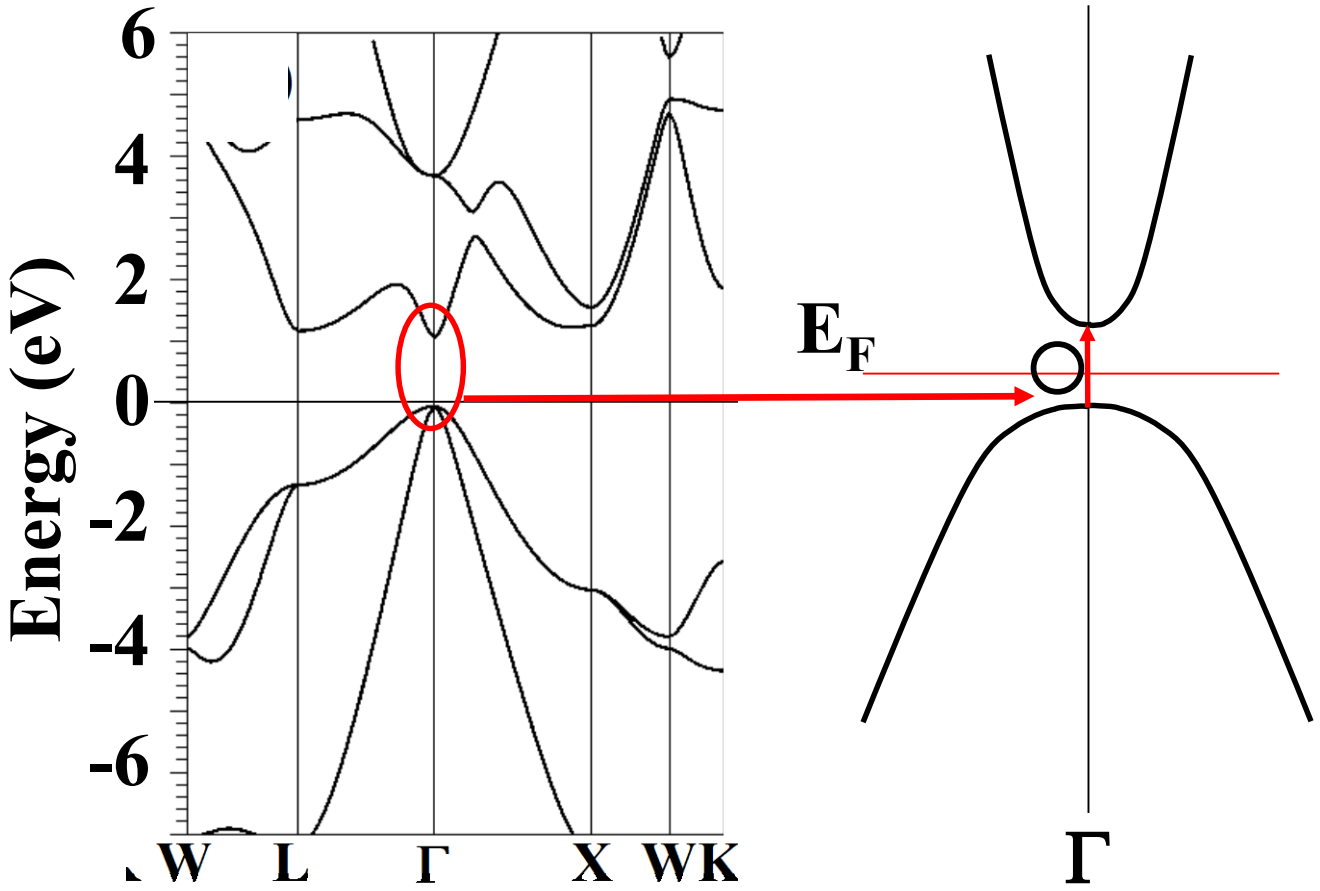
**Non-radiation recombination may be dominant, bad for LED**



# Band structure: Semiconductor

**GaAs Direct-transition type: Strong optical absorption**
**good for solar cell**

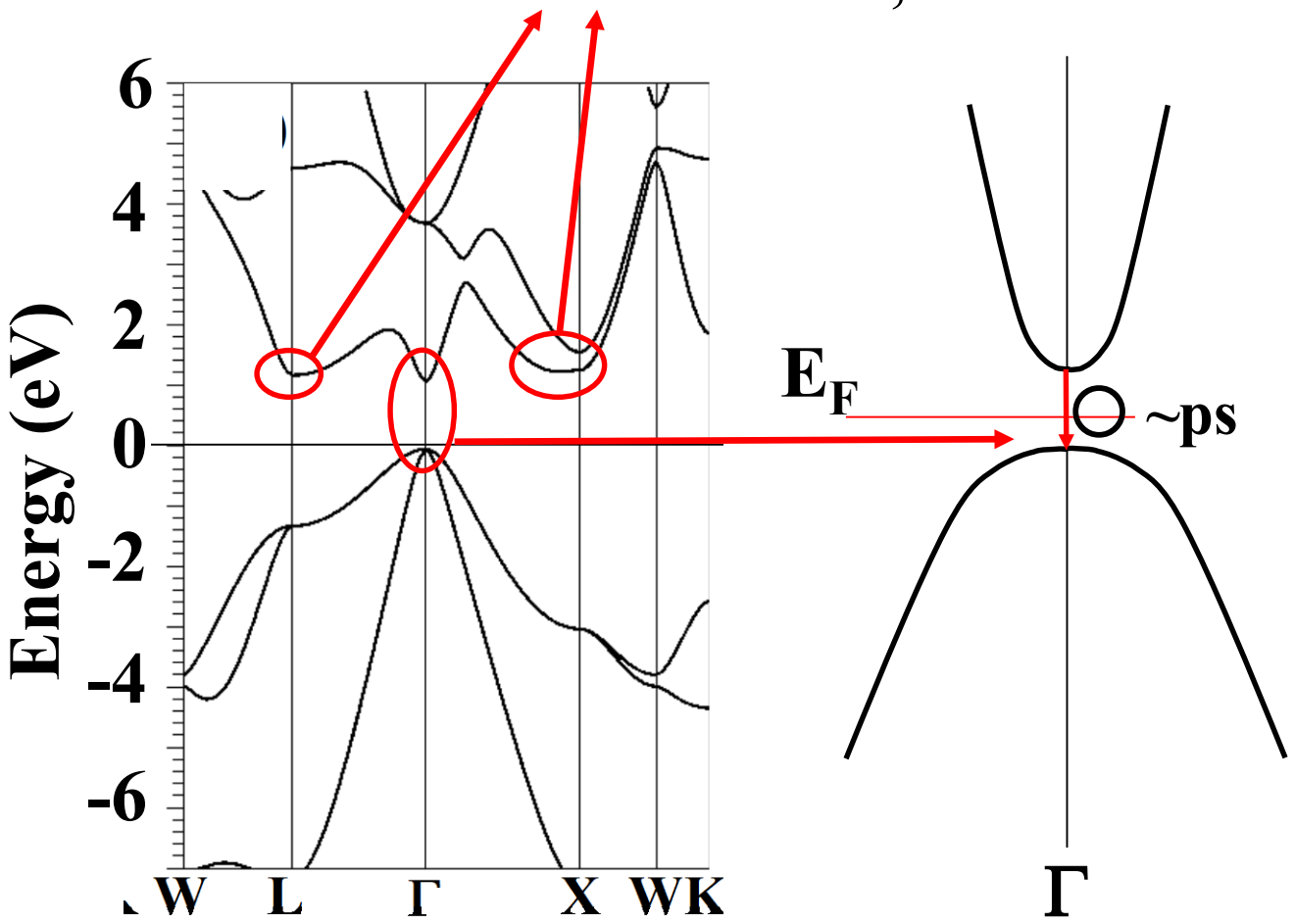


# Band structure: Semiconductor

**GaAs Direct-transition type: Fast recombination**

**Radiative recombination may be dominant, good for LED**

**Indirect-transition at CBM, better for solar cell**



# First-principles calculation: Effective mass

# 第一原理計算: 有効質量

# Effective medium / Effective mass approximation

**Semiconductor have many atoms that may scatter $e^-$, but**

**Thanks to the Bloch's theorem (the band theory),**
**$e^-$ at the Bloch state $E(k)$ is not scattered by the periodic atoms**

- **The host is regarded as a uniform continuous media with the dielectric permittivity ε**
- **Electrons in crystal are treated as free electrons, but it has effective mass $m_e^*$ and the charge $-|e|$**

**If one know ε, $m_e^*$, and $m_h^*$,**
**a variety of properties would be calculated**

# Known from effective mass (free $e^-$ approx.)

Mobility, conductivity $\mu = \frac{e\tau}{m_e^*}$ $\sigma = eN_{free}\mu$

Density of state function $M_C$ is the degeneracy of LUMO

$$N(E) = M_C \frac{\sqrt{2}}{\pi^2} \frac{\sqrt{E - E_C}}{\hbar^3} m_{de}^{3/2}$$

Burstein-Moss shift
($E_F$ of degenerated semiconductor) $\Delta E_g^{BM} = \frac{h^2}{m_{de}} \left( \frac{3N_e}{16\sqrt{2}\pi} \right)^{2/3}$

Effective density of state $N_C$, $N_V$

for isotropic CBM/VBM that does not have extra degeneracy other than spin, density-of-states effective mass $m_{de}$ is equal to carrier effective mass $m_e^*$.

$$N_C = 2\left( \frac{2\pi m_{de} k_B T}{h^2} \right)^{3/2} M_C$$

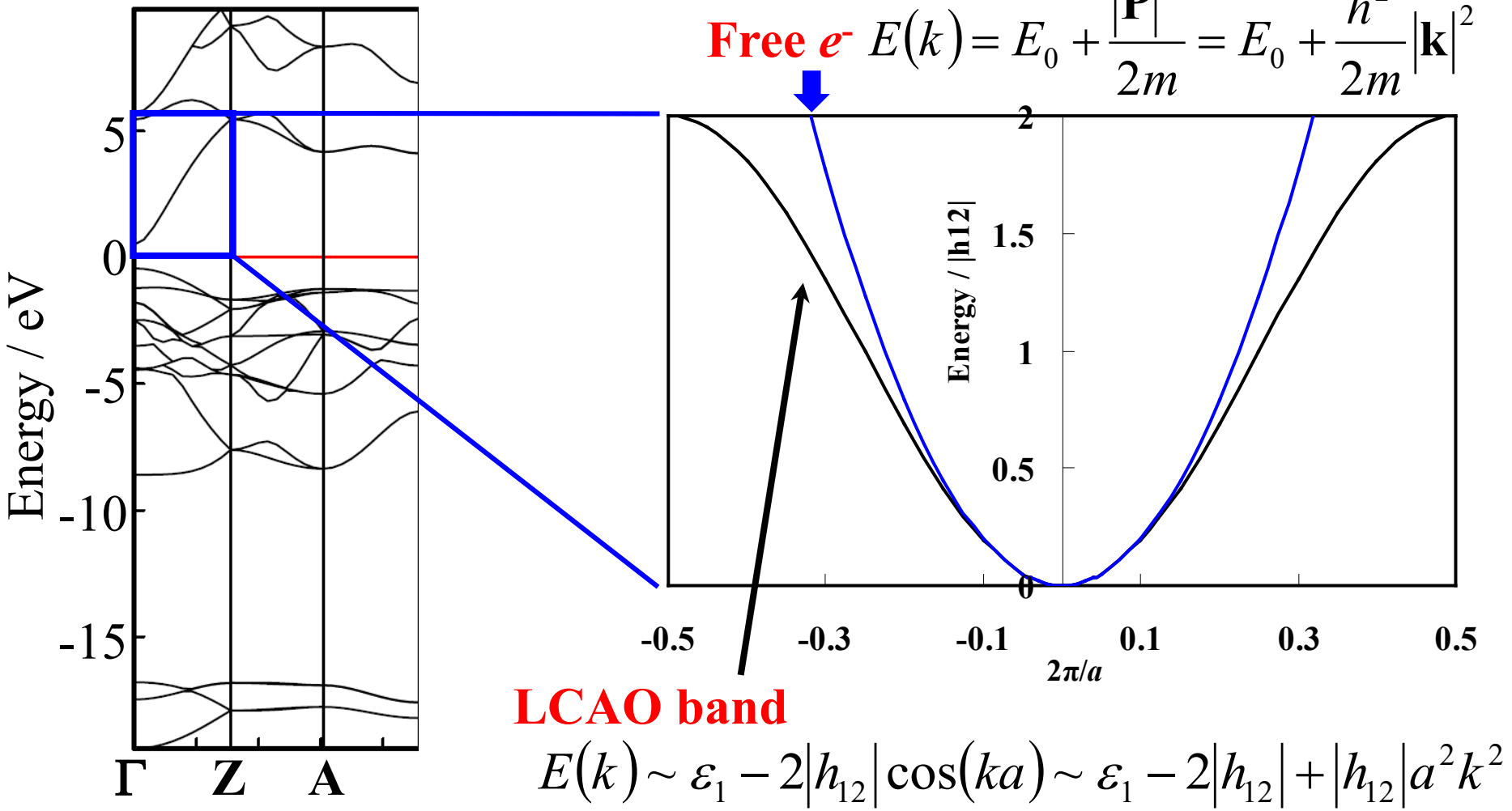
Thermal velocity $\frac{1}{2} m_e^* v_{th}^2 = \frac{3}{2} k_B T$ $v_{th} = \sqrt{3k_B T / m_e^*}$

Fermi velocity $\frac{1}{2} m_e^* v_F^2 = E_F - E_C$ $v_F = \sqrt{2(E_F - E_C)/m_e^*}$

# Effective mass

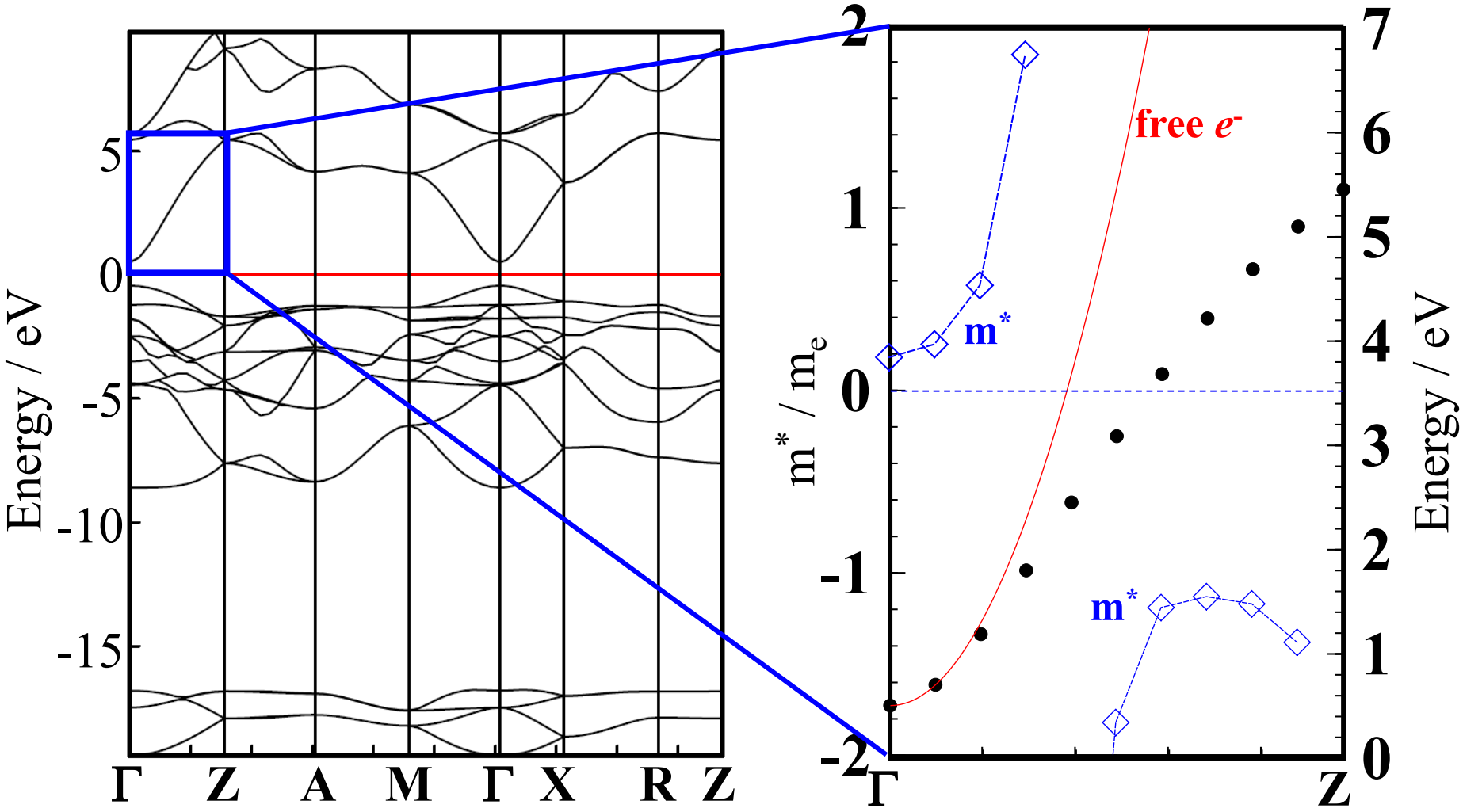
$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 E_n(\mathbf{k})}{\partial k^2}$$

**Band structure of $SnO_2$**

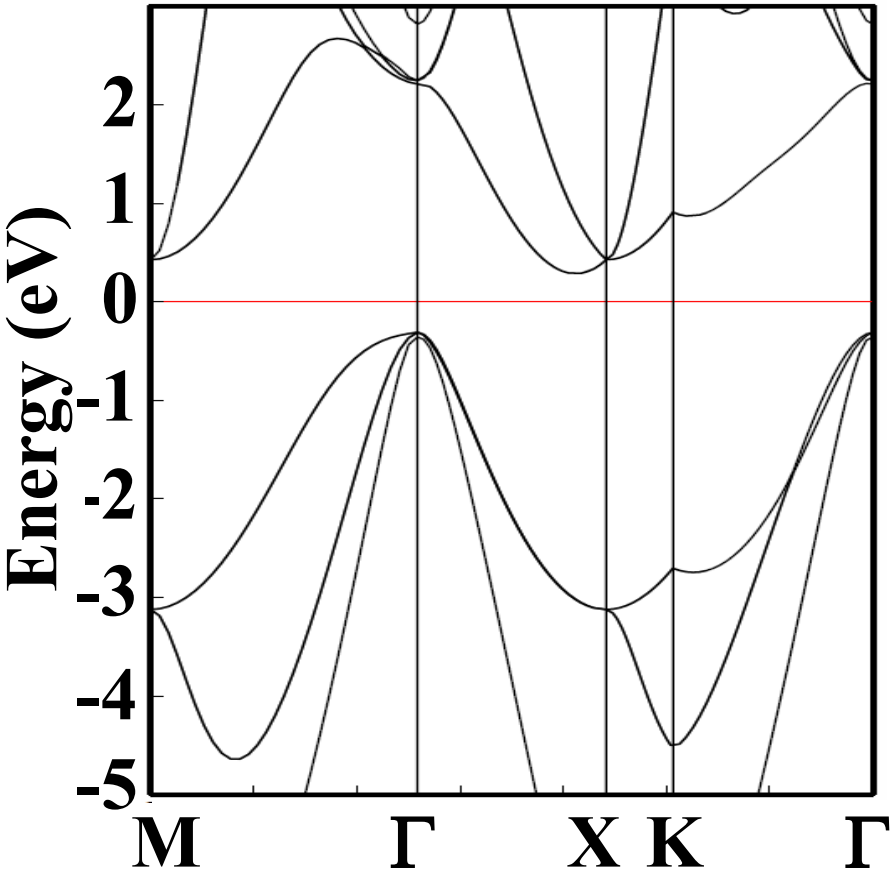


# Effective mass: $SnO_2$

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 E_n(\mathbf{k})}{\partial k^2}$$



# Effective mass in Si




## Experimental

| | | |
|---|---|---|
| $e^-$ | | |
| Longitudinal $m_{le}^* = 0.98$ | Transversal $m_{te}^* = 0.19$ | DOS $m_{de}^* = 0.33$ |
| $h^+$ | | |
| Heavy hole $m_{hh}^* = 0.49$ | Light hole $m_{lh}^* = 0.16$ | |
| Split-off (SO) band (spin-orbit) $m_{soh}^* = 0.29$ | | DOS $m_{dh}^* = 0.55$ |

## Calculated

**$e^-$:**

**$m_{le}^* = 0.96m_e$, $m_{te}^* = 0.09m_e$**

**$h^+$:**

**lh $0.19m_e$ (isotropic)**

**hh $0.83m_e$ (<110>) $0.26m_e$ (<100>)**

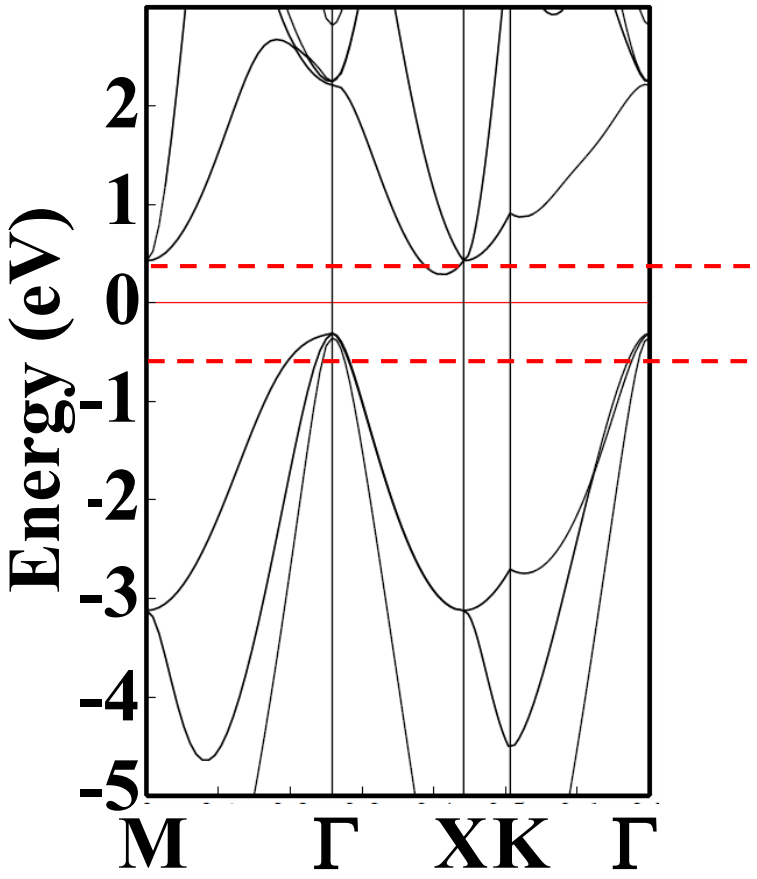
**Split off hole band**

**$0.14m_e$ (<110>) $0.22m_e$ (<100>)**

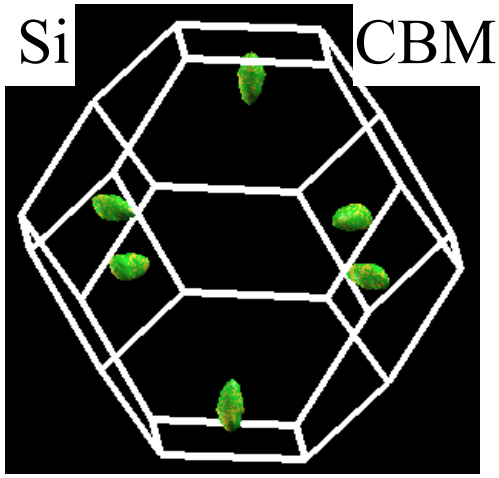
**$k \cdot p$ perturbation method**

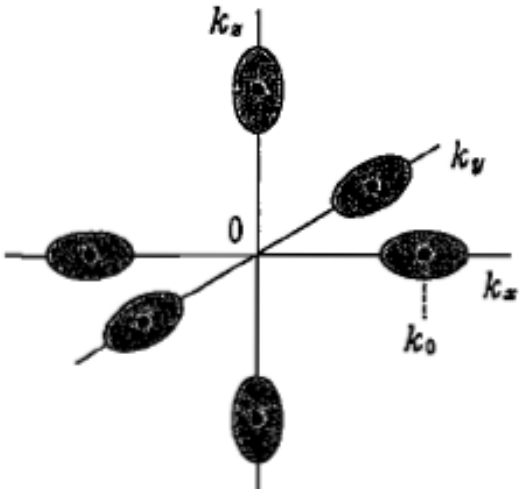
$$m_e^* = \left(1 + 2P^2 / m_e E_g\right)^{-1} m_e$$

# Fermi surface of Si

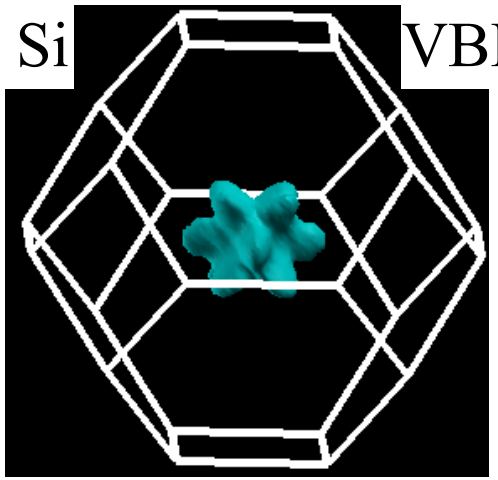


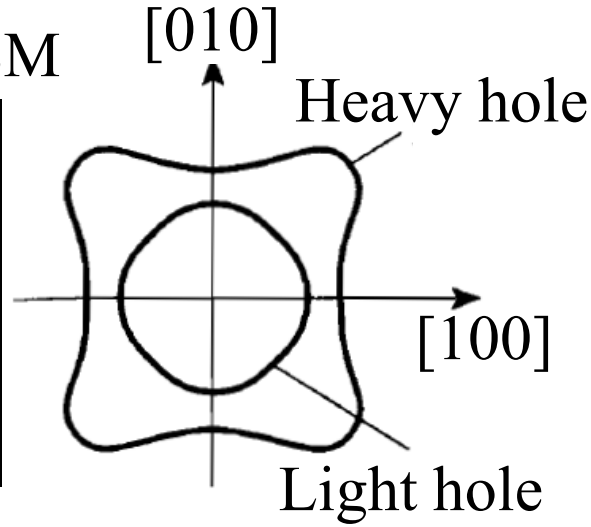

Si CBM






Si VBM






**Widened Fermi surface**

**$\Rightarrow$ $k$ for the same $E = \hbar k^2/2m_e$ is larger**

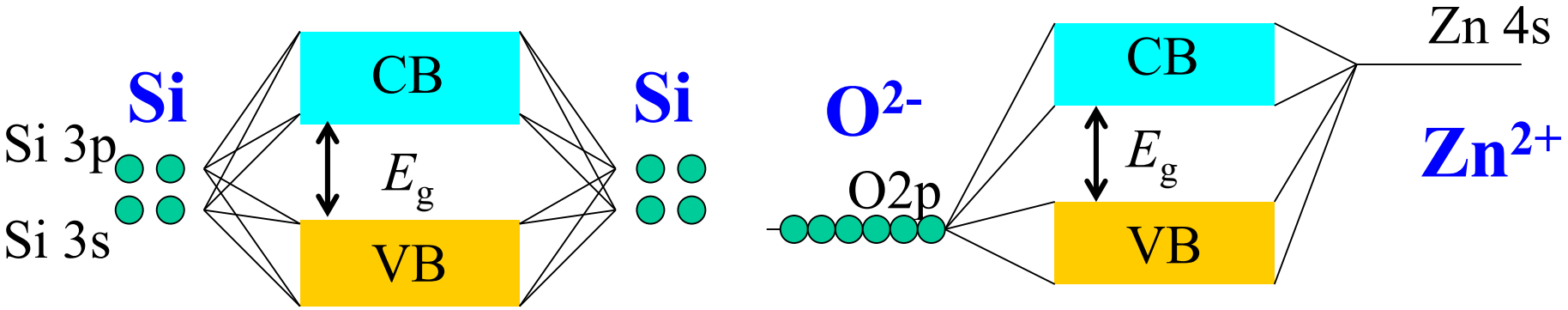
**$\Rightarrow$ Larger effective mass**

# First-principles calculation: Bandgap problem and functional

# 第一原理計算: バンドギャップ問題と汎関数

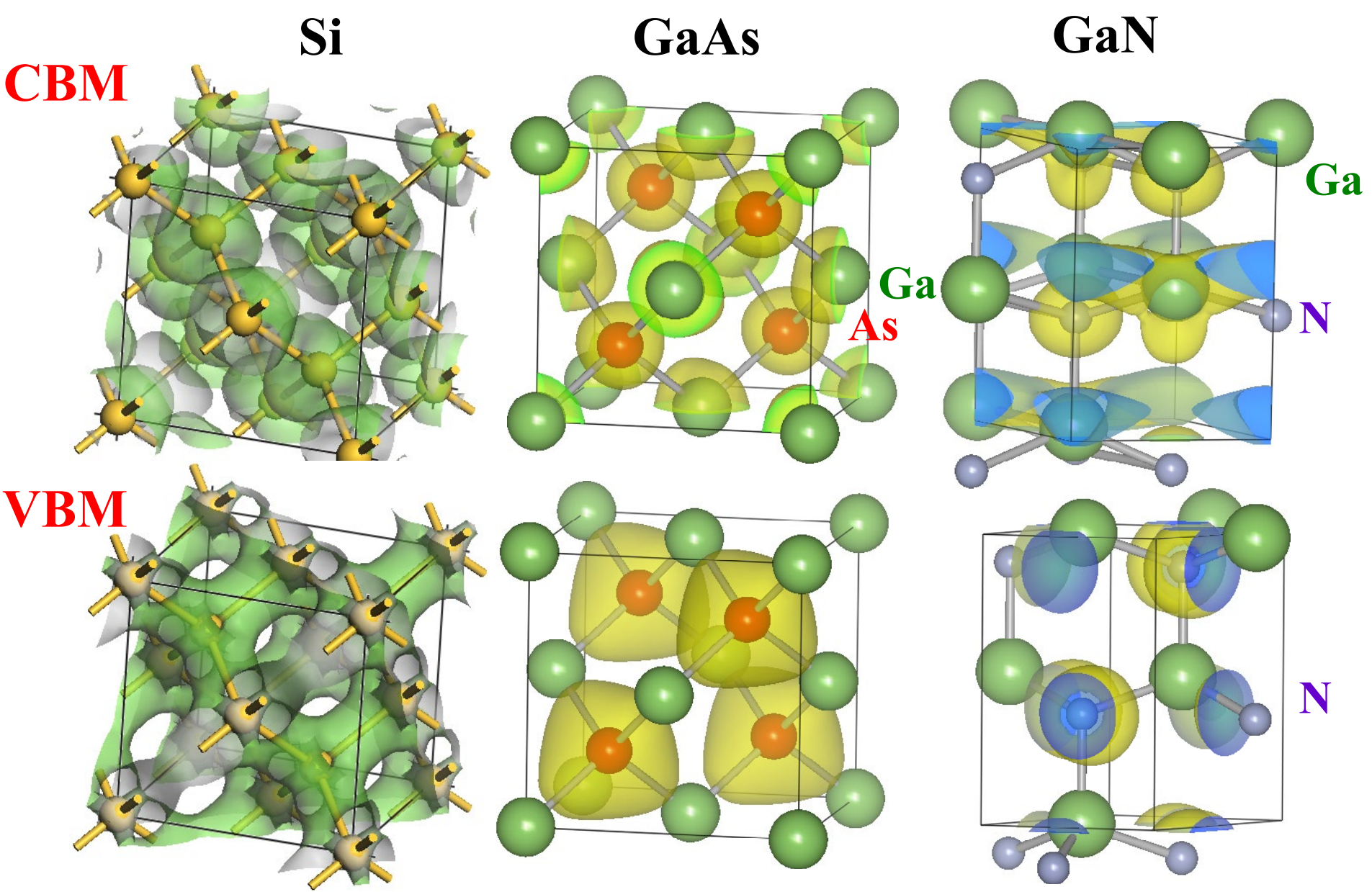
# Origins of bandgap

1. **Covalent materials, e.g. in Si**
   Energy splitting due to bonding and anti-bonding levels
2. **Ionic materials, e.g., in oxides**
   Energy level difference in cation and anion contribut much
   (covalent $E_g$ + ionic $E_g$)



# Wave function (Electron density)

VASP,PBE96



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3. **Interference at BZ boundary**: Bragg diffraction
   appears in (nearly) free electron approximation,
   but usually not appear around $E_F$.
   Important e.g. for Peiels transition
4. Strong electron correlation materials
   Eg can not be explained by one-electron mean-field approximation such as DFT.
   Important for d and f electrons systems.
   Can be treated by beyond DFT methods like LDA/GGA+U, GW approximations.

# Functionals:

## Exchange functionals and correlation functionsl

**Density functional theory (DFT): Kohn-Sham equation**

$$\left\{-\frac{1}{2}\nabla^2 + V_{ext}(\rho(\mathbf{r})) + V_{e-e}(\rho(\mathbf{r})) + V_{XC}(\rho(\mathbf{r}))\right\}\phi(\mathbf{r}) = \varepsilon\phi(\mathbf{r})$$

**$V_{XC}$ is unknown**

**=> Many $V_{XC}$ have been proposed based on a variety of approximations**

# Functionals:

## Exchange functionals and correlation functionsl

**L(S)DA: Local (Spin) Density Approximation**

$$V_{Xc} = -3\alpha\left((3/8\pi)\rho(\mathbf{r})\right)^{\frac{1}{3}}$$

**Local: determined only by the electron density at the point *r***

**Non-local: Incorporate information other than the point *r***

**=> Use derivative of electron densityる**

**GGA: Generalized Gradient Approximation**

$$x_\sigma = \left|\nabla\rho_\sigma\right| / \rho_\sigma^{\frac{4}{3}}$$

$$E_{XC} = E_{XC}^{LSDA} - b\sum_\sigma \int \rho_\sigma^{\frac{4}{3}} \frac{x_\sigma^{\,2}}{1 + 6bx_\sigma \sinh^{-1} x_\sigma} dv + E_X^{NL}$$

**Exact exchange:**

**Hartree-Fock exchange potential**

# Functionals

**LDA/LSDA:**

**CA** (Ceperley-Alder)/PZ (Perdew-Zunger) [Perdew and Zunger, Phys. Rev. B **23** (1981) 5048]

**PW92** (Perdew-Wang 92) [J.P. Perdew and Y. Wang, Phys. Rev. B **45** (1992) 13244]

**GGA:**

**Becke88, PW91**, **PBE (PBE96)**

**revPBE** (Revised PBE) [Y. Zhang and W. Yang, Phys. Rev. Lett. **80** (1998) 890]

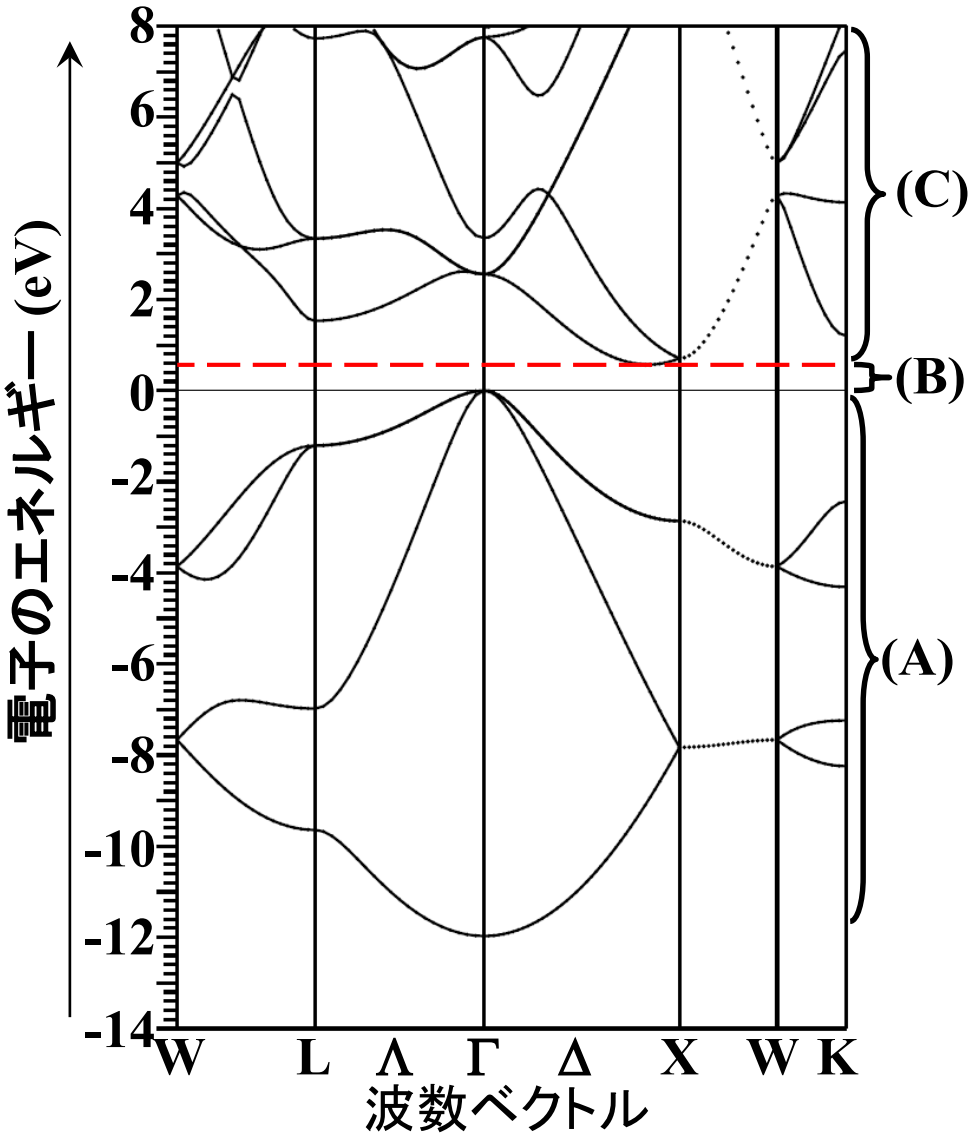
**RPBE** (Revised PBE) [B. Hammer, L. B. Hansen, and J. K. Nørskov, Phys. Rev. B **59** (1999) 7413]

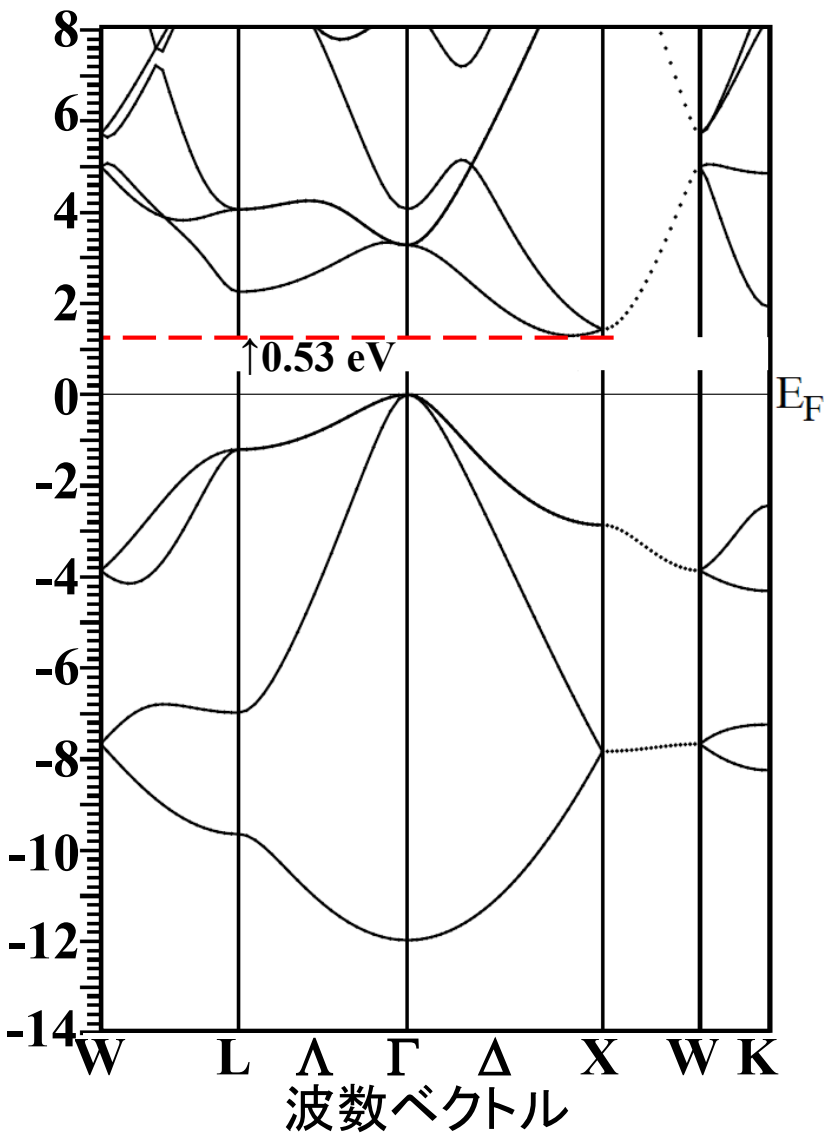
**PBEsol** (PBE for solids) [J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou and K. Burke, Phys. Rev. Lett. **100** (2008) 136406]

**WC** (Wu-Cohen modification of PBE) [Z. Wu and R.E. Cohen, Phys. Rev. B **73** (2006) 235116]

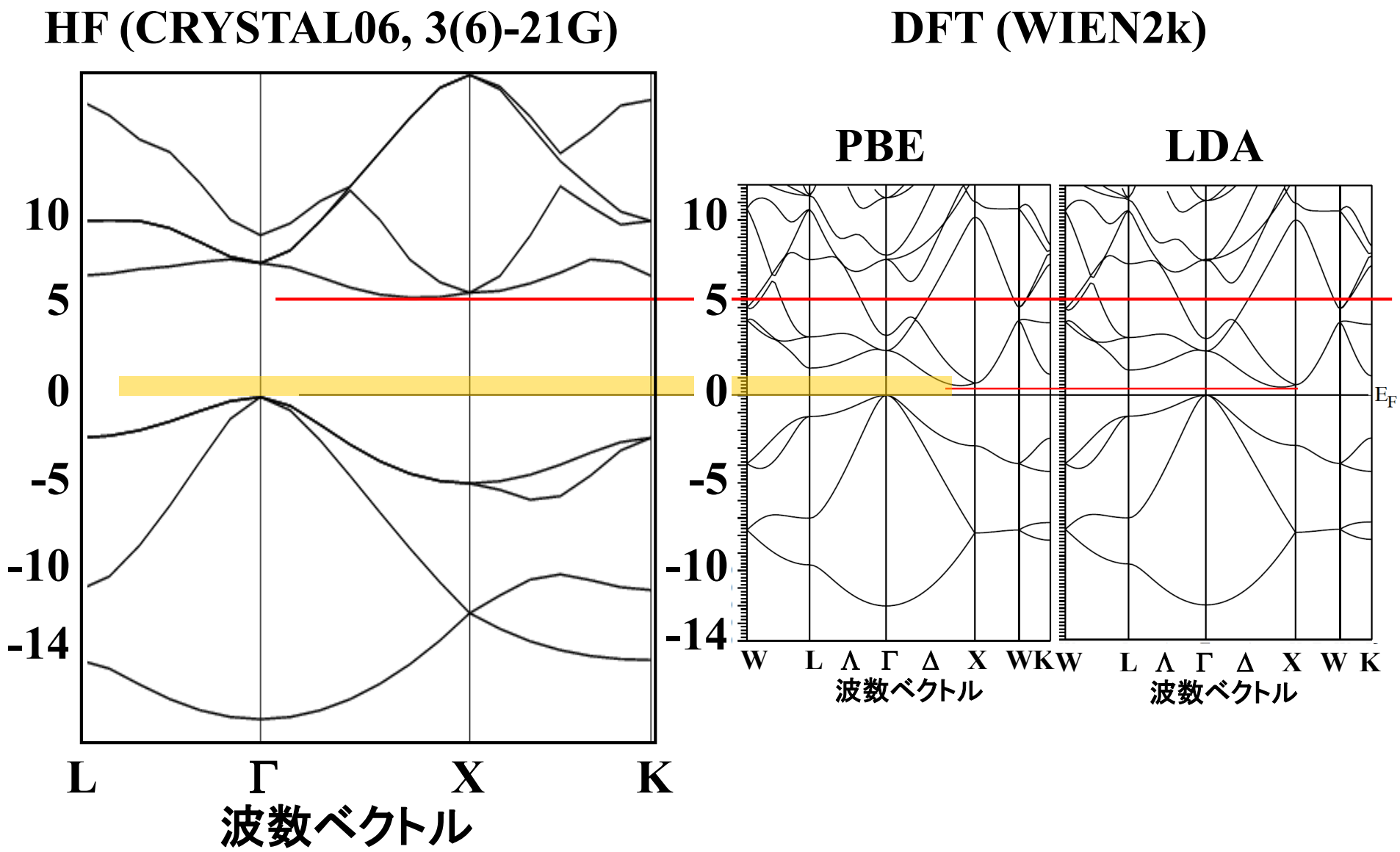
# Bandgap problem

**Si** (WIEN2k, PBE)  Exp: $E_g$ = 1.12 eV (300K)



# Bandgap problem: HF vs DFT



# Better methods for bandgap − beyond DFT −

(i) Configuration Interaction: CI
Employed for molecular orbital calculations (Gaussian etc).
Very heavy for infinite solids (band calculation)

For band calculations

(i) Self-Interaction Correction: SIC

(ii) Incorporate shielding effect to the EE potential
Screened Exchange: sX approximation

(iii) HF and DFT give wrong Eg values in opposite directions
=> Their potentials are mixed at an appropriate ratio: Hybrid DFT
(a) The mixing parameters are determined empirically so as to reproduce observed bandgaps for many molecules / crystals.
B3PW91, B3LYP etc.
(b) The mixing parameters are determined theoretical.
PBE0 and its shielding derivative (HSE)

(iv) GW approximation (quasi-particle approximation)

# Hybrid functionals: PBE0, HSE

## PBE0 hybrid functional

$$E_{xc}^{SR,HF\,PBE0} = aE_x^{HF,SR} + (1-a)E_x^{PBE} + E_c^{PBE}$$

Mixing parameter $a = 1/4$

## HSE hybrid functional

$$E_{xc}^{\omega PBEh} = aE_x^{HF,SR}(\omega) + (1-a)E_x^{PBE,SR}(\omega) + aE_x^{PBE,LR}(\omega) + E_c^{PBE}$$

Mixing parameter $a = 1/4$

Shielding param $\omega \to 0$: **PBE0** $\omega \to \infty$: **PBE96 (GGA)**

(sometimes adjusted so as to reproduce observed bandgap)

HSE03 : $\omega = 0.15$

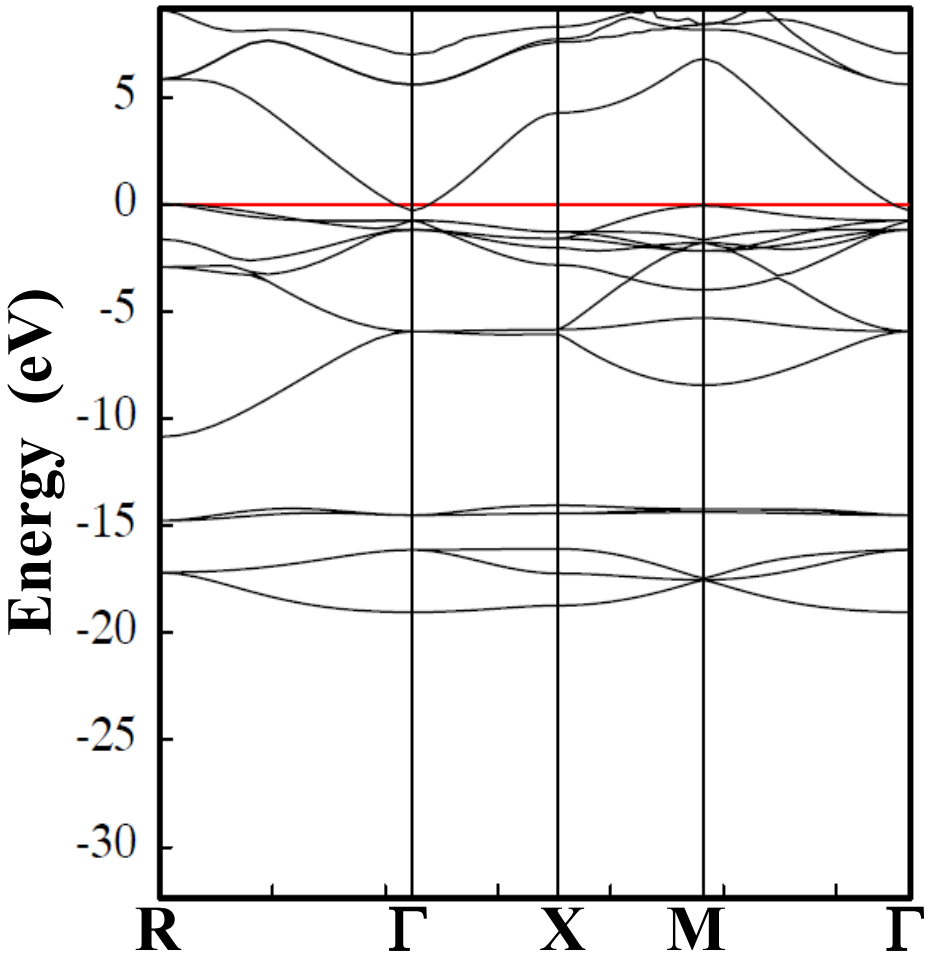
HSE06 (HSE03のERRATA): $\omega = 0.15/2^{1/2} = 0.106$ (HF part)

$\omega = 0.15 \times 2^{1/3} = 0.189$ (PBE part)

*John P. Perdew, Matthias Ernzerhof and Kieron Burke*
*J. Chem. Phys.* ***105*** *(1996) 9982*
*Jochen Heyd, Gustavo E. Scuseria, Matthias Ernzerhof*
*J. Chem. Phys* ***118*** *(2003) 8207;* ***124*** *(2006) 219906*

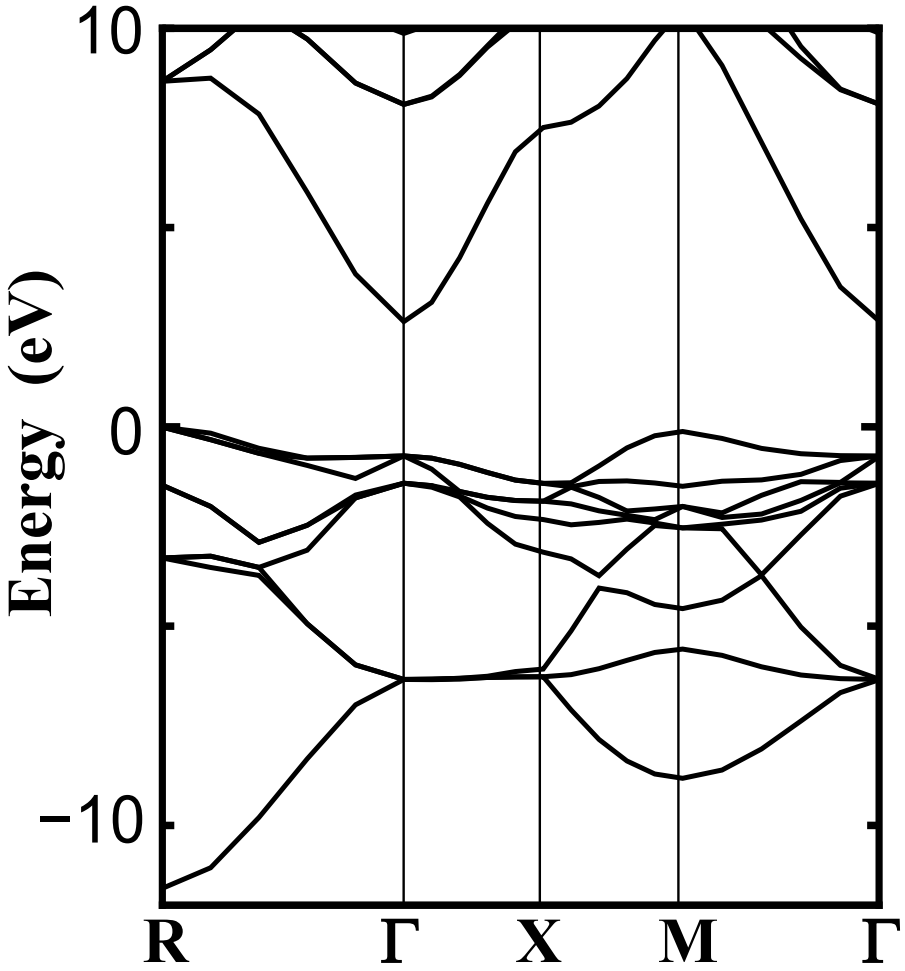
# Band structures of cubic $SrGeO_3$

GGA (PBE96)




Negative bandgap !!

PBE0




Exp. $E_g$ ~ 2.7 eV

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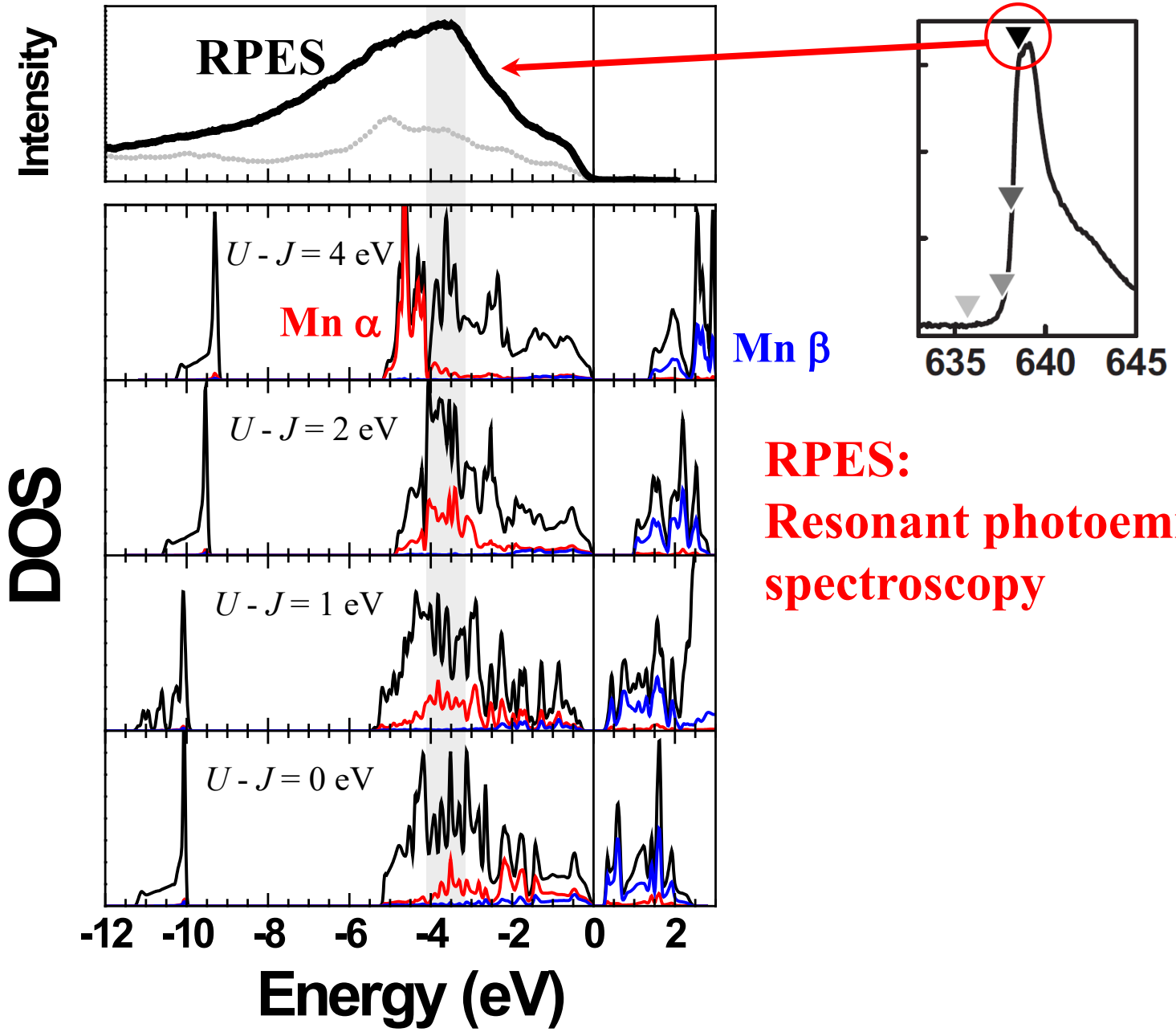
   Important e.g. for Peiels transition
4. Strong **electron correlation** materials
   Eg can not be explained by one-electron mean-field approximation such as DFT.
   Important for d and f electrons systems.
   Can be treated by beyond DFT methods like LDA/GGA+U, GW approximations.

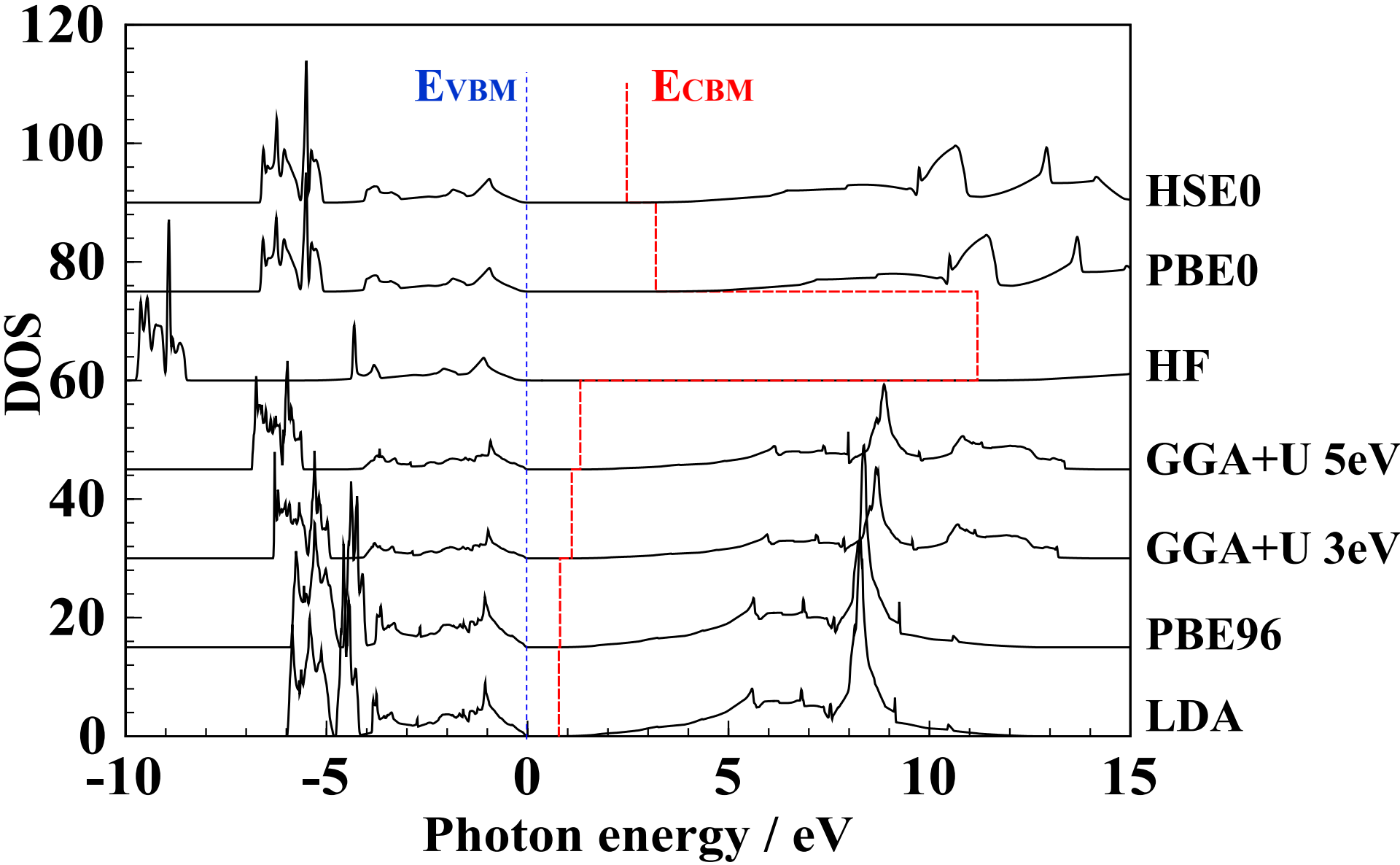
# +$U$ approx.: LaOMnP, AFM, $U - J$ = 0–4 eV




**RPES:**
**Resonant photoemission spectroscopy**

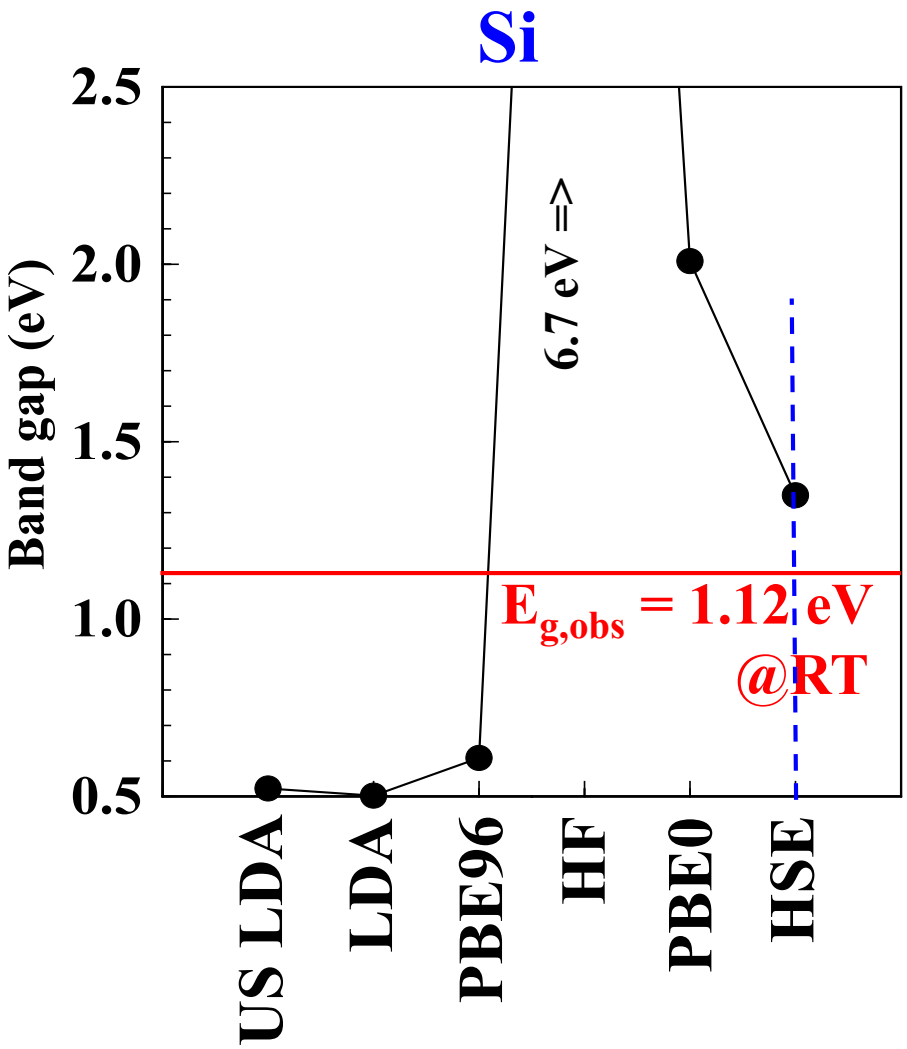
# Effects of functional and *U*: ZnO

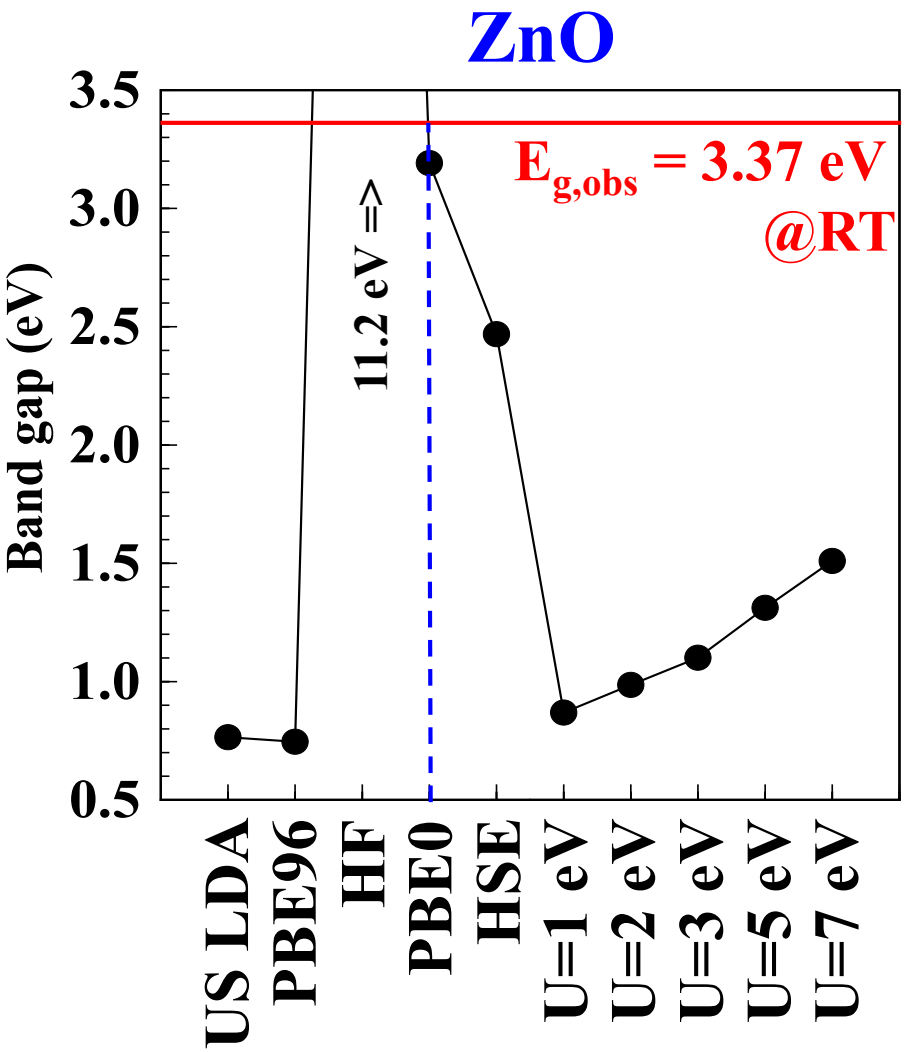
VASP



# $E_g$: Comparison of functional

VASP



**Self-interaction correction to the local-density approximation in the calculation of the energy band gaps …**
N. Hamada and S. Ohnishi, Phys. Rev. B **34**, 9042 (1986)

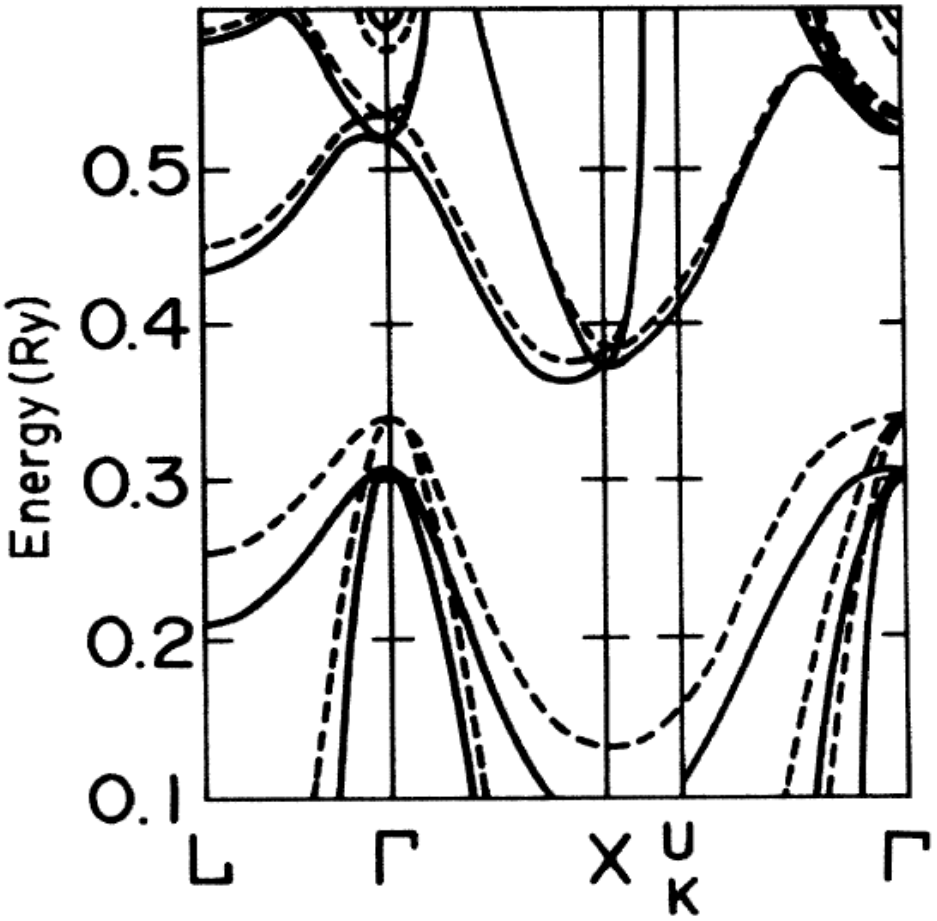


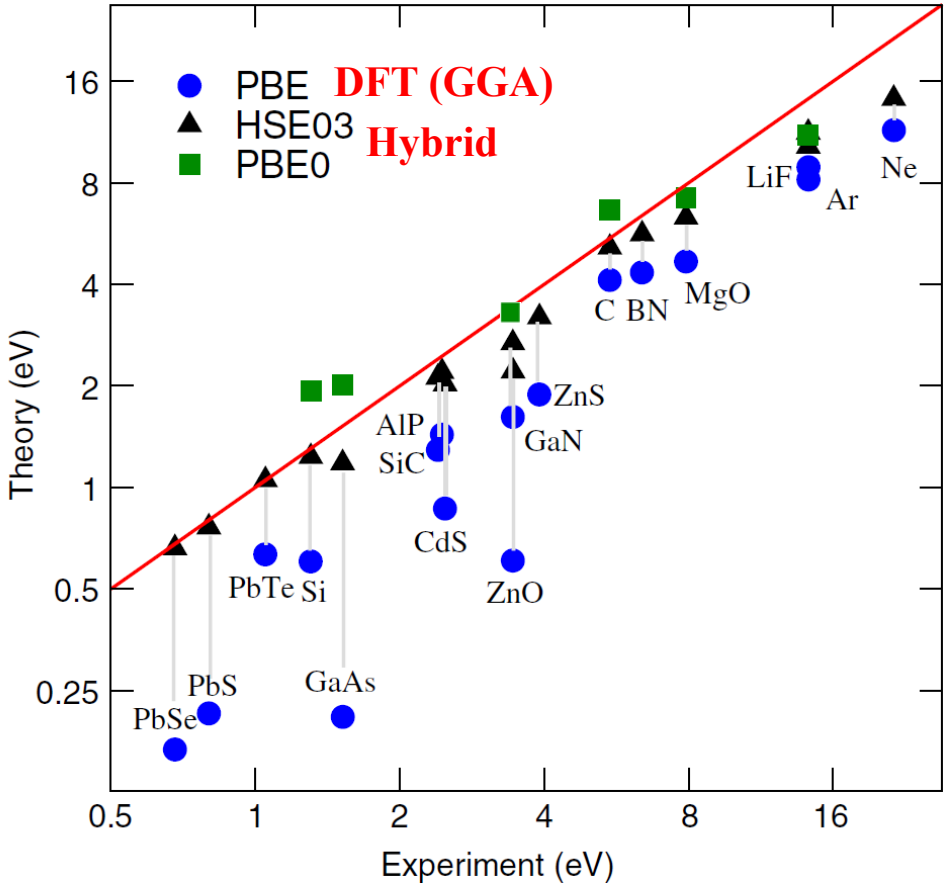

FIG. 1. Energy band structures of Si along high symmetry lines. Solid curves represent the SIC-LDA calculation, and dashed curves the LDA. Fundamental energy band gap is given by the difference between the conduction band minimum near $X$ point and the valence band top at Γ point. Note that the energy gap in SIC-LDA is about two times of that in LDA.

**The error due to LDA is larger for VB than for CB**

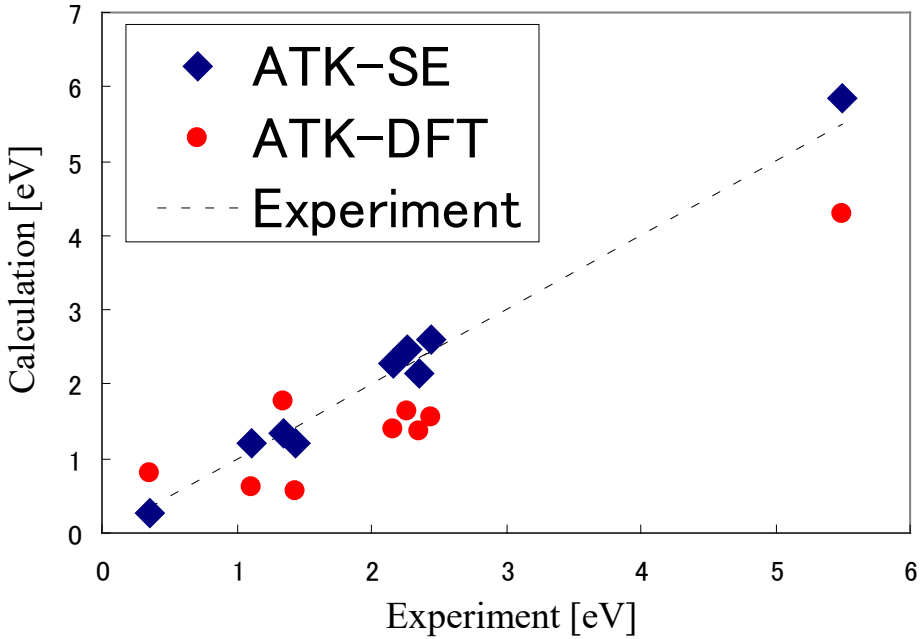
# Calculated $E_g$ for semiconductors

[Japanese] 大橋直樹監修、バンドギャップエンジニアリング －高効率デバイスへの挑戦－
大場史康、*第4章　半導体の物性シミュレーション*(シーエムシー出版)

*M. Marsman et al, J. Phys.:Condens. Matter,* ***20****, 064201 (2008)*



# High-accuracy bandgaps by semi-empirical method (ATK-SE)




| | ATK-SE [eV] | ATK-DFT [eV] | Experiment [eV] |
|---|---|---|---|
| InAs | 0.28 | 0.80 | 0.36 |
| Si | 1.22 | 0.63 | 1.11 |
| InP | 1.35 | 1.78 | 1.35 |
| GaAs | 1.2 | 0.56 | 1.43 |
| AlAs | 2.27 | 1.39 | 2.16 |
| GaP | 2.47 | 1.63 | 2.26 |
| AlP | 2.61 | 1.56 | 2.45 |
| SiC | 2.15 | 1.36 | 2.36 |
| Diamond | 5.84 | 4.29 | 5.5 |

Comparison of calculated and experimental bandgaps.
ATK-SE can provide reasonable bandgap values for a variety of materials

QuantumWise

CYBERNET

# First-principles calculation: Optical spectrum

# 第一原理計算: 光学スペクトル

# Optical spectrum

## (Optical dielectric function ε*, Absorption coefficient α)

$$\mathcal{H} = \mathcal{H}_0 - \boldsymbol{er}\cdot\boldsymbol{E}$$

$$\varepsilon_1(\omega) = 1 + 4\pi \sum_j \frac{e^2 \left|T_{0j}\right|^2}{\hbar} \frac{2\omega_j}{\omega_j{}^2 - \omega^2}$$

$$T_{ij} = \left\langle \Psi_i \left| \mathbf{r} \right| \Psi_j \right\rangle = \int \Psi_i{}^* \mathbf{r} \Psi_j d\mathbf{r}$$

**Kramers-Kronig conversion**

$$\varepsilon_2(\omega) = \frac{4\pi N e^2}{m} \sum_j f_j \pi \delta\left(\omega^2 - \omega_j{}^2\right)$$

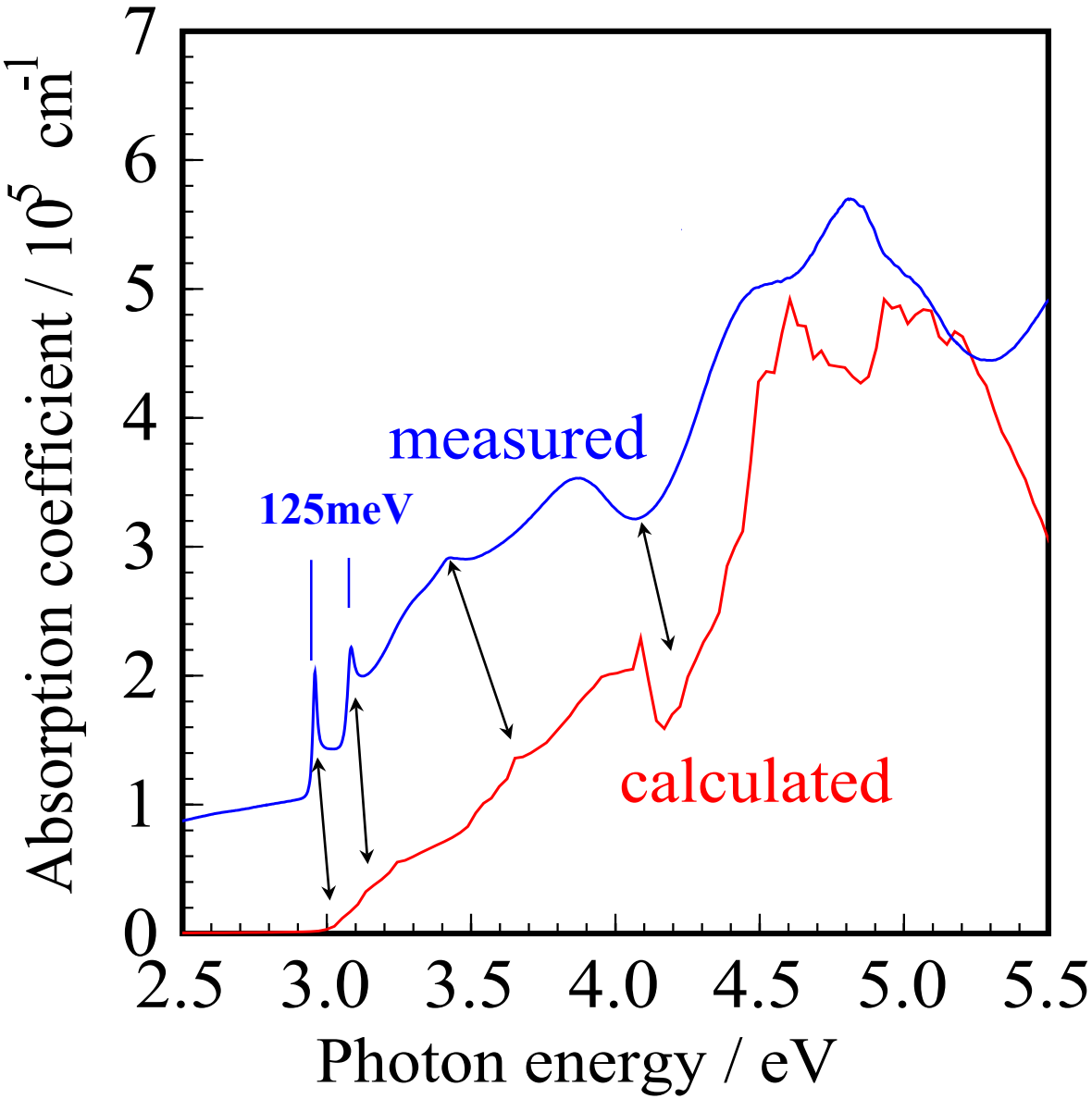
$$= \frac{4\pi N e^2}{m} \sum_j f_j \frac{\pi}{2\omega} \left[\delta(\omega - \omega_j) + \delta(\omega + \omega_j)\right]$$

$$n(\omega) + i\kappa(\omega) = \sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega)}$$

$$\alpha(\omega) = \frac{4\pi}{\lambda}\kappa(\omega)$$

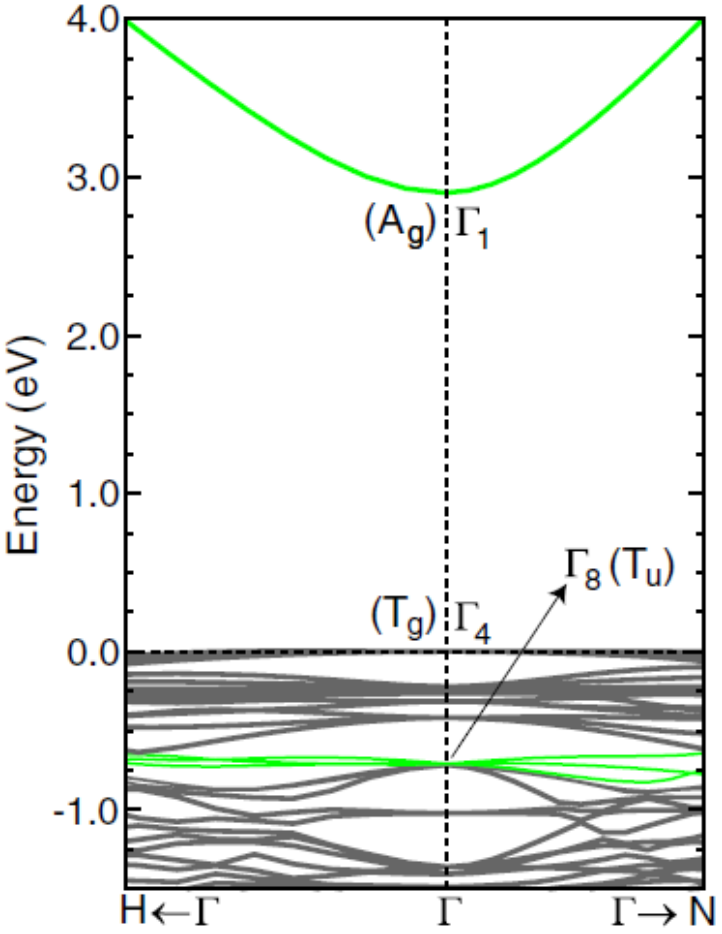
# Optical spectra: LaCuOSe

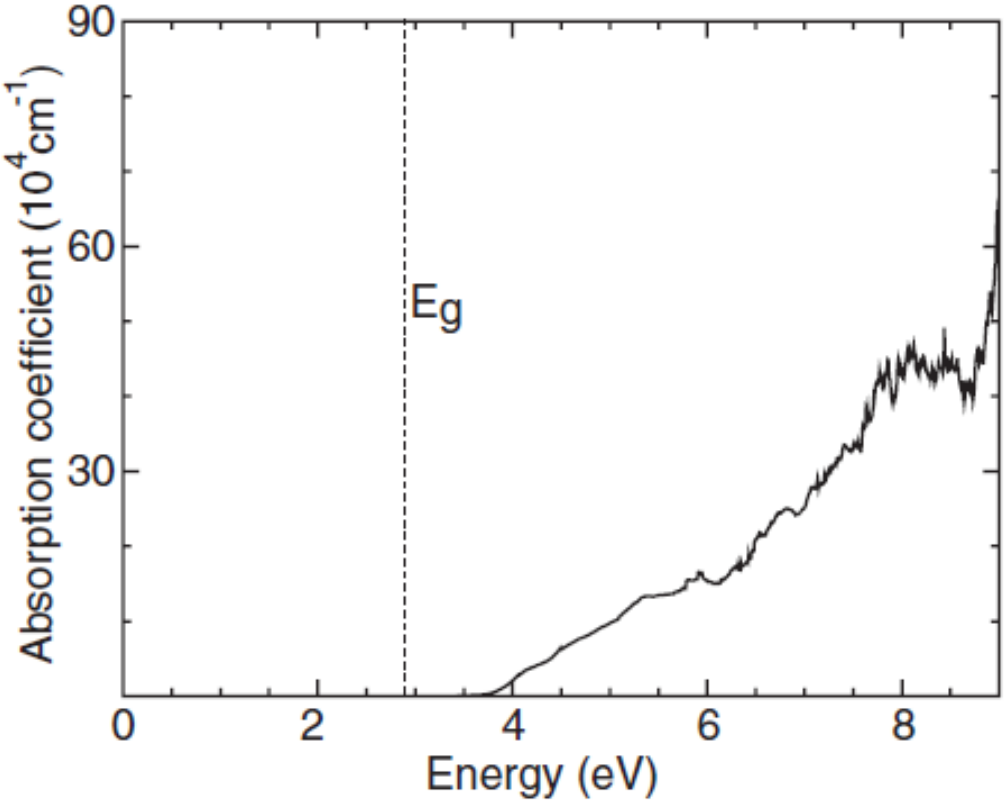
WIEN2k+OPTICS



# Bandgap of $In_2O_3$

Nature of the band gap of $In_2O_3$ revealed by first-principles calculations and x-ray spectroscopy
Aron Walsh, Juarez L.D.F.Da Silva, Su-Huai Wei, C. Korber, A. Klein, L.F.J. Piper, Alex DeMasi, Kevin E. Smith, G. Panaccione, P. Torelli, D.J. Payne, A. Bourlange, and R.G. Egdell
Phys. Rev. Lett. 100 (2008) 167402



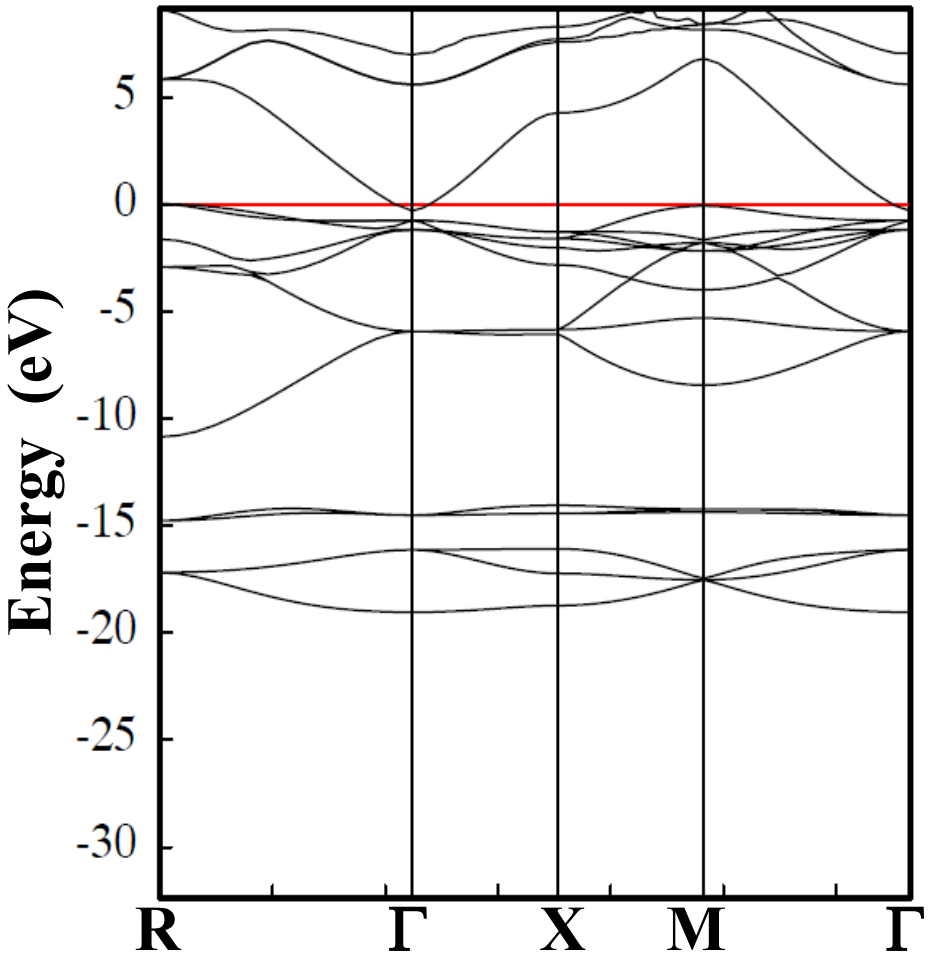




$E_{\text{ind}} = 2.89$ eV

$E_{\text{dir}} = 3.70$ eV

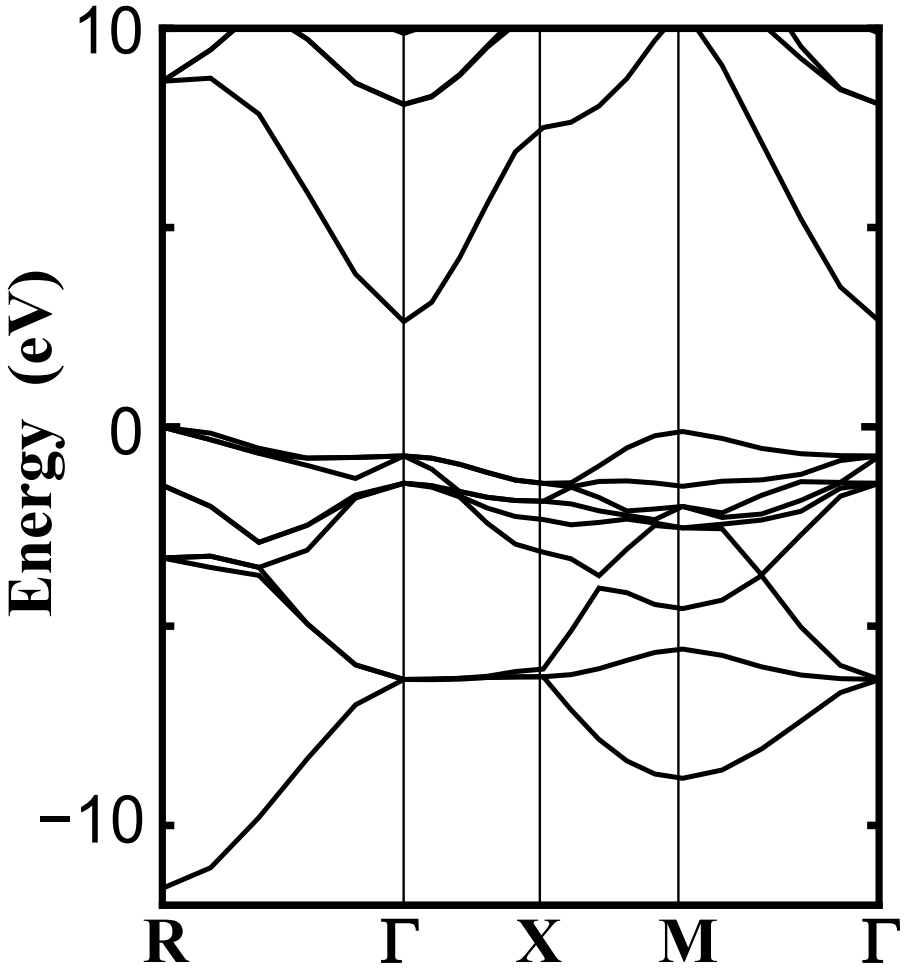
# Band structures of cubic $SrGeO_3$

GGA (PBE96)




Negative bandgap !!

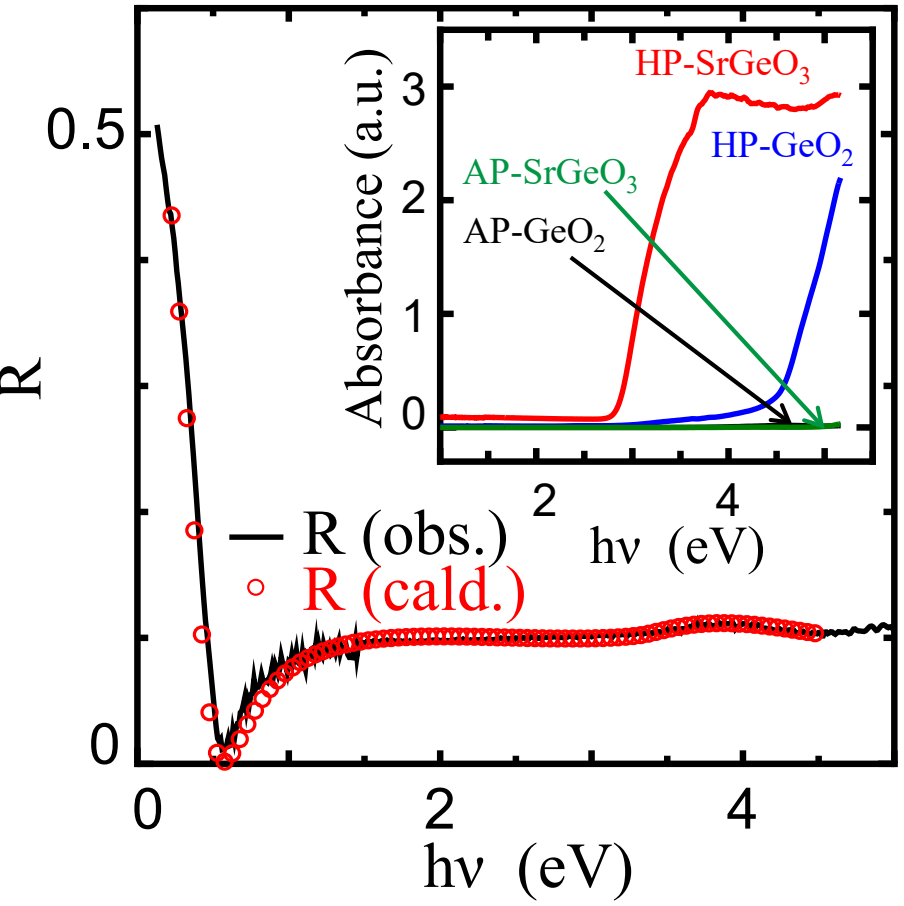
PBE0




Exp. $E_g$ ~ 2.7 eV

# Optical spectra og Ge-based oxides

**Observed**




**PBE0**